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Electrochemical and photoelectrochemical treatment of 1-aminonaphthalene-3,6-disulphonic acid

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Abstract

1-Aminonaphthalene-3,6-disulphonic acid (ANDS) is one of the components in the wastewater produced during the synthesis of H-acid used in production of various dyes. Electrochemical oxidation of this wastewater can be an interesting alternative to other treatment methods, especially if it is combined with photochemical oxidation. Cyclic and differential pulse voltammetry was used in the determination of the kinetic parameters of the process. EIS method was used in the investigation of the adsorption at a platinum electrode. The first step of the ANDS electrooxidation proceeds in at least one step and is irreversible. The substrate is adsorbed at an electrode with the maximum coverage of its surface at the potential of 0.25 V. At the potential of 0.6 V the substrate is desorbed from the surface. An increase in pH causes the reaction of the first step to proceed easier but does not change its rate. Electrochemical oxidation of the substrate causes a decrease in TOC and COD by 18 and 36%, respectively. Results of the ANDS electrochemical oxidation can be improved by combining this method with photochemical oxidation. This yields a decrease in TOC and COD by 40.0 and 58.3%, respectively.

Keywords: 1-Aminonaphthalene-3,6-disulphonic acid; Electrochemical oxidation; Photoelectrochemical oxidation

1. Introduction

1-Aminonaphthalene-3,6-disulphonic acid (ANDS) is one of the by-products formed during the synthesis of H-acid (1-amino-8-hydroxynaphthalene-3,6-disulphonic acid) which is commonly used in the synthesis of azo, reactive dyes, etc. Pure ANDS can be obtained by reductive hydrolysis of Koch acid (1-aminonaphthalene-3,6,8-trisulphonic acid) [1]. ANDS is easily soluble in water and alcohol. Salts of ANDS are also easily soluble in water and show slight blue fluorescence. This compound is one of the components of wastewater produced during the synthesis of H-acid. Wastewater formed during this synthesis is toxic to the living organisms and is characterised by high values of COD and low BOD/COD ratio [2–4]. Biological, physical and chemical methods commonly used in the treatment of industrial wastewater are not efficient in the case of wastewater from H-acid production [4]. This wastewater is hazardous to the environment. Electrochemical oxidation of sulphonic derivatives of naphthalene can be an interesting alternative to other treatment methods, especially if it is combined with photochemical oxidation at titanium electrode covered with TiO_2/RuO_2. This method does not require application of additional chemicals as opposed to other methods [5].

The aim of the investigation was to improve the effectiveness of ANDS treatment using electrochemical oxidation combined with photoelectrochemical oxidation.

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2. Materials and methods

2.1. Chemicals

1-Aminonaphthalene-3,6-disulphonic acid is one of the intermediate products used in the production of azo dyes. Solution of ANDS was obtained by dissolving this substrate (Institute of Dyes & Organic Products in Zgierz, Poland) in 0.1 mol L^{-1} $NaClO_4$ (Fluka). The concentration of ANDS solutions was in the range from 1×10^{-3} to 8×10^{-3} mol L^{-1}. Solutions used in the determination of the effect of pH on ANDS 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. Analytical methods

Determination of the kinetic parameters of the ANDS oxidation was carried out using staircase cyclic and differential pulse voltammetry methods. Voltammetric curves were recorded at platinum, titanium covered with TiO_2/RuO_2 and hanging mercury drop electrode (HMDE) using Autolab (EcoChemie, Holland) analytical instrument. Prior to the measurements the solutions were deoxidised by purging with argon for 15 min. The electrode potential was measured vs. saturated calomel electrode (SCE). Differential capacity was determined by electrochemical impedance spectroscopy (EIS) using a FRA Autolab module.

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 [6]. UV–vis spectra were recorded in the wavelength range from 190 to 800 nm using UV–vis spectrophotometer Shimadzu UV-24001 PC.

2.3. Electrolytic and photocatalytic degradation experiments

Investigation of the electrochemical oxidation of the substrate was carried out in an electrochemical cell with undivided electrode compartments. Platinum or titanium covered with TiO_2/RuO_2 was used as an anode. Platinum was used as a cathode. Photoelectrochemical oxidation of the substrate was carried out in the same electrochemical cell placed in the photochemical reactor Rayonett RPR-200 (Southern New England Ultraviolet Co.). The reactor was equipped with 8 lamps emitting radiation at the wavelength of 254 nm.

3. Results and discussion

The preliminary information about the course of the reaction can be obtained by investigating the dependence of the reaction current on the electrode potential. Example voltammograms of ANDS oxidation and reduction are presented in Fig. 1.

The oxidation of ANDS at the platinum electrode proceeds in at least one step before potentials reach the value at which the oxygen evolution starts and is irreversible. The process starts at the potential of 0.6 V vs. SCE. In the reverse scan a current peak at the potential of 0.3 V is formed. The presence of the current peak indicates reduction of the products formed during oxidation. The substrate is reduced at the mercury electrode (HMDE). Peaks in the voltammograms prove that at least two electrode processes take place. Reduction of ANDS starts at the potential of −1.25 V (Fig. 1).

An application of the voltammetric method with the higher resolution, e.g. differential pulse voltammetry, yields voltammograms of ANDS oxidation with one peak which corresponds to at least one electrode step of the reaction (Fig. 2, curve 1).

The electrochemical impedance spectroscopy method used in the experiments revealed that ANDS was adsorbed starting with the initial values of the electrode polarisation potential (Fig. 2). An increase in the electrode potential causes an increase in the adsorption with the maximum coverage of platinum at 0.25 V. A Faradaic reaction starts at the potential of 0.6 V. At this potential also an adsorptive–desorptive peak is observed in the curves of differential capacity. The presence of this peak confirms desorption of the substrate from the electrode surface. The adsorption within the potential range where peaks of ANDS oxidation are formed had no effect. This fact can be confirmed by observing the linear dependence of the peak current on the square root of the scan rate (Fig. 3). The dependence

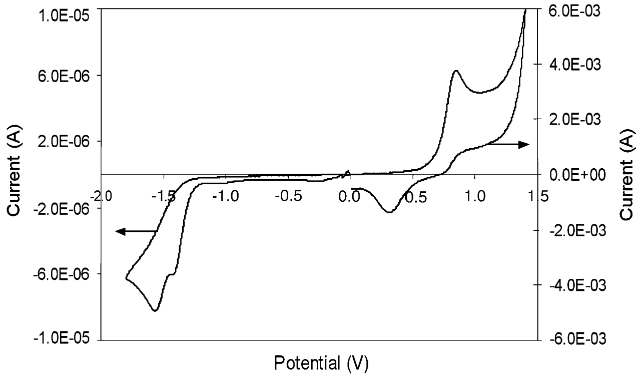

Fig. 1. Voltammograms of ANDS oxidation at platinum and ANDS reduction recorded at a mercury electrode; $c = 1.0 \times 10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v = 0.01$ V s^{-1}.

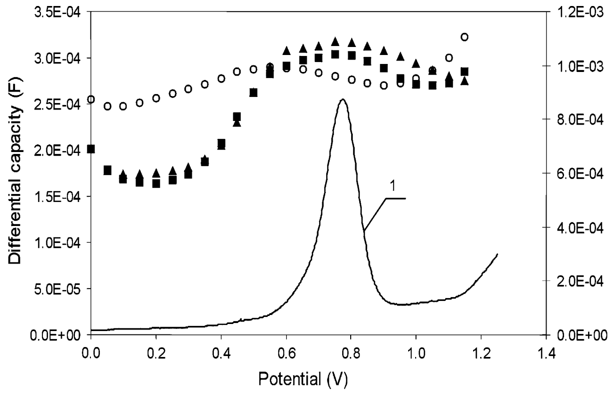

Fig. 2. Differential pulse voltammogram (curve 1) of ANDS oxidation recorded at platinum; $c = 5.0 \times 10^{-3}$ mol L^{-1} (0.1 mol L^{-1} $NaClO_4$), $v = 0.01$ V s^{-1}. Differential capacity dependence on the electrode potential; ○ – electrolyte, ■ – ANDS $c = 1.0 \times 10^{-3}$ mol L^{-1}, ▲ – ANDS $c = 2.0 \times 10^{-3}$ mol L^{-1}.

shows that the peak current of the ANDS oxidation at platinum is proportional to the square root of the scan rate. The process is controlled by diffusion because the dependence crosses the origin of the coordinates. Almost complete desorption of the substrate at the potential, at which the Faradaic reaction starts, enables the analysis of the peak currents obtained as a result of the substrate diffusion to the electrode.

Concentration of the substrate in the wastewater can vary. Thus, its effect on the reaction rate is important. A dependence of the logarithm of the current at the specified potential on the logarithm of the substrate concentration presents an order of the reaction (Fig. 4). The order of the substrate oxidation at platinum and titanium covered with TiO_2/RuO_2 does not change with the change in the potential. The lack of changes in the curve slope at various potentials indicates that there are no changes in the mechanism of the electrode reaction. The value of the order is 0.79 at platinum electrode and 0.74 at titanium electrode covered with TiO_2/RuO_2. Thus, it is possible to determine the constant rate of the first step of the oxidation. Heterogeneous rate constant k_{bh} [7] for the first step of the oxidation, determined at a half-wave potential at platinum electrode is 1.05×10^{-3} cm s^{-1}.

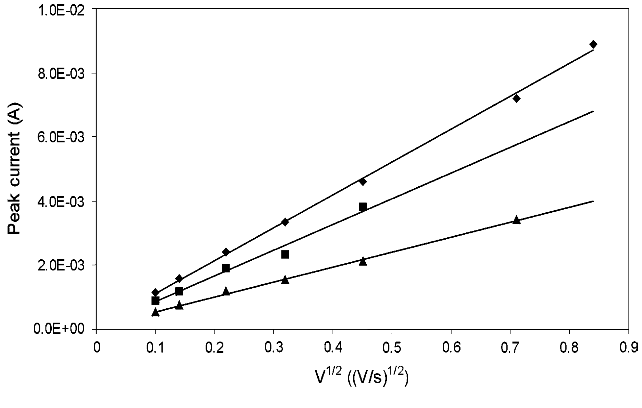

Fig. 3. Dependence of the peak current in ANDS oxidation at platinum on the square root of the scan rate; ▲ – $c = 3.0 \times 10^{-3}$ mol L^{-1}, ■ – $c = 5.0 \times 10^{-3}$ mol L^{-1}, ◆ – $c = 8.0 \times 10^{-3}$ mol L^{-1}.

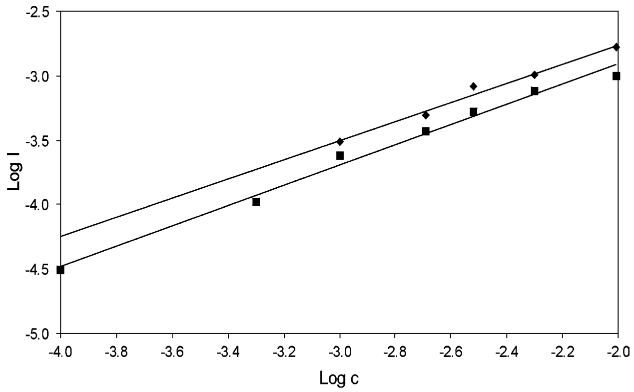

Fig. 4. Dependence of the current logarithm in oxidation of ANDS at a constant potential ($E = 0.74$ V) on the logarithm of the substrate concentration; $v = 0.01$ V s^{-1}, ■ – platinum electrode, ◆ – titanium electrode covered with TiO_2/RuO_2.

Wastewater formed during the production of H-acid is acidic. Before the disposal of the wastewater to the surface water receiver, it is necessary to neutralise it. It is also important to decide if the wastewater should be neutralised before or after electrochemical oxidation. Thus, investigation of the pH effect on the ANDS oxidation (one of wastewater components) was carried out. pH of the solutions was varied from 0.3 to 13.7. Some cyclic voltammograms of the ANDS oxidation in solutions at different pH values are presented in Fig. 5. An increase in pH of the solutions causes the reaction of the ANDS oxidation to proceed easier.

A dependence of a half-wave potential on pH of solutions in the ANDS oxidation (Fig. 6) can be divided

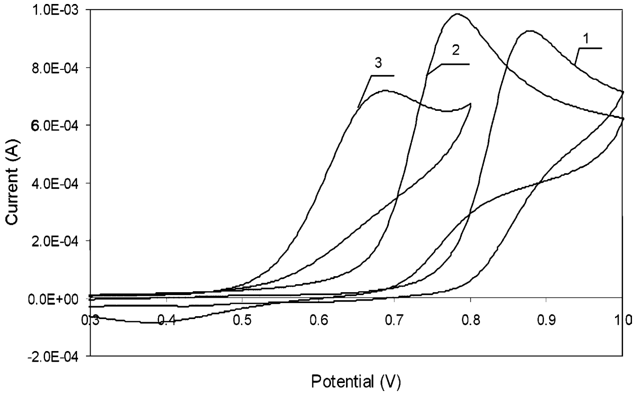

Fig. 5. Cyclic voltammogram of ANDS oxidation at platinum electrode; $c = 5.0 \times 10^{-3}$ mol L^{-1}, $v = 0.01$ V s^{-1}, curve 1 – pH = 0.6, 2 – pH = 7.0, 3 – pH = 12.5.

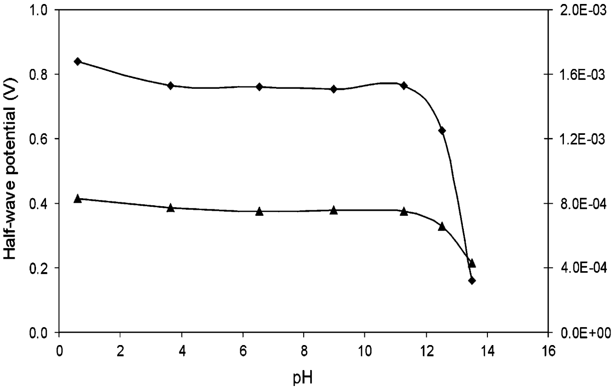

Fig. 6. Dependence of $E_{1/2}$ (◆ – left axis) and the limiting current (▲ – right axis) on pH in ANDS oxidation; $c = 5 \times 10^{-3}$ mol L^{-1}, $v = 0.01$ V s^{-1}, platinum electrode.

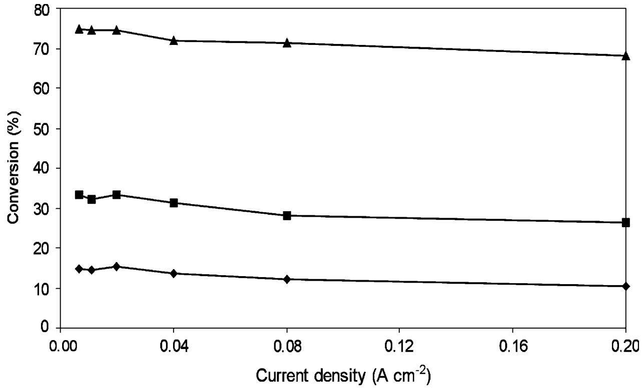

Fig. 7. Dependence of the ANDS conversion on the current density. Conversion was calculated as a change in TOC – ◆, COD – ■ and absorbance – ▲; platinum anode, $c = 1 \times 10^{-3}$ mol L^{-1}, volume of solution – 60 mL.

into three regions. In the range of low pH values (lower than 3.5), d$E_{1/2}$/dpH totals 29. Half-wave potential is almost constant in the pH range from 3.5 to 11.0. At pH values higher than 11, d$E_{1/2}$/dpH = 262. The rate of the first step of the substrate oxidation is almost independent of the pH. In the pH range from 0 to 11 the order of the oxidation vs. concentration of hydrogen ions is almost 0.

Oxidation proceeds easier in the solutions with pH values of 7.0. Thus, taking into consideration the necessity of the wastewater neutralisation, further investigation was carried out in the neutral medium.

Current density in the first step of the ANDS oxidation at the platinum electrode and with low scan rate is 0.9×10^{-3} A cm^{-2}. In order to verify the suggested current density, electrolyses were carried out at the current intensity in the range from 0.05 to 0.70 A. It appeared that the current intensity of 0.4 A should be used in further investigations (at constant electrode surface of 20 cm^2, which corresponds to the current density of 2.0×10^{-2} A cm^{-2}) for the specified cell geometry. This current density is sufficient for the consecutive steps of substrate oxidation, which takes place before the potential of oxygen evolution during the short duration electrolyses.

In order to determine the effect of the current density on the conversion of the substrate, electrolyses at the current intensity of 0.4 A and at anodes with surface area 2–60 cm^2 were carried out. An increase in the anode surface from 2 to 20 cm^2 causes almost linear increase in the conversion of the substrate. Further increase in the anode surface yields slight changes in the conversion (Fig. 7). Thus, further investigation was carried out at the current density of 2×10^{-2} A cm^{-2}.

Temperature has a significant influence on the efficiency of the process. The effect of temperature on the conversion of ANDS was investigated at the anode with surface area of 20 cm^2 (current density of 2.0×10^{-2} A cm^{-2}) used in 4 h electrolyses. The results of the experiments are presented in Table 1. An increase in the temperature causes slight increase in the efficiency of the substrate oxidation.

An application of platinum and titanium electrode covered with TiO_2/RuO_2 in the process of electrochemical oxidation yields comparable results. In order to intensify the electrochemical oxidation of ANDS, experiments with application of the titanium electrode covered with TiO_2/RuO_2 were carried out in a photoelectrochemical reactor. Under the parameters optimal for the electrochemical process (i.e. current density of 2.0×10^{-2} A cm^{-2}, anode surface area of 20 cm^2, temperature of 70 °C), investigation of photoelectrochemical oxidation was conducted. An effect of the dispersed TiO_2 on electrochemical oxidation of ANDS was also determined. The comparison of the results of electrochemical oxidation with photoelectrochemical oxidation is presented in Table 2.

The conversion of ANDS (calculated as a change in COD) in the photoelectrochemical oxidation (58%) is higher than in the process of electrochemical oxidation (36%). The application of the dispersed TiO_2 as a catalyst in the photoelectrochemical oxidation causes slight increase to 62% in ANDS conversion (Table 2). Electrolyses at various electrical charges, i.e. durations (Fig. 8) were carried out in the investigation of photoelectrochemical oxidation of ANDS.

Table 1
Dependence of ANDS conversion on the electrooxidation temperature

Temperature (°C)	η_{TOC} (%)	η_{COD} (%)	η_{Abs} (%)
30	13.83	35.14	76.76
40	16.45	33.78	76.76
50	15.67	33.58	77.82
60	15.23	35.14	78.21
70	17.63	36.48	78.93
80	18.75	36.48	78.93

Conversion of ANDS is presented as a change in TOC – η_{TOC}, COD – η_{COD} and absorbance – η_{Abs}; platinum anode, $c = 1 \times 10^{-3}$ mol L^{-1}, volume of solution – 60 mL.

Table 2
Dependence of ANDS conversion on the type of the process

Process type	η_{TOC} (%)	η_{COD} (%)	η_{Abs} (%)
Electrochemical oxidation	18.01	36.10	78.20
Photoelectrochemical oxidation	40.02	58.34	85.11
Photoelectrochemical oxidation + TiO_2	44.30	62.11	88.83

Conversion of ANDS is presented as a change in TOC – η_{TOC}, COD – η_{COD} and absorbance – η_{Abs}; titanium electrode covered with TiO_2/RuO_2, $c = 1 \times 10^{-3}$ mol L^{-1}, volume of solution – 60 mL, current density – 2.0×10^{-2} A cm^{-2}, temperature of 70 °C, electrolysis duration – 4 h.

The dependence presented in Fig. 8 shows that the conversion increases with an increase in the electrolyses duration (electrical charge) up to 4 h. Further increase in the duration causes only a slight increase in the conversion.

4. Conclusions

The investigation of the ANDS oxidation using electrochemical and photoelectrochemical methods resulted in the following conclusions:

1. Electrochemical oxidation of ANDS at the platinum electrode starts at the potential of 0.6 V vs. SCE and proceeds in at least one step. The reaction is irreversible. The substrate is reduced at HMDE also irreversibly and in at least two steps.
2. The substrate is adsorbed at platinum electrode beginning with the initial scan potentials with the maximum coverage at the potential of 0.25 V. At the potential of 0.6 V, the Faradaic reaction starts and the substrate is desorbed from the electrode surface. Linear dependence of the peak current on the scan rate crosses the origin of the coordinates and proves the diffusion control of the process.
3. The order of the reaction for the first step of the ANDS oxidation under conditions similar to the conditions of the linear diffusion at a platinum electrode does not change with electrode potential and totals 0.79. In the case of titanium electrode covered with TiO_2/RuO_2, the order of the reaction totals 0.74. Heterogeneous rate constant at the half-wave potential equals 1.05×10^{-3} cm s^{-1}.
4. If pH increases from 1 to 11, the reaction proceeds easier ($dE_{1/2}/dpH = 29$). The rate of the first step of the ANDS oxidation is almost independent of pH. In the range of pH values higher than 11, the slope $dE_{1/2}/dpH$ equals 262 and the reaction rate decreases significantly.
5. Two concurrent reactions, electrochemical and photochemical, result in an increase in the effectiveness of ANDS destruction. Electrochemical oxidation of the substrate causes a decrease in TOC by 18% and COD by 36%. Photoelectrochemical oxidation yields a decrease in TOC by 40% and COD by 58%. An application of dispersed TiO_2 as a catalyst in the photochemical reaction causes a decrease in TOC by 44% and COD by 62%. This indicates catalytic effect of TiO_2, which is present at electrode surface and in the solution in the dispersed form.

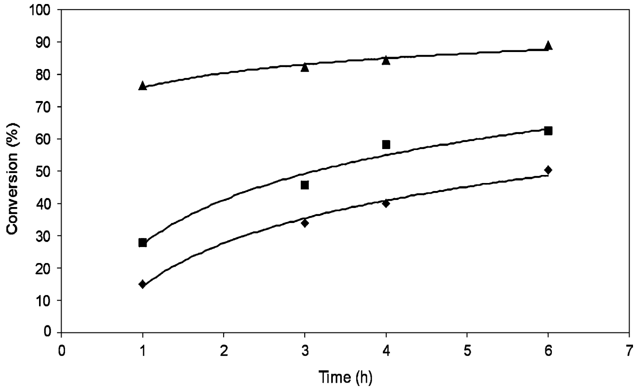

Fig. 8. Dependence of ANDS conversion on electrolysis duration (electrical charge) in photoelectrochemical process. Conversion was calculated as a change in TOC – ◆, COD – ■ and absorbance – ▲; TiO_2/RuO_2 anode, $c = 1 \times 10^{-3}$ mol L^{-1}, volume of solution – 60 mL; $j = 2 \times 10^{-2}$ A cm^{-2}, $t = 70$°C.

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