STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, L, 1, 2005

ELECTROCHEMICAL BEHAVIOR OF PHENOLS IN AQUEOUS SOLUTION – FUNDAMENTS FOR THEIR ELECTROCHEMICAL DEGRADATION IN WASTE WATERS

MARIA JITARU, LUISA ROXANA MANDOC, CRISTINA MIHAI, OANA TUDORAN

"Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering,
11, Arany Janos street, 400028 Cluj-Napoca, Phone: 00 40 264 59383, Romania
mjitaru@chem.ubbcluj.ro

ABSTRACT. The main objective of this work is to bring information (influence of the nature of the electrode material, of pH, nature of the organic molecules) on the electrochemical parameters (peak potentials, current density) concerning the electrochemical behavior of some phenols, in different aqueous solution, having pH between 4 and 12 on different electrode materials (glassy carbon, Au, Hg, PbO_2). Both electrochemical processes on the level of hydroxyl and nitro group (in p-nitrophenol) have been studied.

Different phenols (phenol, p-nitrophenol, p-metoxyphenol and 1-naphtol) derivatives have been of interest in this work, in order to establish their electrochemical behavior, useful for the electrochemical degradation.

In this work, cyclic voltammetry (using BAS 100W and AUTOLAB PGSAT computer aided electrochemical systems) and UV-Vis spectrophotometry (UNICAM Helios β) were used for the control of phenols concentration during the electro-oxidation.As compared to the electrochemical oxidation of naphtols, the electrochemical oxidation of phenols, having a strong aromatic character, takes place more difficult. The oxidation processes on the level of phenolic group strongly depends on the pH. On the other hand, the nitrophenols could be reduced on the level of nitro group and their oxidation is also possible.

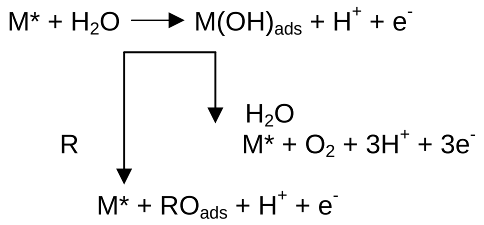
Keywords: Phenols, electrochemical oxidation, cyclic voltammetry, nitrophenols

INTRODUCTION

Removal or modification of the organic impurities in waste-waters is a major challenge for environmental science. Pollutants such phenols and their derivatives have been attracted special attention.

Phenol and related compounds are considered to be very toxic to humans through oral exposure. Ingestion of 1 g was reported to be lethal, with symptoms including muscle weakness and tremors, loss of coordination, paralysis, convulsions, coma, and respiratory arrest. Inhalation and dermal exposure to phenol is highly irritating to the skin, eyes, and mucous membranes in humans. The hydroquinone is probably carcinogen, toxic and severe skin irritant [4].

The destruction of the organic pollutants from the waste waters can be achieved either through chemical methods using different oxidant agents e.g. the ozone which is considered "a clean" reactive, or by unconventional alternatives with environmental favorable impact, like direct or indirect electrochemical oxidation. It has been proposed [5,6] that the mechanism involves the adsorption of OH species, produced from the oxidation of water molecules, or the oxides produced from electrochemical oxidation on the surface. Considering the participation of OH species, the reaction taking place on the electrode, may be written as:



where: M* corresponds to an adsorption site and R is the organic compound.

In order to evaluate electrocatalytic activity of the electrode for the oxidation of R, contributions of both processes to the total current has to be determinate.

According to Bonfatti and co-workers [7] the electrochemical oxidation index (EOI) proposed by Comninellis [8] could be a measure towards the oxidative degradation of the organic substrates.

EXPERIMENTAL

In order to obtain the voltamperommetric data, fundaments for the electrochemical phenols oxidation, cyclic voltammetry (BAS 100W and AUTOLAB PGSAT 12 computer aided electrochemical systems) have been used. The control of the electrochemical processes was achieved using UV-Vis spectrophotometer (UNICAM Helios β). Voltammograms were recorded in different buffer solution of ionic strength 0.1. The pH of buffer solution was measured using the JENWAY 3330 pH meter, after standardization with potassium hydrogen phthalate and borax buffers. Controlled potential and current electrolysis of 0.1- 0.5 mM solution of the dye was carried out both in a conventional divided H-type cell. The electrodes for cyclic voltammetry (from BAS Co.) had an area of 0.2826 cm^2 and PbO_2 for preparative scale oxidation of phenols had an area of 4.2 cm^2; it has been electrochemically preformed, according to our previous method [9]. All potentials refer to Ag/AgCl,KCl at an ambient temperature of 20±2 °C.

Voltamperometric behavior of studied compounds on glassy carbon electrode – influence of the background and pH

Cyclic voltammograms on glassy carbon electrode, in alkaline media (NaOH 0.1M, pH = 13), reveal that the oxidation of 1-naphtol takes place easier (100-300mV) comparing to phenol oxidation (350–600 mV), due to different conjugation effects of the phenol comparing with 1-naphtol.

The oxidation potential slowly decrease at the same time with growing of phenols concentration, due to the increasing of the coverage degree, both for phenol (Fig. 1a) and p-nitrophenol (Fig. 1c) oxidation. Nitro group is more difficult to be adsorbed on glassy carbon, may be because of the expanded conjugation and of the stabilization of the molecule by resonance. The reduction of NO_2 group was performed on MDE (mercury drop electrode) with hanging drop (Fig. 1d).

The difference of the electrochemical reactivity of the investigated phenols cannot be explained by a simple steric hindrance of the π –electrons interaction of the benzene ring with the electrode.

The effect of the electrons withdrawal of nitro group in p-nitrophenol, correspond to the decrease of the pK_a value (7.14 for p-nitrophenols comparing to 9.95 for phenol, 10.0 for p-metoxyphenol and 0.2-0.4 for 1-naphtol) [10]. The oxidation of the hydroxyl group in p-nitrophenols takes place more difficult (at about

960 mV most positive value) - Fig.2 and Table 1, comparing to phenol (525 mV) and p-metoxyphenol (540 mV). The weakest acid (1-naphtol) could be the easiest oxidized (247 mV).

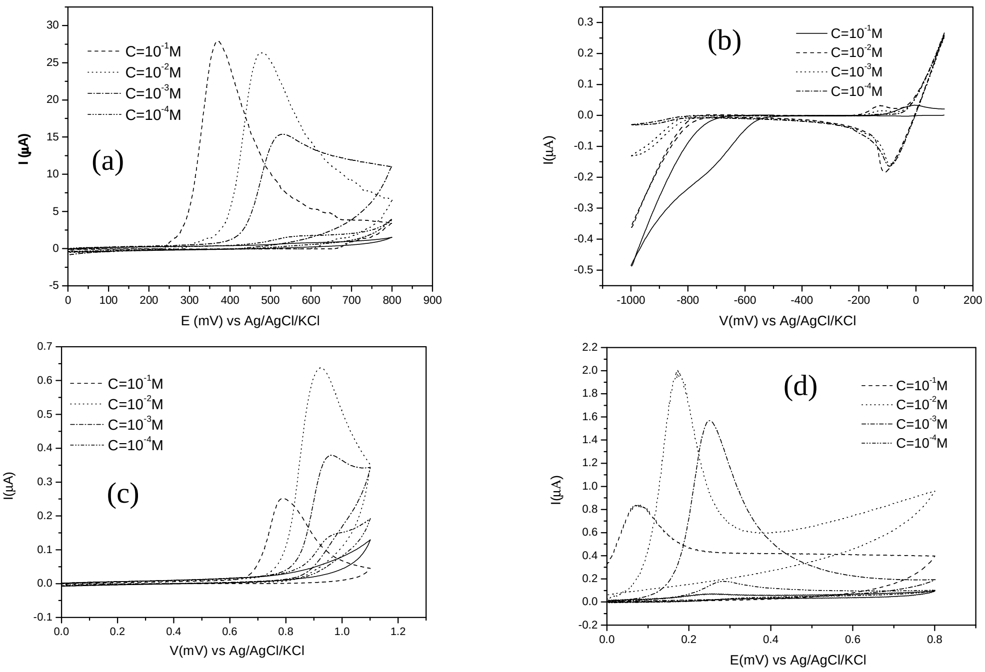


Figure 1. VOC in alkaline media, NaOH 0.1M, pH = 13 ± 0,2 of (a) phenol; (b) 1-naphtol; (c) p-nitrophenol; (d) reduction of p-nitrofenol; WE: GC; RE: Ag/AgCl,KCl; AE: Pt; v=50mV/s;

Phenoxide anion can be adsorbed on the electrode surface either due to the electrostatic interactions of the negatively charged oxygen and the anode surface or due to the π- electron interaction between the aromatic ring and the electrode. As a result of these two possibilities, phenoxide anions are oriented parallel or a certain angle to the electrode surface, influenced by the electronic effects of the substitutes on the aromatic ring [10].

Because the stronger withdrawal exerted by the nitro group the negative charge of the oxygen atom diminishes and weakens electrostatic interaction between the phenoxide anion and the anode, maintaining the unfavorable flat orientation of the molecule at the electrode and the oxidation of hydroxyl group becomes more difficult.

In excited-state higher acidity of 1-naphtol (pKa = 0.2 - 0.4) might be manifested in higher reactivity of 1-naphtol for electrochemical reaction, requiring excited-state naphtolate ions. A common explanation for the value of pK_a in 1-naphtol is intramolecular charge transfer (ICT) in the excited of acid, from the hydroxyl oxygen to the aromatic ring. It was subsequently realized that the ICT effect must be even larger in the conjugate anionic base [9]. According to this behavior, our results show that the oxidation of 1-naphtol takes place at lower positive potentials.

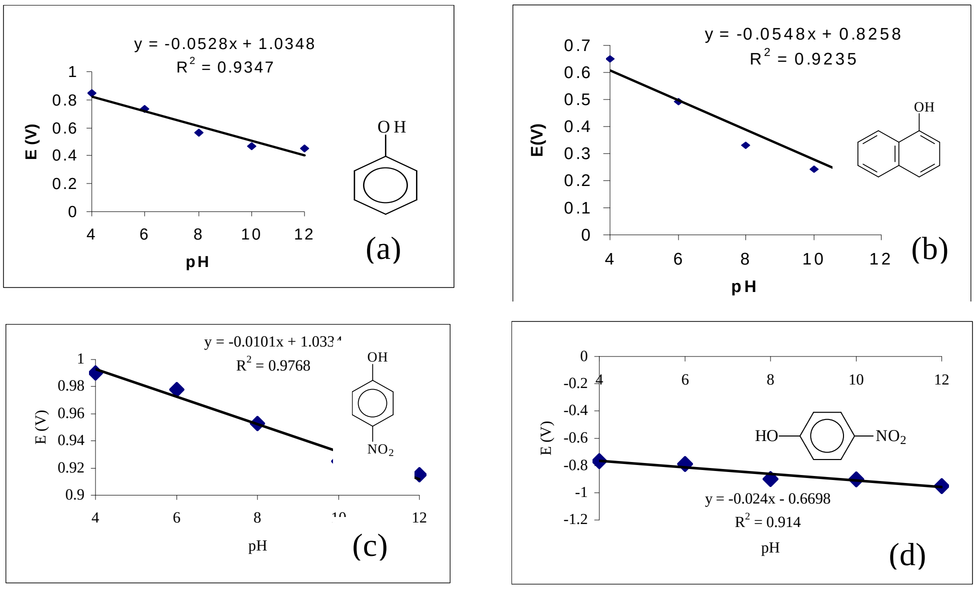


Figure 2. Potential – pH correlation for 10^{-3}M (a) phenol ; (b) 1-naphtol; (c) p-nitrophenol oxidation and (d) p-nitrophenol reduction WE: GC; RE: Ag/AgCl,KCl; AE: Pt; v=50mV/s; electrolyte Na_2SO_4 0.33 M with aliquots of H_2SO_4 or NaOH

	ε_{ox} (V)
Phenol	0.525
1-naphtol	0.247
p-nitrophenol	0.960
p-metoxyphenol	0.540

Table 1. Oxidation peaks potentials of the studied compounds in alkaline media (NaOH, 0.1 M) on GC electrode

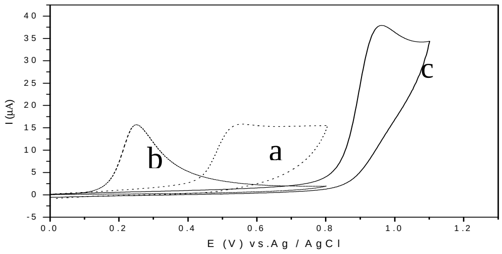


Figure 3. VOC on GC in alkaline media, NaOH 0.1M, pH = 13 ± 0,2 of (a) phenol; (b) 1-naphtol; (c) p-nitrophenol;

Determination of EOI for the oxidation of phenol and 1-naphtol

The electrochemical oxidation index (EOI), according to Bonfatti [7] and Comninellis [8] has been determinate, like a measure towards the oxidative degradation of phenol and 1-naphtol, using an experimental installation equipped with a divided cell described earlier [9]. The best results have been obtained on pre-formed PbO_2. Cyclic voltammetric determinations on PbO_2 are strongly affected by the oxidation.

For all the investigated phenols the high EOI have been obtained at lower pH values. The oxidation of the 1-naphtol seems to be more intensive, but the pH dependence is similar – Fig. 4.

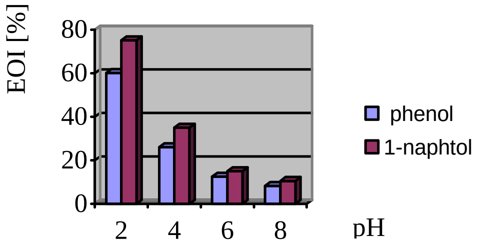


Figure 4. Dependence of the EOI as a function of pH. T= 20±0.2 ^{0}C; Na_2SO_4 0.33 M with aliquots of H_2SO_4 or NaOH, on PbO_2 electrode, c_i=1 g/l and i = 100 Am^{-2}.

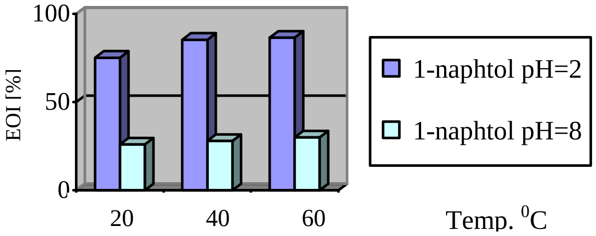


Figure 5. Dependence of the EOI on the temperature; electrolyte Na_2SO_4 0.33 M with aliquots of H_2SO_4 or NaOH on PbO_2 electrode, initial concentration 1 g/l; i = 100 Am^{-2}.

On the other hand in the investigated temperature range, between 40-60 ^{0}C the EOI is practically constant, for different pH - Fig. 5.

CONCLUSIONS

The electrochemical behavior of different phenols, depending of their nature, pK_a, pH, etc. and the EOI on PbO_2 have been reported. The oxidative capacity of the investigated phenols strongly depends on pK_a:

1-naphtol > phenol ≅ p-metoxyphenol > p-nitrophenol

Electrochemical decontamination of waste water containing phenols on PbO_2 becomes more efficient when the pH≈2, when the competitive oxygen formation diminishes. The electrochemical mineralization of the phenols on PbO_2 could be realized at accessible temperatures. These data are important for the electrochemical degradation of phenols in waste waters.

ACKNOWLEDGMENTS

We are grateful for the financial support from AUF-2700PL309& MATNANTECH-227(405) projects.

REFERENCES

1. M.Jitaru, A.Katona, N.Dulamita, M.Stanca and M.Birca, *Annales scientifiques de l’Université d’Etat de Moldova* (serie chimie-biologie), 282, 2001.
2. M.Stanca, M.Jitaru, N.Dulamita, *Annales scientifiques de l’Université d’Etat de Moldova* (serie chimie-biologie), 277, 2000.
3. M.Jitaru, M.Stanca and N. Dulamita, Series - SICHEM’2000, Ed. MATRIX ROM, 9-15 Oct., Bucureşti, ISBN 973-685-163-X, p. 401, 2000**.**
4. U.S. Environmental Protection Agency. Drinking Water Health Advisory on Phenol. Office of Drinking Water, Washington, DC. 1990.
5. O.Simond, V.Schaller, Ch.Comninellis, *Electrochim. Acta,* 42, 2, 2009, 1997.
6. G.Foti, D.Gandini, Ch.Comninellis, *Current Topics in Electrochemistry*, 5, 71, 1997.
7. F.Bonfatti, S.Ferro, F.Lavezzo, M.Malacarne, G.Lodi and A.DeBattisti, *J. Electrochem.Soc*, 146(6) 217, 1999.
8. Ch. Comninellis and C. Pulgarin *J.Appl.Electrochem.,* 21, 1403, 1991.
9. L. Oniciu, Maria Jitaru I. A. Silberg, F. Ciomos, D. A. Lowy, and O. H. Oprea, Rom. Pat. RO 91210, Mar 30, 1987; Chem. Abstr., 1987, 107, 245180q.
10. F. Lu, G.N. Salaita, L. Languren-Davidson, D.A. Stern, E. Wellner, D. G. Frank, N. Batina, D. C. Zapien, A. T. Hubbard, *Langmuir* ***4,*** 1988, 637.