



Application of TiO₂–RuO₂/Ti electrodes modified with transition metal oxides in photoelectrochemical degradation of H-acid - synergetic effect

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ABSTRACT

Results of investigation of H-acid degradation in photoelectrochemical process with the application of TiO₂–RuO₂/Ti electrodes modified with transition metals oxides like: Nb₂O₅, ZrO₂ and Y₂O₃, are described. Comparison of H-acid conversion calculated as a change in COD and TOC in photocatalytic, electrochemical and photoelectrochemical process shows that the highest conversion was achieved in the photoelectrochemical process due to a significant synergetic effect. The synergetic effect in the photodegradation of H-acid was estimated as a parameter – synergetic factor (SF). It appeared that SF depended on current intensity applied in the photoelectrochemical degradation of H-acid and on modification of titanium electrodes. The highest synergetic effect was obtained in the case of TiO₂–RuO₂/Ti electrodes modified with Nb₂O₅ in the atmosphere of nitrogen and applied in the processes carried out at the current intensity of 0.3 A.

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1. Introduction

A lot of organic compounds, which occur in industrial wastewater, are hard biodegradable and very toxic for alive organisms in the aquatic environment. The wastewater often contains mixtures of various compounds arising from dyeing and chemical industry and strongly affects the natural environment [1,2].

1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (H-acid) is a semi-finished product applied mainly in dyeing industry for production of reactive dyes and in pharmaceutical industry for drugs production [3]. Reactive dyes are applied mainly in dyeing and printing of cellulosic fibers as well as in dyeing of polyamide and protein fibers [4,5]. Wastewater arising from H-acid and dyes production as well as formed in dyeing process, contains aromatic compounds with –NH₂, –OH, –NO₂, –SO₃ substituents, which are toxic to alive organisms in the aquatic environment. These compounds are not directly degraded and wastewater are not decolorized in biological treatment. A treatment degree of this wastewater achieved in commonly applied chemical and physical treatment is relatively low. Due to this fact, this wastewater is hazardous for the natural environment.

In the case of electrochemical method, total treatment of this wastewater requires so called “deep oxidation” resulting in high electrical energy consumption and high process costs [6–8]. An

application of a photoelectrochemical treatment and selection of a proper electrode material can be an alternative to currently applied treatment methods for this type of wastewater.

A decrease in process costs could be possible by among others the application of an electrode material with proper oxide semiconductor film which causes photoactivation of this electrode by radiation with the lowest energy including solar radiation. Solar radiation is commonly available and is a renewable energy source.

Nowadays, photoelectrochemistry of semiconductors concerning transformation of solar energy to electrical energy in electrochemical systems is developed [9]. Titanium electrodes belong to the group of electrodes called DSA (dimensionally stable anodes) [10,11]. They can be modified with transition metal oxides and are applied in electrochemical processes assisted by photocatalysis, due to high efficiency of these processes connected with their high synergetic effect [12–16]. These electrodes are obtained in a thermal process of ruthenium and titanium salts decomposition at titanium substrate previously prepared and resistant to oxidation [14,17]. Electrodes with oxide film containing not only TiO₂ (photocatalytic features) [18–21] and RuO₂ (electrocatalytic features) [12,20,22] but also such oxides as Nb₂O₅, ZrO₂, Y₂O₃ draw attention [9,17,18,23–25]. This modification has great influence on photocatalytic features of these electrodes due to shift of Fermi level toward conduction band and an increase of their specific surface. The above mentioned oxides are n-type semiconductors (donors) with band gap energy as follows: 3.4 eV (Nb₂O₅), 3.27 eV (ZrO₂) and 4.1 eV (Y₂O₃). Taking into consideration the potential of conduction band edge for these oxides, introduction of these oxides into electrode film containing TiO₂

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should cause a decrease in energy required for transfer of electrons from the valence band to conduction band. Results of the investigations prove that Ti/TiO₂-RuO₂ electrodes modified with Nb₂O₅, ZrO₂, Y₂O₃ oxides (conduction bands consisting of d-orbitals) are applied in photoelectrochemical processes as anodes and show higher efficiency of the process than electrodes modified with semiconductors with conduction band consisting of only s-orbitals [26]. Investigations of these electrodes activity seem to be very important due to their photocatalytic features and possibility of their application in the photoelectrochemical processes with radiation with the lowest energy, including solar radiation [16,26–29].

Investigations of electrochemical and photoelectrochemical features of H-acid at TiO₂-RuO₂/Ti electrodes modified with transition metal oxides is important due to determination of these compounds degradation mechanism. Preliminary electroanalytical investigations of the electrode reactions at Pt and TiO₂-RuO₂/Ti electrodes have been carried out [13,30]. Electroanalytical methods are suitable in determination of mechanism and kinetics of electrode reactions [31–33]. Results of electroanalytical investigations and degradation of H-acid will enable determination of the optimum parameters of the photoelectrochemical treatment of this type compounds. Moreover, they will allow selection of an electrode material with proper oxide semiconductor film as anode what enables application of radiation with the lowest energy, e.g., solar radiation, in the photoelectrochemical treatment.

The aim of this work was to investigate electrochemical oxidation of H-acid at TiO₂-RuO₂/Ti electrodes modified with Nb₂O₅, Y₂O₃ and ZrO₂. Results of kinetic parameters determination for electrode reactions and results of the investigation of electrode type and current intensity effect on H-acid degradation in photocatalytic, electrochemical and photoelectrochemical process, are also described.

2. Materials and methods

2.1. Chemicals and electrode materials

1-Amino-8-hydroxynaphthalene-3,6-disulphonic acid (H-acid) was obtained from dyestuff works Boruta-Zachem Kolor Co. in Zgierz (Poland). The substrate solutions were prepared by its dissolving in 0.1 mol L⁻¹ NaClO₄ (Fluka). Concentrations of H-acid varied from 1 × 10⁻³ to 5 × 10⁻³ mol L⁻¹. The following reagents were used in chemical oxygen demand (COD) determination: H₂SO₄ (Chempur, Poland) with Ag₂SO₄ (POCh Gliwice, Poland), K₂Cr₂O₇ (POCh Gliwice, Poland) and Fe(NH₄)₂(SO₄)₂ (POCh Gliwice, Poland). Purity of chemicals used in the experiments was analytical grade.

Electrodes: TiO₂(70%)-RuO₂(30%)/Ti, TiO₂(60%)-RuO₂(30%)-Nb₂O₅(10%)/Ti, TiO₂(60%)-RuO₂(30%)-Nb₂O₅(10%)(N₂)/Ti, TiO₂(60%)-RuO₂(30%)-ZrO₂(10%)/Ti and TiO₂(60%)-RuO₂(30%)-Y₂O₃(10%)/Ti were applied in the investigation. These electrodes were prepared by thermal decomposition of metal precursors (Ti, Ru, Nb, Zr and Y salts) on titanium support. Precursors concentrations were matched in such a way that oxide films had nominal content after heating in a temperature of 500 °C in air, except for TiO₂(60%)-RuO₂(30%)-Nb₂O₅(10%)(N₂)/Ti electrode which was heated in nitrogen atmosphere. The surface area of electrodes used in electroanalytical experiments was 2 cm² while their surface in degradation experiments was 20 cm².

In order to compare results of the investigation, platinum electrode with comparable geometric surface was also applied in electroanalytical measurements and degradation processes.

2.2. Electroanalytical methods and degradation experiments

Methods of cyclic (CV) and differential pulse (DPV) voltammetry were used in electrochemical measurements carried out with an AUTOLAB (Ecochemie, Holland) analytical set. A three electrode cell was applied in all experiments. Titanium electrodes covered with TiO₂(70%)-RuO₂(30%), TiO₂(60%)-RuO₂(30%)-Nb₂O₅(10%), TiO₂(60%)-RuO₂(30%)-Nb₂O₅(10%)(N₂), TiO₂(60%)-RuO₂(30%)-ZrO₂(10%), TiO₂(60%)-RuO₂(30%)-Y₂O₃(10%) and platinum electrode were used as a working electrode. Platinum electrode was a cathode in all experiments. 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.

Peak potential (E_{pa}), half-peak potential ($E_{pa/2}$) and half-wave potential ($E_{1/2}$) for the first step of the H-acid electrooxidation was determined from recorded voltammograms. If the electrode process proceeds under linear diffusion condition, then anodic transition coefficient (βn_{β}), heterogeneous rate constant (k_{bh}) and reaction order (z) for the electrode process can be calculated from the following equations [34]:

$$\beta n_{\beta} = \frac{1.857RT}{F(E_{pa} - E_{pa/2})} \quad (1)$$

$$E_{pa} = -1.14 \frac{RT}{\beta n_{\beta} F} - \frac{RT}{\beta n_{\beta} F} \ln \frac{k_{bh}^0}{D_{red}^{1/2}} + \frac{RT}{2\beta n_{\beta} F} \ln \beta n_{\beta} \nu \quad (2)$$

$$k_{bh} = k_{bh}^0 \exp\left(\frac{-\beta n_{\beta} FE}{RT}\right) \quad (3)$$

$$z = \frac{\partial \log i_a}{\partial \log c} \quad (4)$$

where D_{red} – diffusion coefficient of reduced form (cm² s⁻¹); ν – scan rate (V s⁻¹); F – Faraday constant (96,487 C mol⁻¹); R – universal gas constant (8.314 J K⁻¹ mol⁻¹); T – Kelvin temperature (K); k_{bh}^0 – heterogeneous rate constant at a peak potential vs. SCE (cm s⁻¹); i_a – anodic current intensity (A cm⁻²); c – concentration of substrate oxidized form (mol cm⁻³).

Heterogeneous rate constant (k_{bh}) determined for a specified potential E characterizes transfer rate of electron through electrode-solution interface. The electron transition coefficient characterizes symmetry of the activated barrier of an electrode reaction. Reaction order is a parameter necessary for determination of electrode reaction mechanism.

Electrochemical degradation of a substrate was carried out under galvanostatic conditions in a cell with undivided electrode compartments made of quartz glass. Photocatalytic and photoelectrochemical oxidation of H-acid was also carried out in the same cell inserted into a reactor RPR 200 (Southern New England Ultraviolet Co.). The reactor was equipped with 16 lamps (35 W) emitting radiation with the wavelength of 254 nm.

2.3. Analytical methods

The total organic carbon (TOC), chemical oxygen demand (COD) and UV-vis spectra were determined in the solutions before and after the electrolyses. TOC was analyzed with TOC 5050A Shimadzu Total Organic Carbon Analyser. COD was determined according to the procedure described in Refs. [35,36]. UV-vis spectra were recorded in the wavelength range from 190 to 800 nm using UV-vis Spectrophotometer Shimadzu UV-24001 PC.

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