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Photoelectrochemical treatment of 1-amino-8-hydroxynaphthalene-3,6-disulphonic acid at electrode covered with TiO_2/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 TiO_2/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: CO_2, H_2O, NH_3, 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 TiO_2 catalyst in dispersed form to the solution causes further decrease in TOC and COD to 55 and 75%, respectively.

Keywords: H acid; Photoelectrochemical oxidation; Platinum electrode; $Ti/TiO_2/RuO_2$ electrode

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 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 (Fe^{2+}, H_2O_2) combined with coagulation results in 90% decrease in COD (initial value – 60 000 mg O_2/l) [4,5]. Oxidation with Fenton's reagent combined with UV radiation in the presence of TiO_2 yields a 60% decrease in COD from 300 mg O_2/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_2 shows metallic conductivity and electrocatalytic activity. On the other hand, TiO_2 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^{-1} $NaClO_4$ (Fluka). The concentration of (H acid) solutions was in the range from 1×10^{-3} to 5×10^{-3} mol l^{-1}. 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_2SO_4 (Chempur, Poland) with Ag_2SO_4 (POCh Gliwice, Poland), $K_2Cr_2O_7$ (POCh Gliwice, Poland) and $Fe(NH_4)_2(SO_4)_2$ (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_2 (70%) and RuO_2 (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^3 min^{-1}, 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

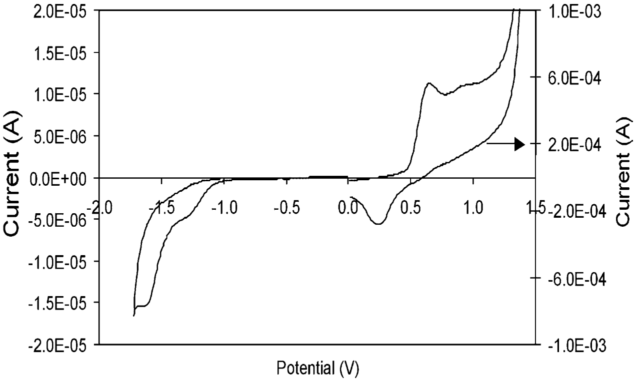


Fig. 1. Cyclic voltammograms of H acid oxidation at platinum (right axis) and reduction at mercury electrode (left axis); $c = 5 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$, $v = 0.01$ V s^{-1}.

irreversible. The substrate is also reduced at a mercury electrode starting from the potential of about −1.0 V. Two peaks of the cyclic curve confirm that there are at least two steps in this reaction. Using a method with higher resolution, e.g. differential pulse voltammetry, it was found that except for two peaks visible in the cyclic voltammograms, the third peak of oxidation at a potential close to the potential of oxygen evolution could be detected. The peaks (Fig. 2 — dependence of the current on the potential) characterise at least three electrode reactions at potentials of 0.5, 0.8 and 1.1 V.

Current densities for the first step of the substrate oxidation at a platinum and titanium electrode covered with TiO_2/RuO_2 are comparable. Comparison of the oxidation effects at both electrodes (Fig. 3) indicates an easier oxidation of the substrate at the titanium electrode covered with TiO_2/RuO_2 by about 100 mV and higher rate of the first step of oxidation at the specified potential. The substrate is adsorbed at the platinum (Fig. 2, curve 3) and titanium electrode covered with TiO_2/RuO_2 (Fig. 3, curve 3) starting with the initial scan potentials (0 V). Increase in the potential of the platinum electrode results in an increase in the adsorption with the maximum coverage at a potential of about 0.2 V. While Faradaic reaction starts at a potential of 0.45 V, pseudo-capacitive adsorptive–desorptive peak is observed in curves $C = f(E)$ (Fig. 2). This fact indicates desorption of the substrate from the electrode surface at the beginning of oxidation of the substrate which diffuses to the electrode.

In the applied potential range, maximum adsorption was observed at a potential of 0 V at the titanium electrode covered with TiO_2/RuO_2 (Fig. 3, curve 3). If potential increases from 0 to about 0.4 V, adsorption decreases, which is proved by an increase in the capacity (Fig. 3, curve 3). Simultaneously, an increase in Faradaic current of the reaction (Fig. 3, curve 2) is observed. While desorption of the substrate is observed at curves $C = f(E)$, a current peak of diffusing substrate is shaped at cyclic voltammograms.

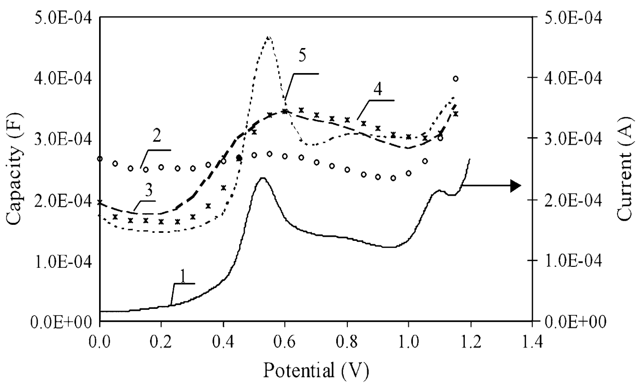


Fig. 2. Differential capacity vs. the electrode potential (left axis); curves: 2 — electrolyte, 3 — $c = 0.1 \times 10^{-3}$ mol dm^{-3}, 4 — $c = 0.5 \times 10^{-3}$ mol dm^{-3}, 5 — $c = 1.0 \times 10^{-3}$ mol dm^{-3} of H acid at platinum electrode. Differential pulse voltammogram of H acid oxidation (right axis); $c = 5 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$ — curve 1.

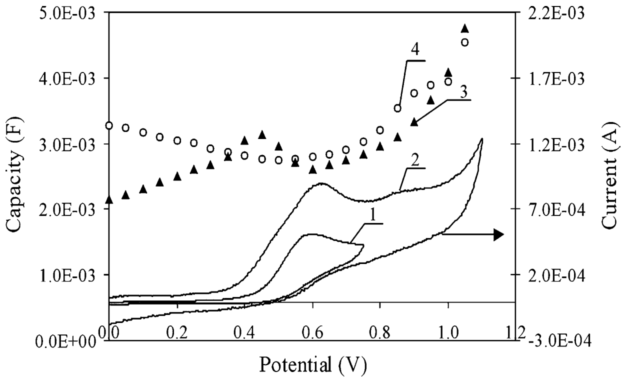


Fig. 3. Cyclic voltammograms of H acid oxidation; $c = 5 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$, $v = 0.01$ V s^{-1}; curves: 1 — recorded at platinum, 2 — at titanium covered with TiO_2/RuO_2. Differential capacity vs. the potential measured at $Ti/TiO_2/RuO_2$ electrode, curves: 3 — H acid $c = 5 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$, 4 — 0.1 mol dm^{-3} $NaClO_4$.

Almost complete desorption of the substrate from the electrode surface with the start of the Faradaic reaction allows to analyse the peak currents as currents resulting from the substrate diffusion. The lack of the effect of the adsorption in the potential range, where peaks are shaped, is also proved by a dependence of the peak current on the square root of the scan, which is linear and crosses the origin of the coordinates. This dependence is linear to scan rate of 0.05 V s^{-1} and about 0.6 V s^{-1} at the titanium electrode covered with TiO_2/RuO_2 and the platinum electrode, respectively (Fig. 4).

3.1. Effect of pH

Wastewater arising from H acid production is acidic (pH about 3). Therefore, it is necessary to neutralise it

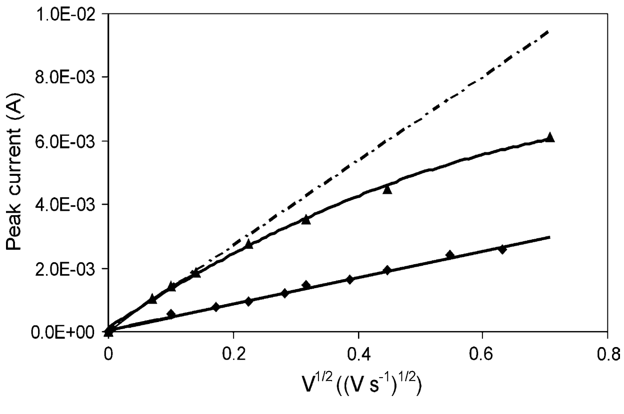


Fig. 4. Dependence of the peak current on the square root of scan rate for H acid solution in 0.1 mol dm^{-3} $NaClO_4$; ◆ — platinum electrode, ▲ — $Ti/TiO_2/RuO_2$ electrode.

before its disposal to surface water. It is important to decide if neutralisation should take place before or after electrochemical oxidation. For that reason determination of pH effect on oxidation of H acid, the main component of the wastewater, is necessary.

It was found that if pH of medium increases, then oxidation of H acid is easier (lower oxidation potential) – Fig. 5, curve 1. Dependence of $E_{1/2}$ on pH can be divided into three regions. For pH values lower than 3.5, $\mathrm{d}E_{1/2}/\mathrm{dpH}$ is 58. $\mathrm{d}E_{1/2}/\mathrm{dpH}$ is almost independent of pH in the range from 3.5 to 10. For pH values higher than 10, $\mathrm{d}E_{1/2}/\mathrm{dpH}$ is equal to 116. The rate of the first step of the substrate oxidation almost does not depend on pH (Fig. 5, curve 2). In the pH range 3.5–10, the limiting current of the reaction vs. concentration of hydrogen ions is almost constant. For pH values lower than 3.5, the reaction rate increases by about 15%.

3.2. Effect of substrate concentration on reaction rate

Concentration of H acid in wastewater can vary. Therefore, the influence of the concentration on the rate of the first step of the substrate oxidation was determined.

This dependence, presented as a change in logarithm of current at the specified potential vs. logarithm of substrate concentration, in fact shows the order of electrode reaction (Fig. 6). Under conditions similar to the conditions of linear diffusion, the order of the reaction is 0.68 and 0.85 at the titanium electrode covered with TiO_2/RuO_2 and the platinum electrode, respectively.

Heterogeneous rate constants k_{bh} [13] determined at the half-wave potential (0.546 V) are equal to 0.967×10^{-3} and 1.04×10^{-3} cm s^{-1} at the titanium electrode covered with TiO_2/RuO_2 and the platinum electrode, respectively.

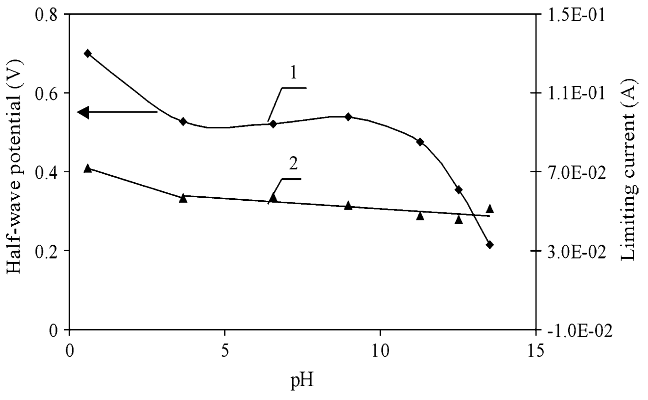


Fig. 5. Dependence of $E_{1/2}$ (curve 1 – the left axis) and the limiting current (curve 2 – the right axis) on pH for H acid; $c = 5 \times 10^{-3}$ mol dm^{-3}, platinum electrode.

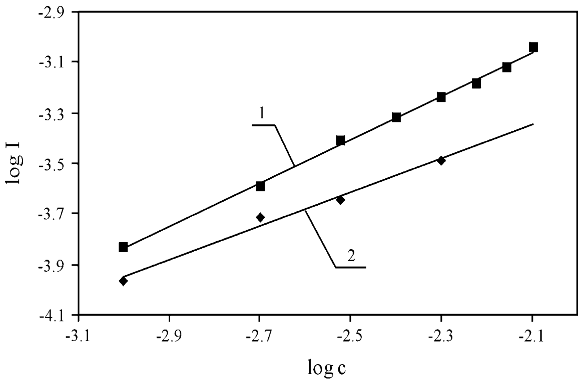


Fig. 6. Dependence of the logarithm of the current for H acid oxidation at constant potential on the logarithm of the substrate concentration; $v = 0.01$ V s^{-1}, $E = 0.5$ V; curves: 1 – titanium covered with TiO_2/RuO_2, 2 – platinum electrode.

3.3. Effect of potential – reaction products

It results from the dependences presented in Figs. 1 and 2, that the substrate is oxidised in at least three steps at potentials lower than the potential of oxygen evolution. Of course, at potentials higher than 1.4 V, the three above mentioned steps take place. However, other possible reactions cannot be identified in curves of potential vs. current, due to the evolution of oxygen. The influence of the potential on the oxidation of H acid was analysed on the basis of changes in the absorbance from UV–VIS spectra, COD, TOC and current of the first peak in cyclic voltammogram. Products of the electrochemical oxidation were analysed using a method of liquid chromatography. Voltammograms recorded at the platinum anode in the solutions after oxidation of the substrate in the potential range from 0.7 to 1.0 V and at electrical charge of 8 As passing through the cell, show a decrease in the current of the peak which characterises the first step of two-electron oxidation of the substrate (Fig. 7, curve 2).

A decrease in 50% of the first peak current with a simultaneous decrease in the absorbance at the wavelength of 234 nm and formation of a new band at the wavelength of 440 nm (Fig. 8, curve 2) show formation of the products of one-electron oxidation. In order to confirm this fact, one-electron oxidation of H acid was carried out in an aqueous solution using a method of pulse radiolysis. Radiation of the aqueous solution of KBr (saturated with nitrogen suboxide) with high-energetic electron beams resulted in formation of anion radical $Br_2^{-\bullet}$ according to the following reactions [14,15]:

$$Br^{-} + HO^{\bullet} \rightarrow (BrOH)^{-\bullet} \qquad (1)$$

$$(BrOH)^{-\bullet} \rightarrow Br^{\bullet} + OH^{-} \qquad (2)$$

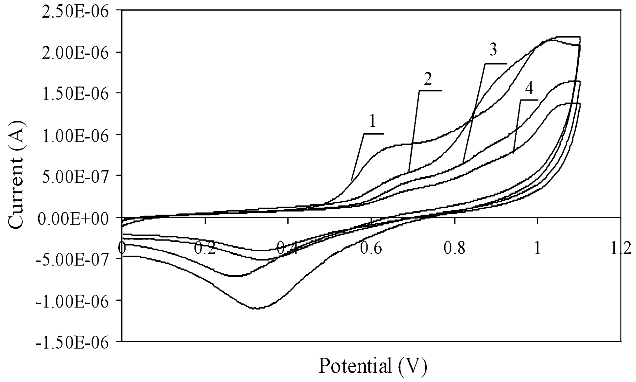


Fig. 7. Cyclic voltammograms recorded in the solutions after H acid oxidation at various potentials; curves 1 – initial solution, 2 – 0.7 V, 3 – 1.2 V, 4 – 1.4 V; $c = 1 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$, platinum electrode.

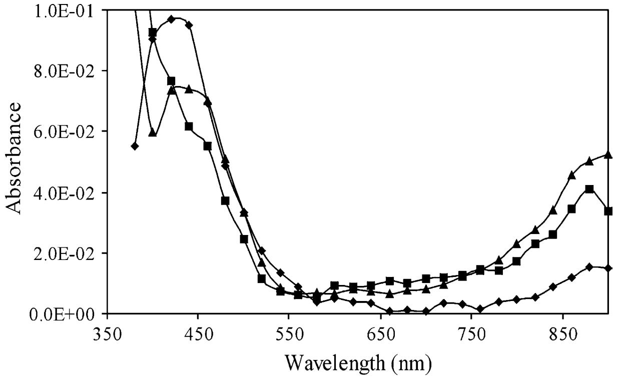


Fig. 9. UV–VIS spectra of the products recorded during one-electron oxidation of H acid using a method of pulse radiolysis; ■ – 3 μs, ▲ – 10 μs, ◆ – 0.6 ms.

$$\overset{\bullet}{Br} + Br^{-} \rightarrow Br_2^{-\bullet} \tag{3}$$

Next, dibromide anion radical oxidised the substrate:

$$Br_2^{-\bullet} + A \rightarrow 2Br^{-} + A^{+\bullet} \tag{4}$$

Products of the process were analysed with the application of UV–VIS spectrophotometry.

Analysis of UV–VIS spectra presented in Fig. 9 yields a conclusion that two products are formed during one-electron oxidation of H acid. The first product is formed in 3 μs and is characterised by absorption bands at the wavelengths of 440 and 870 nm. Concentration of this product increases after 10 μs. A new product is formed in 0.6 ms and its absorbance at the wavelength of 440 nm increases. Simultaneously, the band at 870 nm decreases.

UV–VIS spectrum recorded after 0.6 ms of one-electron oxidation (Fig. 9) is similar to the spectrum recorded in the solution after oxidation at 0.7 V (Fig. 8, curve 2). This indicates the formation of two products (anion radical and anion radical after deprotonation) in one-electron oxidation of H acid at the potential of 0.7 V. The second product (anion radical after deprotonation) is stable.

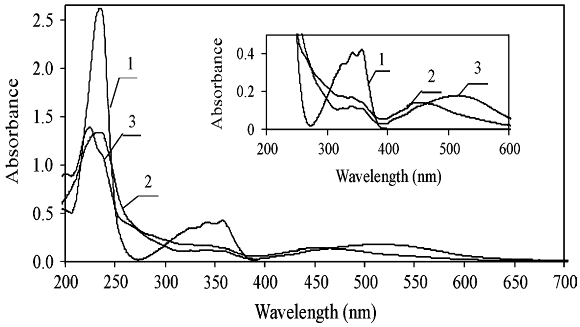
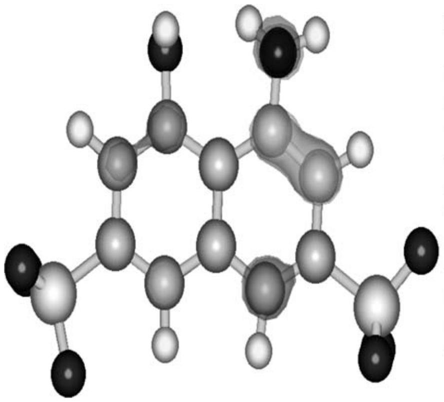


Fig. 8. UV–VIS spectra recorded in the solutions after electrolyses in a cell with divided electrode compartments, at various anode potentials and at anode surface of 20 cm^2; curves: 1 – initial solution, 2 – 0.7 V, 3 – 1.2 V.

Oxidation of the substrate in the potential range from 0.7 to 1.0 V at electrical charge of 8 As (enough to total two-electron conversion of the substrate) is characterised by a significant decrease in the absorbance comparable to a decrease in the current with regard to the character and value. A decrease in COD (about 10%) during oxidation indicates the formation of products, which show less oxygen demand than the substrate. The lack of changes in TOC proves that the substrate does not undergo destruction with evolution of CO_2. Thus, it can be suggested that in the above mentioned potential range only amino and/or hydroxyl group is oxidised and formation of a radical is the first step.

Half-wave potentials ($E_{1/2}$) determined for aminonaphthalene-3,6-disulphonic and hydroxynaphthalene-3,6-disulphonic acids were 0.745 and 0.779 V, respectively. These values show that amino group should be oxidised first. Approximate quantum-chemical calculations (Hyperchem and Amsol [16]) were carried out for an ion of the substrate taking into consideration hydration (SM1 model [17,18]). Hydration allowed to achieve better correlation of oxidation potential ($E_{1/2}$) vs. HOMO energy [19,20]. The results of the calculations indicate that electron density for HOMO orbital (the highest occupied molecular orbital), which shows the susceptibility to oxidation, is the highest at C1–C2 and C1–N bond (Fig. 10). A net charge at nitrogen atom (−0.298) is higher than at oxygen atom in OH group (−0.265). Results of ^{13}C NMR measurements for the substrate also show higher electron density at C1 atom bonded with nitrogen atom than the density at C8 atom, which forms a bond with oxygen atom. This confirms that amino group should be oxidised first.

The band characteristic for radicals is not observed in spectra recorded in solutions after oxidation at potentials in the range from 1.0 to 1.4 V. However, a new band



NMR ^{13}C Spectrum

C	ppm
C1	138,96
C2	106,47
C3	124,59
C4	116,69
C5	116,69
C6	140,52
C7	106,47
C8	151,52
C9	117,63
C10	133,18

Fig. 10. Distribution of electron density of HOMO orbital in H acid anion. Chemical shifts for carbon atoms determined from ^{13}C NMR spectrum.

appears at a wavelength of 520 nm. Simultaneously, absorbance at a wavelength of 234 nm decreases (Fig. 8, curve 3). The value of absorbance at 520 nm increases with an increase in the potentials of the substrate oxidation in the above mentioned potential range. Voltammograms recorded in the solutions after the substrate oxidation at the potential range from 1.0 to 1.4 V show that current of the first peak decreases to about 50%. Currents of weakly shaped II and III peaks also decrease (Fig. 7 curve 3 and 4). These facts indicate formation of other products of the reaction. The changes are accompanied by a decrease in COD what proves “deeper” oxidation of the substrate. Simultaneously, TOC also decreases and this decrease is due to total destruction of the substrate with the evolution of CO_2, H_2O, NH_3 and SO_4^{2-}. Analyses of the solutions obtained after oxidation at the potential range from 1.4 to 2.0 V indicate a decrease in the process effectiveness expressed as a decrease in conversion calculated as a change in COD and TOC. This effect is caused by the fact that an electrical charge is used for more intensive evolution of oxygen.

The influence of oxygen evolution on the process effectiveness is shown by changes in the absorbance, COD and TOC during electrolyses at various electrical charges and at a potential of 1.4 V and 2.0 V. At the potential of 1.4 V, evolution of oxygen is almost not observed in contrary to the potential of 2.0 V. Results of the measurements at various electrical charges and at the above mentioned potentials are presented in Table 1. Data in Table 1 show that at the same electrical charge, process effectiveness at 2.0 V is about 40% lower in absorbance changes and 3 times lower in COD changes than at 1.4 V. Analyses of TOC values prove that only part of the substrate was completely oxidised. At higher potentials (2.0 V) and low electrical charges, TOC almost does not change. In order to obtain destruction degree of the substrate to CO_2 similar to a degree obtained at low potential (1.4 V), it is necessary to carry out electrolyses at the electrical charge 4 or 5 times higher. Electrical charge of 23.3 As applied at the potential of 1.4 V totals 14.1% of theoretical charge (165.6 As) necessary for the total oxidation of the substrate to CO_2, H_2O and NH_3. The conversion of the substrate to the above mentioned products is 11.89% (as a change in TOC). It means that the electrical charge is used in 85% for the total oxidation of the substrate and in 15% for other products present in the solution. Thus, it was found that a significant part of the electrical charge is used for total oxidation of the substrate at potentials in the range from 1.1 to 1.4 V.

Table 1

Conversion of H acid obtained at various electrical charges and analysed as a change in: absorbance – $\eta_{\text{Abs.}}$ (%), COD – η_{COD} (%) and TOC – η_{TOC} (%), anode – Pt, $c = 1 \times 10^{-3}$ mol dm^{-3} in 0.1 mol dm^{-3} $NaClO_4$, $E = 1.4$ and 2.0 V

Q (As)	$\eta_{\text{Abs.}}$ (%), $\lambda = 234$ nm	η_{COD} (%)	η_{TOC} (%)
$E = 1.4$ V			
3.00	13.81	4.82	1.81
6.00	36.78	10.84	4.39
14.40	67.94	33.73	8.56
23.30	72.82	46.98	11.89
$E = 2.0$ V			
6.00	24.12	3.10	4.00
14.40	38.42	9.82	4.20
23.30	54.74	15.66	4.51
40.75	58.79	16.87	5.99
92.75	67.99	22.89	7.85
134.25	70.68	27.71	9.59

Chromatographic analyses yield a conclusion that after electrolyses (23.3 As) the peak which corresponds to the substrate (retention time of 2.6 min.) is not observed at chromatograms. However, seven new peaks appear (Fig. 11). UV spectra were recorded for products characterised by these peaks.

In order to identify reaction products (*P*1–*P*7), theoretical UV–VIS spectrum for possible products of two-electron oxidation of H acid was calculated. A comparison of the spectra obtained as a result of the experiments (scanning) with the theoretical spectra resulted in a

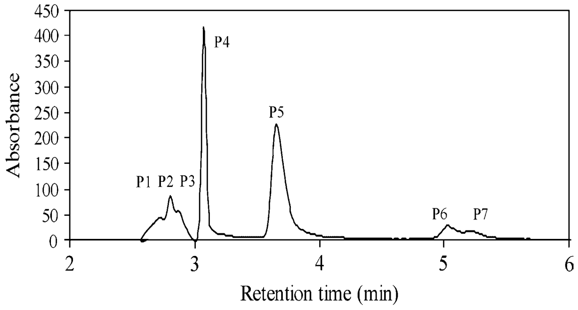
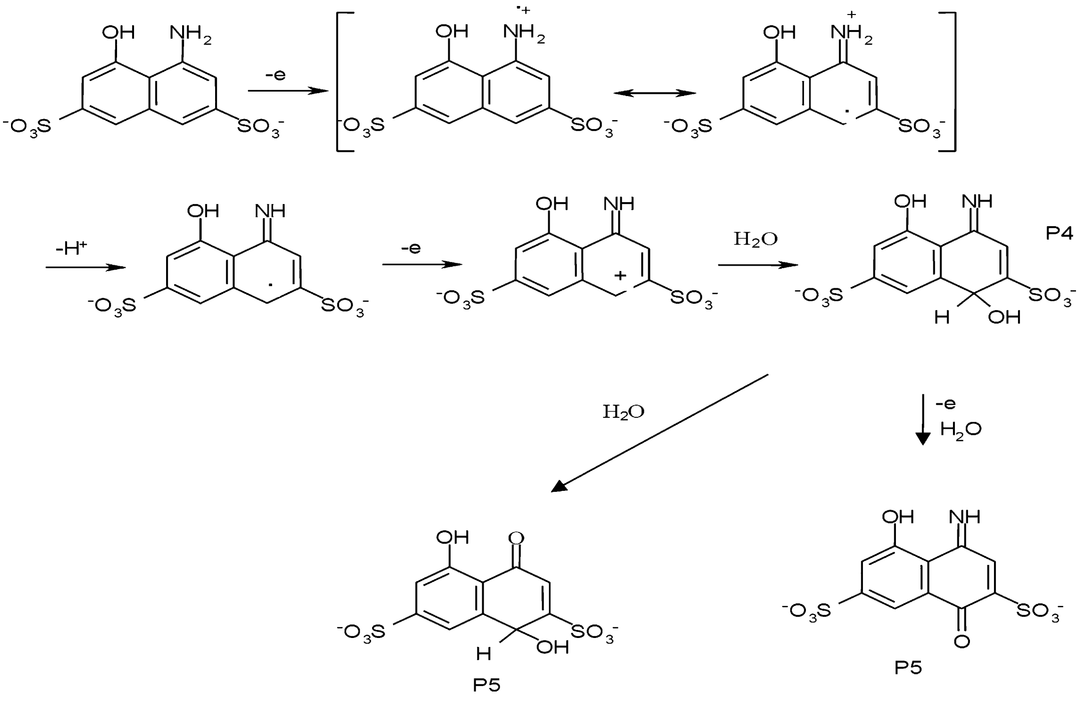


Fig. 11. Chromatogram recorded in H acid solutions after electrochemical oxidation at 1.4 V and 23 As.



Scheme 1.

suggestion of two reaction products: *P*4 – 4-hydro-4,8-dihydroxy-1-iminonaphthalene-3,6-disulphonic acid and *P*5 – 8-hydroxy-1-imino-4-oxynaphthalene-3,6-disulphonic acid or 4-hydro-4,8-dihydroxy-1-oxynaphthalene-3,6-disulphonic acid.

The results of the experiments and calculations allowed to suggest the following scheme of H acid oxidation if two electrons are involved in the process (Scheme 1).

3.4. Photoelectrochemical oxidation

In order to investigate effectiveness of photoelectrochemical oxidation of H acid, influence of various parameters on electrochemical oxidation was determined first.

Results of the voltammetric investigations show that in the first and third step of H acid oxidation the peak current density is about 1.0×10^{-3} A cm^{-2}. These steps take place before the potential at which oxygen evolution starts. In order to determine the effect of the current density on the substrate conversion, the electrolyses were carried out at the current intensity of 0.4 A and with various anode surface area (2–60 cm^{2}).

The dependence of the conversion on the current density is presented in Fig. 12. This dependence shows that the conversion is almost constant for the current density ranging from 0.007 to 0.020 A cm^{-2}. An increase in the current density to 0.1 A cm^{-2} causes a decrease in the conversion. Thus, further experiments were carried out at the current density of 0.02 A cm^{-2}.

The effect of the process temperature on the substrate conversion was determined under the following conditions: anode surface area – 20 cm^{2}, electrolyte volume – 60 cm^{3}, and electrolysis duration – 4 h. Dependence of the H acid conversion on the temperature is presented in Fig. 13. This dependence shows that an increase in the process temperature to 80 °C causes an increase in the substrate conversion.

The effect of the electrical charge on the substrate conversion was determined at the current density of 0.02 A cm^{-2} and temperature of 70 °C. The results of experiments are presented in Fig. 14. The substrate conversion increases with an increase in electrolysis duration (electrical charge) to 4 h. Further increase in duration causes only slight increase in the conversion.

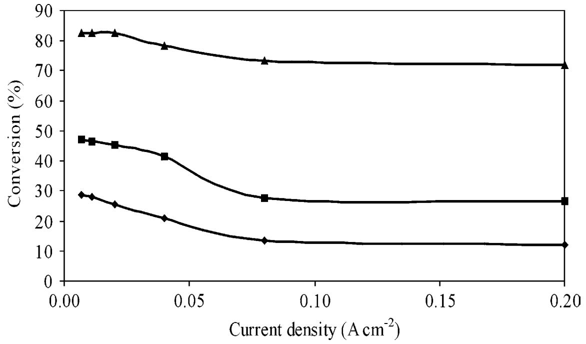


Fig. 12. Dependence of H acid conversion on the electrolysis current density; the conversion was calculated as a change in: ◆ – TOC, ■ – COD, ▲ – absorbance, anode – Pt, electrolyte volume – 60 cm^{3}, temperature – 50 °C, current intensity – 0.4 A.

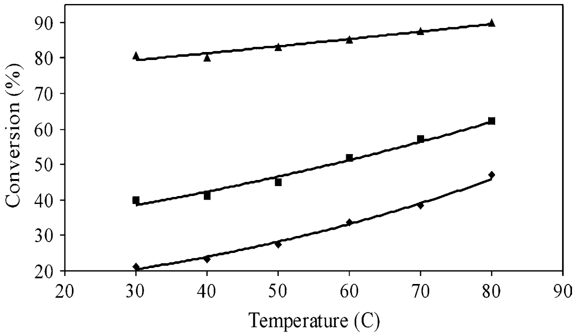


Fig. 13. Dependence of H acid conversion on the electrolysis temperature; the conversion was calculated as a change in: ◆ – TOC, ■ – COD, ▲ – absorbance, anode – Pt, electrolyte volume – 60 cm^3, electrolysis duration – 4 h, current density – 0.02 A cm^{-2}.

Table 2
Dependence of H acid conversion on the process type

Process type	η_{TOC} (%)	η_{COD} (%)	$\eta_{Abs.}$ (%)
Electrolysis, anode – Pt	26.5	42.7	87.6
Electrolysis, anode – $Ti/TiO_2/RuO_2$	25.6	48.1	88.2
UV – $Ti/TiO_2/RuO_2$	1.0	8.3	35.3
UV – $Ti/TiO_2/RuO_2$ + TiO_2 catalyst	7.9	23.8	42.4
Electrolysis + UV, anode – Pt	36.5	55.9	87.1
Electrolysis + UV, anode – $Ti/TiO_2/RuO_2$	48.6	67.9	92.4
Electrolysis + UV, anode – $Ti/TiO_2/RuO_2$ + TiO_2 catalyst	54.3	75.0	97.5

Conversion was calculated as a change in: TOC – η_{TOC} (%), COD – η_{COD} (%) and absorbance – $\eta_{Abs.}$(%), anode – Pt or $Ti/TiO_2/RuO_2$, electrolyte volume – 60 cm^3, temperature – 70 °C, current density – 0.02 A cm^{-2}, electrolysis duration – 4 h, λ = 254 nm (8 lamps).

Intensification of the electrochemical oxidation was achieved by an application of the titanium electrode covered with TiO_2/RuO_2 inserted into a photochemical reactor.

Effects of photoelectrochemical oxidation on the substrate conversion were determined under the same parameters as in the electrochemical oxidation, i.e., current density – 0.02 A cm^{-2}, anode surface area – 20 cm^2, process temperature – 70 °C. The results of the experiments are presented in Table 2.

The substrate conversions achieved in the electrochemical oxidation at the platinum electrode and titanium electrode covered with TiO_2/RuO_2 are comparable. The conversion calculated as a change in TOC and obtained in simultaneous oxidation at a platinum electrode and photochemical reaction is equal to 36.5% and is higher than the conversion (25.6%) achieved in the electrochemical oxidation under the same conditions. This fact proves easier electrochemical oxidation of the excited substrate. Photoelectrochemical oxidation at the titanium electrode covered with TiO_2/RuO_2 resulted in the substrate conversion of 48.6%, which is higher in comparison to the conversion (36.5%) achieved in the photoelectrochemical oxidation at the platinum electrode. This proves photocatalytic effect of TiO_2 present at the anode surface. An addition of TiO_2 in dispersed form to the substrate solution causes further increase in the conversion to about 54.3%. The comparison of H acid oxidation effects achieved in the electrochemical and photoelectrochemical reaction is presented in Fig. 14.

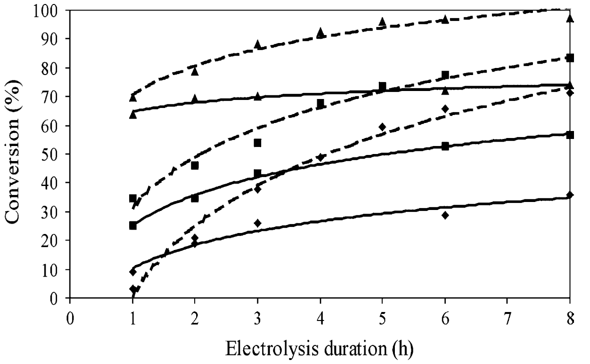


Fig. 14. Dependence of H acid conversion on the electrolysis duration (electrical charge); conversion was calculated as a change in: ◆ – TOC, ■ – COD, ▲ – absorbance; — electrochemical process, - - - photoelectrochemical process, electrolyte volume – 60 cm^3, temperature – 70 °C, current density – 0.02 A cm^{-2}, $Ti/TiO_2/RuO_2$ electrode.

The rate of decrease in TOC, COD and absorbance vs. reaction time is higher in the photoelectrochemical process than in electrochemical process.

4. Conclusions

The oxidation of the substrate is irreversible and starts at the potential of 0.5 V vs. SCE. The reaction proceeds in at least three electrode steps before the potential of oxygen evolution.

The substrate is oxidised easily in the first step at a titanium electrode covered with TiO_2/RuO_2 than at a platinum electrode. The rate of the first step of the substrate oxidation at the specified potential is also higher at a titanium electrode covered with TiO_2/RuO_2. This rate is almost independent of pH. The order of the reaction vs. substrate concentration is 0.68 and 0.85 at a platinum electrode and a titanium electrode covered with TiO_2/RuO_2, respectively.

Heterogeneous rate constants k_{bh} determined at half-wave potentials are equal to 0.967×10^{-3} and 1.04×10^{-3} cm s^{-1} at a titanium electrode covered with TiO_2/RuO_2 and a platinum electrode, respectively.

The process of total oxidation of the substrate should be carried out at potentials lower than the potential at which oxygen evolution starts.

The conversion of H acid in the electrochemical oxidation with application of the platinum electrode and titanium electrode covered with TiO_2/RuO_2 is comparable. Under the specified parameters of the electrochemical oxidation, the conversion of the substrate calculated as a change in TOC, COD and absorbance is about 26, 45 and 88%, respectively.

Simultaneous application of the electrochemical and photochemical oxidation causes an increase in the effectiveness of H acid treatment analysed as a change in TOC and COD to 49 and 68%, respectively.

An application of dispersed TiO_2 as the catalyst in the photoelectrochemical oxidation causes further increase in the conversion of H acid. This fact proves catalytic effect of TiO_2 present at the anode surface and in the solution – in dispersed form.

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References

[1] Knaul SN, Nandy T, Deshpande CV, Srivastava A, Shastry S, Szpyrkowicz L. Application of full-scale evaporation–incineration technology for hazardous wastewater. Water Sci Technol 1998;38: 363–72.

[2] Vilas AM, Suresh K. Adoption of cleaner technologies for manufacturing H-acid. Chem Eng World 1999;34:51–4.

[3] Yu G, Zhu W, Yang Z, Li Z. Semicondutor photocatalytic oxidation of H-acid aqueous solution. Chemosphere 1998;36(12): 2673–81.

[4] Wanpeng Z, Yang ZY, Li W. Application of ferrous–hydrogen peroxide for the treatment of H-acid manufacturing process wastewater. Water Res 1996;30(12):2949–54.

[5] Socha A, Chrzescijanska E, Kusmierek E, Paryjczak T, Farbotko J. In: Morais C, Texeira F, Vasconcelos L, editors. Proceeding of international water conference IWC2001; Porto. p. 423–9.

[6] Xiao Y, Wang G, Liu H, Zhao H, Chang J, Sun C, et al. Treatment of H-acid wastewater by photo-Fenton reagent combined with a biotreatment process: a study on optimum conditions of pretreatment by a photo-Fenton process. Bull Environ Contam Toxicol 2002;69:430–5.

[7] Chen YH, Chang CY, Huang SF, Chiu CY, Yi D, Shang NC, et al. Decomposition of 2-naphthalenesulfonate in aqueous solution by ozonation with UV radiation. Water Res 2002;26: 4144–54.

[8] Pelegrini R, Peralta-Zamora P, De Andrade AR, Reyes J, Duran N. Electrochemically assisted photocatalytic degradation of reactive dyes. Appl Catal B Environ 1999;22:83–90.

[9] Socha A, Chrzescijanska E, Kusmierek E. Electrochemical and photoelectrochemical treatment of 1-aminonaphthalene-3,6-disulphonic acid. Dyes Pigments 2005;67:71–5.

[10] Ardizzone S, Trasatti S. Interfacial properties of oxides with technological impact electrochemistry. Adv Colloid Interface Sci 1996;64:173–251.

[11] Seralathan M, Osteryoung RA, Osteryoung JG. General equivalence of linear scan and staircase voltammetry. Electroanal Chem 1987;222:69–100.

[12] Hermanowicz W, Dojlido J, Dozanska W, Koziorowski B, Zerbe J. Fizyczno-chemiczne badanie wody i sciekow. Warszawa: Arkady; 1999.

[13] Galus Z. Fundamentals of electrochemical analysis. Horwood: PWN; 1994. p. 242–44, 284–304.

[14] Hasagawa K, Neta P. Rate constants and mechanisms of reaction of Cl_2^- radicals. J Phys Chem 1978;82:854–7.

[15] Mamou A, Rabani J, Behar D. On the oxidation of aqueous Br^- by OH radicals, studied by pulse radiolysis. J Phys Chem 1977;81:1447–8.

[16] HyperChem v. 7.0 and Amsol v. 6.5.1. manuals.

[17] Cramer CJ, Truhlar DG. An SCF solvation model for the hydrophobic effect and absolute free energies of solvation. Science 1992;256:213–7.

[18] Cramer CJ, Truhlar DG. General parameterized SCF model for free energies of solvation in aqueous solution. J Am Chem Soc 1991;113:8305–11.

[19] Socha A. Electrochemical reaction of anthraquinone-1,5-disulphonate sodium salt. Pol J Chem 1995;69:756–65.

[20] Socha A. Electrochemical reaction of 1,8-anthraquinonedisulphonate potassium salt. Pol J Chem 1998;72:766–76.