

ENVIRONMENTAL ASPECTS OF PURIFICATION OF PHENOLIC WASTE WATERS BY MEDIATED ELECTROOXIDATION WITH Ce^{4+}/Ce^{3+} AND MONITORED BY HPLC

— research paper —

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Abstract: The purification of industrial phenolic waste waters by mediated electrooxidation with Ce^{4+}/Ce^{3+} on a platinum anode in H_2SO_4 solution was performed. The conversion degree of phenol and its toxic oxidation derivatives, which are further oxidized to non-toxic compounds, was monitored by high performance liquid chromatography (HPLC).

Keywords: purification, phenolic waste waters, mediated electrooxidation, Ce^{4+}/Ce^{3+} , high performance liquid chromatography

INTRODUCTION

Phenol and its derivatives are toxic substances nearly omnipresent in the environment. They can often be found in relatively high concentrations in industrial waste waters, consequently polluting rivers, soil and, through irrigation, even ground-water (Czuczwa et al., 1987).

Many treatment technologies are in use for the purification of industrial waste waters, aiming either recovery or degradation of phenol. The most usual methods are as follow: activated carbon adsorption (Keinath, 1976), extraction

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with organic solvents (Plattner et al., 1988), biological purification (Paris et al., 1982), chemical oxidation (Hayek et al., 1985) and direct and mediated electrooxidation (Comninellis et al., 1991, 1992, 1993, Pulgarin et al., 1994, Bringmann et al., 1995, Hwang et al., 1996). The purification methods are used separately or in combination, depending on the nature of phenol derivatives, on the concentration of phenol and its derivatives in waste waters. The paper presents the mediated electrooxidation with Ce^{4+}/Ce^{3+} of traces of phenol in residual waste waters. The conversion degree of phenol and the formation of its oxidation products were monitored by HPLC method. The toxic compounds were UV detected at 280 nm.

MATERIALS AND METHODS

Reagents

Phenol, hydroquinone, quinhydrone, H_2SO_4 and methanol were purchased from Merck. $Ce(SO_4)_2 \cdot 4H_2O$ was purchased from Chimopar, Bucharest. All chemicals used were p.a. grade and methanol was liquid chromatography gradient grade. There were used samples of industrial phenolic waste waters from the Chemical Plant Victoria (Romania).

Methods

The mediated electrooxidation of phenolic waste waters was performed with Ce^{4+}/Ce^{3+} redox system in concentration of $6 \times 10^{-4} M$, in $2.5 \times 10^{-1} M H_2SO_4$ solution. The concentration of phenol in waste waters was $6.42 \times 10^{-4} M$.

The mediated electrooxidation with Ce^{4+}/Ce^{3+} of phenolic waste waters was performed by galvanostatic electrolysis at room temperature ($20^\circ C$), for 4 h. An H-shaped stipler cell of 250 cm^3 capacity was used. Both anode and cathode were platinum plates (4 cm^2). Stirring was made by a magnetic bar.

The current density (0.35 A cm^{-2}) was controlled by a Princeton Applied Research model 173 galvanostat.

The disappearance of phenol and the formation of its oxidation products were monitored by high performance liquid chromatography (HPLC) and the conversion degree of phenol and the concentration of its main oxidation product (hydroquinone) were determined.

The initial sample of phenolic waste water and the samples taken during the mediated electrooxidation with Ce^{4+}/Ce^{3+} at 2 hours intervals, were analysed with an HPLC instrument (Jasco PU-980), equipped with a high pressure pump unit (PU-980) with ternary gradient (LG-980-02), 3-lines degaser (DG-980-50), Nucleosil 120 column and a 975 UV-VIS variable wavelength detector.

The detection of phenol and its derivatives was realized in UV at $\lambda = 280$ nm (Baiocchi et al., 1995), using the Nucleosil 120 column (silica gel C₁₈, grain diameter 5 μ m, column size 25x0.4 cm), with a mobile phase of methanol:water (40:60, v/v) (Corcia et al., 1996), having a temperature of 20°C and a flow of 1 ml min⁻¹.

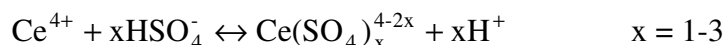
Volumes of 1 ml sampled from the phenolic waste waters, before and during the mediated electrooxidation with Ce⁴⁺/Ce³⁺, were passed through a Polyspher RP-18 Cat cartridge activated with 5 ml methanol and 5 ml bidistilled water. The compounds to be analyzed (phenol, hydroquinone, benzoquinone) were retained on the cartridge and then were eluted with 5 ml methanol and separated by HPLC.

RESULTS AND DISCUSSION

During the electrooxidation of phenol, the formation of the polymer films on Pt anode is inhibited in acid medium. But, high phenol concentration (5×10^{-2} M), high temperature (>50 °C) and low current density (< 30 mA cm⁻²) favored the formation of polymer film on Pt (Comminellis et al., 1991).

In the mediated electrooxidation with Ce⁴⁺/Ce³⁺ of phenolic residual waste waters on platinum anode in H₂SO₄ solution, the phenol is almost completely oxidized (94.60%) after 2 hours to hydroquinone and benzoquinone, but its oxidation products are also completely oxidated in 4 hours to non-toxic compounds, i.e. CO₂ and H₂O, as seen in Figure 1. The peaks noted uk (from unknown) in Figure 1 correspond to certain impurities in the phenolic waste waters and to certain sulfate complexes of Ce⁴⁺.

In H₂SO₄ medium, Ce⁴⁺ forms several sulfate-complexes:



At concentrations of H₂SO₄ greater than 0.05 M, several anionic sulfate-complexes can be found: Ce(SO₄)₃²⁻, HCe(SO₄)₃⁻, H₃Ce(SO₄)₄⁻. The largest amount is represented by Ce(SO₄)₃²⁻ formed at the equilibrium:

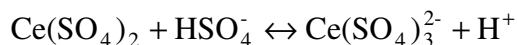


Table 1 presents the conversion degree of phenol and the concentration of the formed hydroquinone, as a function of mediated electrooxidation time.

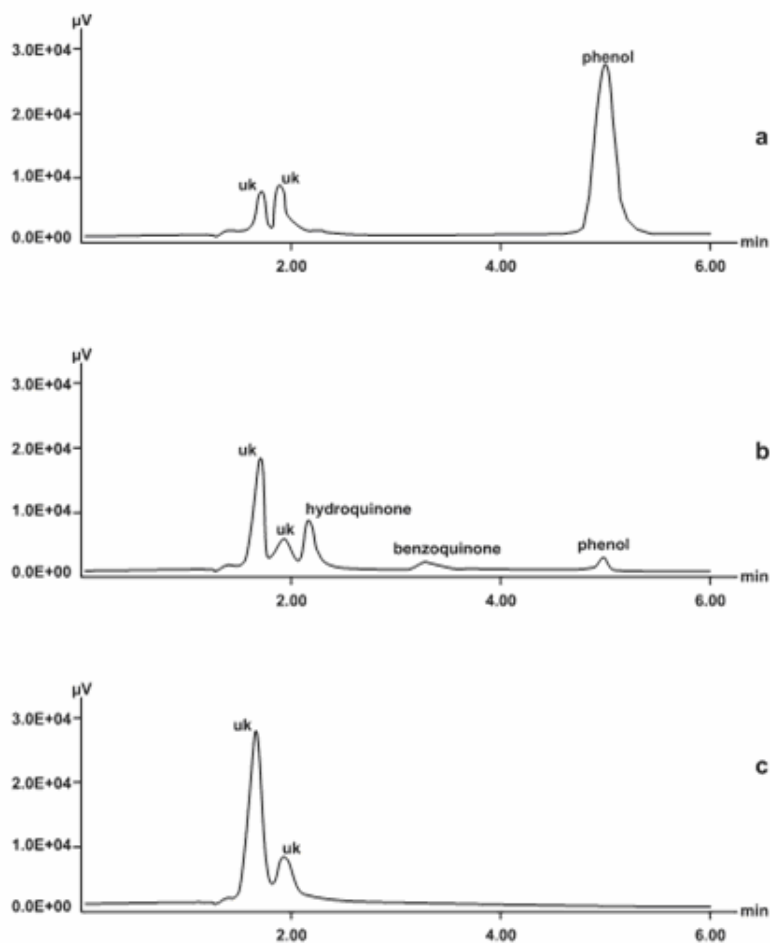


Figure 1. Chromatograms registered during the mediated electrooxidation with $\text{Ce}^{4+}/\text{Ce}^{3+}$ of phenolic waste waters after 0, 2 and 4 hours (a, b, c): Pt anode, $i = 0.35 \text{ A cm}^{-2}$; concentrations: phenol = $6.42 \times 10^{-4} \text{ M}$, $\text{H}_2\text{SO}_4 = 2.5 \times 10^{-1} \text{ M}$, $\text{Ce}^{4+}/\text{Ce}^{3+} = 6 \times 10^{-4} \text{ M}$.

Table 1. The conversion degree of phenol and the concentration of hydroquinone after 2 and 4 hours of mediated electrooxidation with $\text{Ce}^{4+}/\text{Ce}^{3+}$ of phenolic waste waters: Pt anode, $i = 0.35 \text{ A cm}^{-2}$, concentrations: phenol = $6.42 \times 10^{-4} \text{ M}$, $\text{H}_2\text{SO}_4 = 2.5 \times 10^{-1} \text{ M}$, $\text{Ce}^{4+}/\text{Ce}^{3+} = 6 \times 10^{-4} \text{ M}$.

Time (h)	Conversion degree of phenol (%)	Concentration of hydroquinone (x 10 ⁴ M)
2	94.60	0.54
4	100	0

It is observed that, for instance, after 2 hours, the conversion degree of phenol is 94.60%.

The phenol existing in the waste waters is totally oxidized after 4 hours, the conversion degree being 100%. It is also noticed that hydroquinone as main oxidation product is absent after 4 hours in the mediated electrooxidation with Ce⁴⁺/Ce³⁺ of waste waters.

Ce⁴⁺/Ce³⁺ is an efficient mediator redox system for the purification of phenolic waste waters, because the conversion degree of phenol is higher and the concentration of the formed and unoxidized hydroquinone is lower.

As can be noticed, the optimal values of the current density, concentration of H₂SO₄ and concentration of the redox mediator system Ce⁴⁺/Ce³⁺ were chosen after a complete study with a high number of trials. These values correspond to a maximum conversion degree of phenol in the industrial waste waters and of its toxic oxidation derivatives, in particular hydroquinone.

CONCLUSIONS

Industrial phenolic waste waters can be successfully purified by mediated electrooxidation with the Ce⁴⁺/Ce³⁺ redox system on platinum anode in H₂SO₄ solution. The stages of oxidation and the conversion degree of phenol to nontoxic compounds was monitored by HPLC.

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