

# Photoelectrochemical treatment of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid at electrode covered with $\text{TiO}_2/\text{RuO}_2$

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## Abstract

Results of electrochemical oxidation of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid (H acid) show that the substrate is easily oxidised at titanium electrode covered with  $\text{TiO}_2/\text{RuO}_2$  than at platinum. The process should be carried out at potentials lower than the potential at which oxygen evolution starts. The reaction rate does not depend on pH in the range from 3.5 to 10. H acid is destroyed by 25% during electrochemical oxidation. Anion radical is one of the products of one-electron oxidation of the substrate. It quickly undergoes deprotonation. The final products of H acid oxidation are as follows:  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{SO}_4^{2-}$  and at least 7 other organic compounds – naphthalene derivatives. Electrochemical oxidation combined with photochemical reaction causes an increase in the conversion (calculated as a change in TOC) to about 50%. At the same time, COD value decreases by about 70%. Addition of  $\text{TiO}_2$  catalyst in dispersed form to the solution causes further decrease in TOC and COD to 55 and 75%, respectively.

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## 1. Introduction

1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (H acid) is one of the most important intermediate products used in the production of azo, direct and reactive dyes. Production of 1 ton of H acid results in  $18 \text{ m}^3$  of wastewater [1]. The wastewater contains, in addition to H acid, also various derivatives of naphthalene with amino, hydroxy, sulphonic and nitro substituents. The components of the wastewater are hard or not even biodegradable. Commonly used chemical and physico-chemical methods of treatment do not yield required results. Due to the lack of treatment methods for this kind of wastewater, much amount of production of H acid has been moved from European countries to

East and Southern-East Asia in the last 20 years [2]. Many methods for treatment of the wastewater from H acid production were suggested as a solution to this problem.

Photocatalytic oxidation decreases H acid content by 90% (initial concentration – 50 mg/l) during 5 h process [3]. Oxidation with Fenton's reagent ( $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ ) combined with coagulation results in 90% decrease in COD (initial value – 60 000 mg  $\text{O}_2/\text{l}$ ) [4,5]. Oxidation with Fenton's reagent combined with UV radiation in the presence of  $\text{TiO}_2$  yields a 60% decrease in COD from 300 mg  $\text{O}_2/\text{l}$  [6]. In the case of treatment of 2-naphthalenesulphonate sodium at the concentration of 26 mg/l, application of ozonation results in 15% decrease in TOC. A combination of ozonation with UV radiation leads to almost total mineralization of the substrate [7]. Application of electrochemical method and coagulation results in a decrease of TOC by 90% [5].

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None of the above mentioned methods were used on a large scale. In the case of reactive dyes and 1-aminonaphthalene-3,6-disulphonic acid, combination of the electrochemical oxidation with the photocatalytic degradation yields in higher effectiveness of the treatment method [8,9]. Thus, the application of these two combined methods can be suggested for treatment of especially toxic H acid.

Platinum electrode and titanium electrode covered with a mixture of titanium and ruthenium oxides called as dimension stable anodes (DSA) were applied in experiments [10]. RuO<sub>2</sub> shows metallic conductivity and electrocatalytic activity. On the other hand, TiO<sub>2</sub> is a photochemically active semiconductor.

## 2. Materials and methods

### 2.1. Chemicals

1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (H acid) is one of the intermediate products used in the production of azo dyes. Solution of H acid was obtained by dissolving the substrate (Institute of Dyes & Organic Products in Zgierz, Poland) in 0.1 mol l<sup>-1</sup> NaClO<sub>4</sub> (Fluka). The concentration of (H acid) solutions was in the range from 1 × 10<sup>-3</sup> to 5 × 10<sup>-3</sup> mol l<sup>-1</sup>. Solutions used in the determination of the effect of pH on H acid oxidation were prepared by dissolving the substrate in buffers. Solutions of H<sub>2</sub>SO<sub>4</sub> (Chempur, Poland) with Ag<sub>2</sub>SO<sub>4</sub> (POCh Gliwice, Poland), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (POCh Gliwice, Poland) and Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub> (POCh Gliwice, Poland) were used in the determination of COD.

### 2.2. Electrolytic and photocatalytic degradation experiments

Cyclic and differential pulse voltammetries [11,12] were used in electrochemical measurements with an AUTOLAB (Ecochemie, Holland) analytical set. A three electrode cell was applied in all experiments. Titanium electrode covered with TiO<sub>2</sub> (70%) and RuO<sub>2</sub> (30%) and platinum electrode was used as a working electrode. Platinum electrode was a cathode. Potential of the working electrode was measured vs. saturated calomel electrode (SCE). Before the measurements, the solutions were purged with argon in order to remove dissolved oxygen. During measurements argon blanket was kept over solutions.

Differential capacity was measured using a method of electrochemical impedance spectroscopy (module FRA in AUTOLAB set). Electrode potential was changed every 25 mV in the applied potential range.

Preparative oxidation of a substrate was carried out in a cell with undivided electrode compartments under

galvanostatic conditions. Photoelectrochemical oxidation was also carried out in the same cell inserted into a reactor RPR 200 (Southern New England Ultraviolet Co.). The reactor was equipped with 8 lamps (35 W) emitting radiation with the wavelength of 254 nm. Results of the substrate oxidation were analysed by determining the changes in the chemical oxygen demand (COD), total organic carbon (TOC) and absorbance from UV–VIS spectra.

### 2.3. Analytical methods

The total organic carbon (TOC), chemical oxygen demand (COD) and UV–VIS spectra in the solutions were determined before and after the electrolyses. TOC was analysed with TOC 5050A Shimadzu Total Organic Carbon Analyser. COD was determined according to the procedure described in Ref. [12]. UV–VIS spectra were recorded in the wavelength range from 190 to 800 nm using UV–VIS Spectrophotometer Shimadzu UV-24001 PC. Products of the electrochemical oxidation were analysed using a method of liquid chromatography. Chromatographic data were collected and recorded using a Spectra System (Thermo Separation System, USA) with C18 Vydac column. The chromatographic conditions were as follows: flow-rate 1 cm<sup>3</sup> min<sup>-1</sup>, detection – UV adsorption at 232 nm, volume injected – 100 μl, room temperature. The mobile phase composition was water and trifluoroacetic acid (0.05%).

## 3. Results and discussion

Basic information about the course of electrochemical reaction is provided by the dependence of the current on the potential. The dependence presented in Fig. 1 shows that oxidation of the substrate starts at a potential of about 0.5 V. Oxidation of H acid at platinum electrode proceeds in at least two steps and is

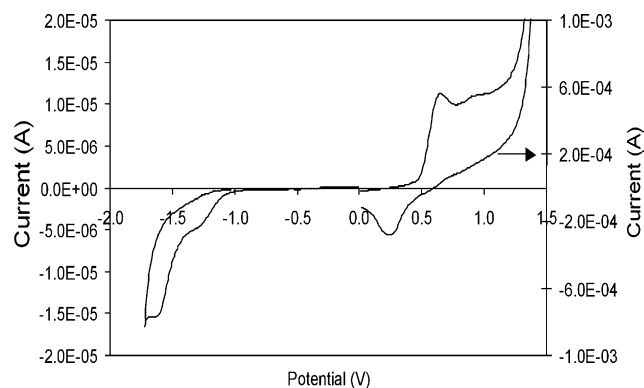


Fig. 1. Cyclic voltammograms of H acid oxidation at platinum (right axis) and reduction at mercury electrode (left axis);  $c = 5 \times 10^{-3}$  mol dm<sup>-3</sup> in 0.1 mol dm<sup>-3</sup> NaClO<sub>4</sub>,  $v = 0.01$  V s<sup>-1</sup>.

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