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# Degradation of N-Methyl-*p*-aminophenol by Indirect Electrochemical Oxidation with Active Oxygen at Different pH Values

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## Abstract

Indirect electrochemical oxidation of N-methyl-*p*-aminophenol (metol) with active oxygen generated *in situ* on graphite cathodes and different metal oxide anode materials has been studied at different pH. Indirect oxidation of N-methyl-*p*-aminophenol with active oxygen at different pH values has been demonstrated to result in effective mineralization to $CO_2$ and $H_2O$. In acidic electrolyte in presence of $Fe^{2+}$ ions the oxidation is accompanied with formation of oxalate complexes of iron stable to oxidation.

## INTRODUCTION

Aromatic amines are employed as starting compounds in production of dyes and medicines, as well as developers in photography, and, therefore, they are typical hydrosphere pollutants. The permissible level of pollution with N-methyl-*p*-aminophenol (metol) in water is 0.05 mg/L. It is generally accepted that for organic substances the most promising method of waste treatment is the oxidation with eco-friendly oxidizers ($O_3$, $H_2O_2$, UV), which do not afford additional compounds in the purified water.

It is known that electrochemical waste treatment with highly reactive intermediates generated *in situ* from $O_2$, $H_2O_2$ and $H_2O$ currently acquires growing popularity due to high efficiency and ecological safety [1–3]. The occurrence of coupled electrochemical reactions results in generation of highly reactive radicals $HO^•$, $HO_2$, which act as active centres involving organic substrates in chemical oxidation of varying depth. These reactions proceed either through addition of the $HO^•$ radical to the acceptor molecule S, or through hydrogen atom abstraction from the acceptor molecule SH:

$$^•OH + S \rightarrow {}^•SOH \rightarrow \text{products} \quad (1)$$

$$^•OH + SH \rightarrow {}^•S + H_2O \rightarrow \text{products} \quad (2)$$

It is known [3] that on Pt, $Pb/PbO_2$, $Sn/SnO_2$, $Mn/MnO_2$ and similar anodes the formation of $HO^•$ and $HO_2$ radicals occurs by the following reactions:

$$H_2O - \bar{e} \rightarrow HO^• + H^+ \quad (3)$$

$$HO_2^- - \bar{e} \rightarrow HO_2^• \quad (4)$$

$$H_2O_2 - \bar{e} \rightarrow HO_2^• + H^+ \quad (5)$$

On introduction of $Fe^{2+}$ ions in the solution the electrochemical variation of the Fenton scheme is realized yielding the most reactive $HO^•$ radicals by the reaction

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^• \quad (6)$$

Apart from participation in oxidation processes, $HO^•$ radicals are also involved in recombination affording hydrogen peroxide:

$$HO^• + HO^• \rightarrow H_2O_2 \quad (7)$$

Metol is known to undergo destructive oxidation with hydrogen peroxide according to the following scheme:

$$2C_7H_9NO + 35H_2O_2 \rightarrow 14CO_2 + N_2 + 44H_2O \quad (8)$$

References [4–6] present the results of oxidation of N-methyl-*p*-aminophenol under photo-Fenton reaction conditions $UV/H_2O_2$ at 60 °C and photocatalytic oxidation with $TiO_2/H_2O_2$.

It has been found that under these conditions metol oxidation is accompanied by formation of a number of intermediate products – different cyclic carbonyl compounds, carboxylic acids, which further are oxidized to $CO_2$ and water.

The purpose of this study is the investigation of indirect electrochemical oxidation of N-methyl-*p*-aminophenol with active oxygen generated *in situ* from $H_2O_2$, $O_2$ and $H_2O$ in alkaline and acidic electrolytes with employment of platinum, lead dioxide anodes, as well as oxide ruthenium-titanium anodes (ORTA).

## EXPERIMENTAL

The experiments were carried out in an electrochemical cell having no separator. A graphite rod was used as the cathode ($S$ = 3 $cm^2$) with Pt, Pb/$PbO_2$ and ORTA anodes. The lead anode was prepared by anodic oxidation of a lead plate 2 × 10 × 25 mm in 0.7 M solution of $H_2SO_4$ at current 1 A during 1 h [7]. According to powder XRD, the composition of the coating was a mixture PbO–α-$PbO_2$ (3 : 1).

0.1 M and 0.2 M NaOH solutions were used as alkaline electrolytes, and 1 M solution of $Na_2SO_4$ acidified with 10 % $H_2SO_4$ to pH 2–3 with addition of iron (II) sulphate ($C_{Fe}^{2+}$ = $0.4 \cdot 10^{-3}$ mg/L) was used as the acidic electrolyte, electrolyte temperature was (35±2) °C.

The oxidation of test solutions of metol was carried out at currents 300 and 600 mA. The starting concentration of metol was 100, 500, 1000, and 2000 mg/L.

The evolution of the concentration of metol and other organic intermediates during the electrolysis was monitored by measuring chemical oxygen demand (COD) [8]. The composition of the oxidation products was analysed by UV spectroscopy.

## RESULTS AND DISCUSSION

During interpretation of the obtained results the dependence of Faradic efficiency on the amount of transferred charge was used, as represented by the formula given in Refs. [9–11]:

$\eta = \Delta \mathrm{COD} V F/(8 I \Delta t)$

where COD is chemical oxygen demand, mg/L; $V$ is the volume of the electrolyte, L; $F$ is the Faraday's constant; $I$ is current, A; $\Delta t$ is electrolysis time, s.

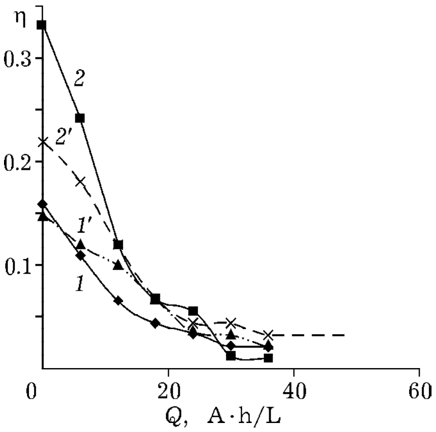

Fig. 1. Faraday efficiency (η) of metol oxidation at different pH values *vs.* amount of transferred charge (metol concentration 500 mg/L, Pt anode). Hydrogen peroxide concentration, mol/L: 0(1, 1′), 0.1 (2, 2′); pH value: 2–3 (*1*, *2*), 9–10 (*1*′, *2*′).

Figure 1 illustrates the dependencies of evolution of Faraday efficiency on the amount of transferred charge for anodic oxidation of metol and indirect electrochemical oxidation with addition of hydrogen peroxide ($C_{H_2O_2}$ = 0.1 mol/L); the initial concentration of metol was 500 mg/L. It can be seen that on direct anodic oxidation the efficiency η is relatively low and equals to 0.15 in the beginning of the electrolysis, apparently, due to low concentration of $HO^{\bullet}$. On addition of $H_2O_2$ the efficacy of oxidation increases and reaches 0.22 at pH 9–10 and 0.33 at pH 2–3 in the beginning of the electrolysis.

The variation of Faraday efficiency with hydrogen peroxide concentration is shown in Fig. 2. As one can see, the increase in hydrogen peroxide concentration from 0.1 to 0.2 mol/L does not significantly affect the oxidation efficiency either in acidic ($\eta_{init}$ = 0.33) or alkaline electrolytes ($\eta_{init}$ = 0.22–0.26). Most likely, such a low efficiency of the process is related to the competition between the anodic oxidation of hydrogen peroxide and the processes of direct oxidation of metol. Similar results have been obtained by us earlier on oxidation of phenol in 0.1 M NaOH solution at $C_{H_2O_2}$ = 0.1 mol/L [12].

Figure 3 presents the dependence of Faraday efficiency of metol oxidation on its initial concentration with addition of hydrogen per-

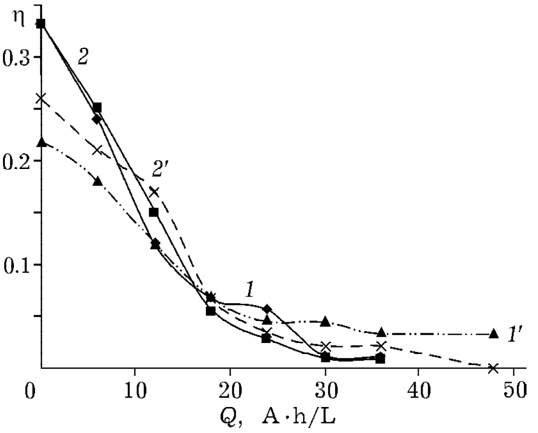

Fig. 2. Faraday efficiency (η) of metol oxidation at different pH values *vs.* hydrogen peroxide concentration (current 600 mA, metol concentration 500 mg/L, Pt anode). $C_{H_2O_2}$, mol/L: 0.1 (*1*, *1'*), 0.2 (*2*, *2'*); pH value: 2–3 (*1*, *2*), 9–10 (*1'*, *2'*).

oxide and at different pH values. Apparently, the efficiency of metol oxidation depends on the substrate concentration. So, for example, at metol concentration 500 mg/L the value of η is 0.33, while at metol concentration of 2000 mg/L the Faraday efficiency approaches 0.98 in solutions with pH 2–3. For solutions with pH 9–10 with metol concentrations 500 and 2000 mg/L the value of η is 0.18 and 0.96, respectively. The shape of the curves prompts the existence of a correlation between the Farady efficiency of oxidation and the substrate concentration.

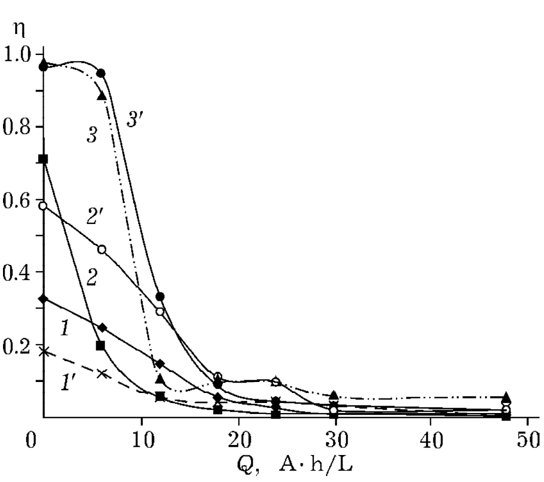

Fig. 3. Faraday efficiency (η) of metol oxidation with hydrogen peroxide ($C_{H_2O_2}$ = 0.2 mol/L) at different pH values *vs.* metol concentration (current 600 mA, Pt anode). Metol concentration, mg/L: 500 (*1*, *1'*), 1000 (*2*, *2'*), 2000 (*3*, *3'*); pH value: 2–3 (*1*–*3*), 9–10 (*1'*–*3'*).

The variation of efficiency of metol oxidation in dependence on the nature of the anode material at different pH values is shown in Fig. 4. Indirect oxidation was carried out with addition of hydrogen peroxide ($C_{H_2O_2}$ = 0.1 mol/L) at initial concentration of metol equal to 1000 mg/L. It is evident that at pH 2–3 the most effective anode material is platinum (η = 0.82). Lead dioxide anodes and ORTA have lower but close efficiency (0.52 and 0.5, respectively). Most likely, the electrochemical variant of the Fenton scheme is realized on oxidation of metol with the platinum anode (reaction (4)). At pH 9–10 the Pb/PbO$_2$ anode material appears to be the most efficient (η = 0.93). When ORTA and Pt anodes are used, the value of η is 0.88 and 0.68, correspondingly.

Figure 5 presents the results of determination of Faraday efficiency of metol oxidation with molecular oxygen, when, apart from di-

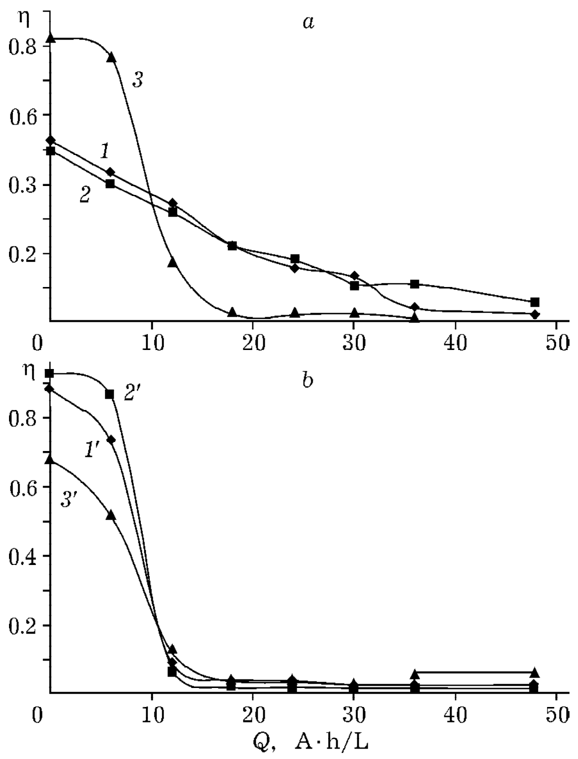

Fig. 4. Faraday efficiency (η) of metol oxidation with hydrogen peroxide ($C_{H_2O_2}$= 0.2 0.2 mol/L) at pH 2–3 (*a*) and 9–10 (*b*) *vs.* anode material (current 600 mA, metol concentration 1000 mg/L): *1*, *1'* – ORTA; *2*, *2'* – Pb/PbO$_2$; *3*, *3'* – Pt.

rect oxygen oxidation, reactions (1)–(3) occur in the solution. When oxygen is bubbled through the cell solution, the reaction of reduction of oxygen to hydrogen peroxide takes place at the graphite cathode, concentrations being 0.002 mol/L at pH 2–3 and 0.006 mol/L at pH 9–10. The starting concentration of metol was 1000 mg/L. The dependencies of Faraday efficiency on the amount of transferred charge indicate that at pH 9–10 the oxidation is more efficient on $Pb/PbO_2$ anodes ($\eta$ = 0.93), then on ORTA ($\eta$ = 0.91)) and Pt ($\eta$ = 0.78); at pH 2–3 – on $Pb/PbO_2$ anodes ($\eta$ = 0.95), ORTA ($\eta$ = 0.85) and Pt ($\eta$ = 0.7).

To verify that metol is oxidized to $CO_2$ and water, the evolved gas was collected and analysed according to [8]. The results obtained give evidence that in the alkaline electrolyte metol mineralization yields $CO_2$ and $H_2O$ with efficiency of 98 %.

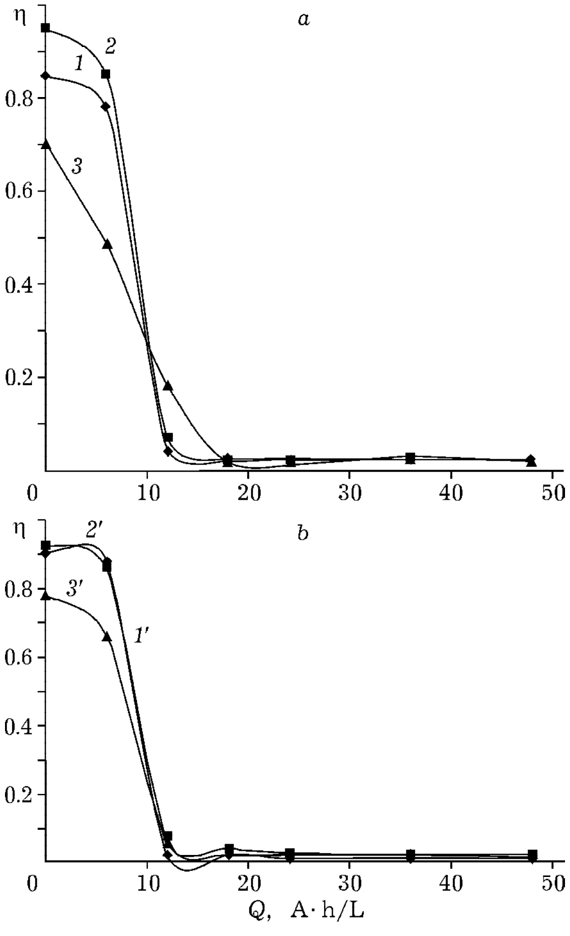

Fig. 5. Faraday efficiency ($\eta$) of metol oxidation with oxygen at pH 2–3 (*a*) and 9–10 (*b*) *vs.* anode material (current 600 mA, metol concentration 1000 mg/L): *1, 1′* – ORTA; *2, 2′* – $Pb/PbO_2$; *3, 3′* – Pt.

UV spectroscopy data indicate that metol oxidation through oxidative polymerisation of the starting material does not dominant. Oxidation of metol at different pH values occurs through different pathways of sequential oxidation: at pH 2–3 carboxylic intermediates are predominantly formed, at pH 9–10 – metol hydroxylation products further transforming into aliphatic acids, which are oxidized into $CO_2$ and water.

A similar scheme of metol oxidation was reported in Refs. [6, 13]. When $Fe^{2+}$ cations are present in the initial solution, the oxidation of the organic substrate is accompanied with appearance of $Fe^{3+}$ cations having absorption bands of their own in the UV region. These transitions overlap with absorption bands of organic products and have higher intensities, hampering the identification of organic materials. The presence of oxalic acid in the product of the substrate oxidation was confirmed by the qualitative reaction [14]. $Fe^{2+}$ cations are known to form stable complexes with oxalic acid anions.

## CONCLUSIONS

It has been demonstrated that N-methyl-*p*-aminophenol can be oxidized at different pH with active oxygen generated *in situ* from oxygen, hydrogen peroxide and water using graphite cathodes and different anode materials. Indirect electrochemical oxidation on a platinum anode with employment of hydrogen peroxide is more efficient in acidic electrolyte than direct anode oxidation (98 and 60 %, respectively).

Indirect oxidation of metol with hydrogen peroxide has been found to occur efficiently in alkaline electrolyte affording $CO_2$ and $H_2O$ with mineralization extent 98 %, while in acidic electrolyte it is 80 % due to formation of oxidation-proof iron oxalate complexes.

It has been shown that the best anode material for metol oxidation with hydrogen peroxide at pH 2–3 is platinum, and at pH 9–10 – $Pb/PbO_2$ (oxidation efficiency is 99 and 95 %, respectively).

On oxidation with oxygen at various pH values the best performance is demonstrated with $Pb/PbO_2$ anode material (oxidation efficiency is 98 %).

It has been established with UV spectroscopy that in the acidic electrolyte intermediate oxidation products of metol are different organic materials of carboxylic nature, and on addition of iron ions oxalate complexes are predominantly formed. In alkaline electrolyte the intermediate products are quinone, hydroquinone and organic acids.

## REFERENCES

1 D. Pletcher, *Acta Chem. Scand.*, 53 (1999) 754.

2 M. A. Oturan, *J. Appl. Electrochem.*, 30 (2000) 475.

3 E. Brillas, E. Mur, J. Casado, *J. Electrochem. Soc.*, 143 (1996) 49.

4 R. Andreozzi, V. Caprio, A. Insola, R. Marotta, *Water Res.*, 34 (2000) 463.

5 L. Lunar, D. Sicilia, S. Rubio, D. Perez-Bendito, *Ibid.*, 34 (2000) 1791.

6 M. Aceituno, C. D. Stalikas, L. Lunar *et al.*, *Ibid.*, 36 (2002) 3582.

7 E. A. Dzhafarov, Elektroosazhdeniye, svoystva i primeneniye okisi svintsa, Nauka, Moscow, 1967.

8 Yu. Lurie (Ed.), Unifitsirovannye metody analiza vod, Khimiya, Moscow, 1971.

9 M. Panizza, C. Bocca, G. Cerisola, *Water Res.*, 34 (2000) 2601.

10 J. Iniesta, P. A. Michaud, M. Panizza *et al.*, *Electrochim. Acta*, 46 (2001) 3573.

11 F. Montilla, P. A. Michaud, E. Morallon *et al.*, *Ibid.*, 47 (2002) 3509.

12 G. V. Kornienko, N. G. Maksimov, V. L. Kornienko, N. I. Pavlenko, *Chem. Sustain. Develop.*, 15 (2002) 303. http://www.sibran.ru/English/csde.htm

13 L. Lunar, D. Sicilia, S. Rubio *et al.*, *Water Res.*, 34 (2000) 3400.

14 R. Poludek-Fabini, T. Beirich, Organic Analysis [in Russian], Khimiya, Leningrad, 1981.