Bulletin of Dnipropetrovsk University. Series Chemistry, 2017, *25*(1), 27–35

Вісник Дніпропетровського університету. Серія Хімія
Bulletin of Dnipropetrovsk University. Series Chemistry

p-ISSN 2306-871X, e-ISSN 2313-4984
journal homepage: http://chemistry.dnu.dp.ua

UDC 544. 653.2

THE ELECTROCHEMICAL OXIDATION OF 4-NITROANILINE AND 4-NITROPHENOL ON MODIFIED PbO_2-ELECTRODES

Olesia B. Shmychkova,[1] Tatiana V. Luk'yanenko,[1] Rossano Amadelli,[2] Alexander B. Velichenko[1,*]

[1]Ukrainian State University of Chemical Technology, 8, Gagarin Ave., 49005 Dnipro, Ukraine
[2]ISOF-CNR u.o.s Ferrara c/o Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via Luigi Borsari, 46–44121 Ferrara, Italy

Received 03 January 2017; revised 14 February 2017; accepted 28 June 2017, available online 05 December 2017

Abstract

The electrochemical oxidation of *p*-nitroanilline and *p*-nitrophenol on lead dioxide anodes, modified by different ionic dopants has been investigated. The general mechanism of the oxidation of organic compounds of aromatic nature includes oxidizing of compounds to the intermediates with quinoid structure, reactions of aromatic ring opening and formation of aliphatic products (mainly acids) and in ideal case – the complete mineralization to CO_2 and H_2O. According to obtained results one can conclude that both reactions occur via formation of *p*-benzoquinon. Calculations, based on kinetic studies of the reaction, have shown that the rate constant of the degradation of the organics involved depends on the composition of the electrode material and varies due to the nature and the content of ionic additives in lead dioxide. The maximum interest for the electrochemical destruction of organic substances represents lead dioxide electrodes modified by bismuth to which a rate constant of p-nitroaniline oxidation increases in 1.6 times compared with nonmodified electrodes. Maximum electrocatalytic activity is achieved by increasing the proportion of α-phase, on the one hand, and increase the crystalline zone of oxide on the other, which leads to increased amounts of oxygen containing particles strongly bounded to the electrode surface that participate in the electrochemical oxidation of aromatic compounds.

Keywords: electrochemical oxidation, hydroxyl radicals, lead dioxide, methanesulfonate electrolyte.

ЕЛЕКТРОХІМІЧНЕ ОКИСНЕННЯ 4-НІТРОАНІЛІНУ ТА 4-НІТРОФЕНОЛУ НА МОДИФІКОВАНИХ PbO_2-ЕЛЕКТРОДАХ

Олеся Б. Шмичкова,[1] Тетяна В. Лук'яненко,[1] Россано Амаделлі,[2] Олександр Б. Веліченко[1,*]

[1]ДВНЗ «Український державний хіміко-технологічний університет», пр. Гагаріна 8, м. Дніпро, 49005 Україна
[2]ISOF-CNR відділення в Феррарі, департамент хімії та фармації, Університет Феррари, вул. Л. Борсарі, 46–44121 Феррара, Італія

Анотація

Досліджено електрохімічне окиснення п-нітроаніліну та *п*-нітрофенолу на діоксидносвинцевих анодах, модифікованих різними іонними добавками. Загальний механізм окиснення органічних сполук ароматичної природи включає окиснення до проміжних сполук із хіноїдною будовою, реакції ароматичного розімкнення кільця та формування аліфатичних продуктів (головним чином, кислот) і в ідеальному випадку – повна мінералізація до CO_2 і H_2O. Результати досліджень показали, що обидві реакції проходять через утворення п-бензохінону. Розрахунки, засновані на кінетичних дослідженях, показали, що константи швидкості руйнації досліджуваних органічних сполук залежать від складу електроду та варіюються залежно від природи та кількості модифікуючих добавок у плюмбум діоксиді. Найбільший інтерес для електрохімічної руйнації органічних сполук представляють модифіковані Бісмутом діоксидносвинцеві аноди, для яких константа швидкості окиснення *п*-нітроаніліну збільшується в 1.6 разів порівняно з немодифікованим покриттям. Максимальна електроактивність каталізатора досягається за збільшення частки α-фази, з одного боку, та збільшення кількості лабільних оксигеновмісних часточок на поверхні електроду, які беруть участь в електрохімічному окисненні ароматичних сполук, з іншого боку.

Ключові слова: електрохімічне окиснення, гідроксил-радикали, плюмбум діоксид, метансульфонатний електроліт.

**Corresponding author: tel.: +380562473627; e-mail address: velichenko@ukr.net*

doi: 10.15421/081705

Bulletin of Dnipropetrovsk University. Series Chemistry, 2017, *25*(1), 27–35

ЭЛЕКТРОХИМИЧЕСКОЕ ОКИСЛЕНИЕ 4-НИТРОАНИЛИНА И 4-НИТРОФЕНОЛА НА МОДИФИЦИРОВАННЫХ PbO_2-ЭЛЕКТРОДАХ

Олеся Б. Шмычкова,[1] Татьяна В. Лукьяненко,[1] Россано Амаделли,[2] Александр Б. Величенко[1,*]
[1]*ГВУЗ «Украинский государственных химико-технологический университет», пр Гагарина 8, г. Днепр, 49005, Украина*
[2]*ISOF-CNR отделение в Ферраре, департамент химии и фармации, Университет Феррары, ул. Л. Борсари, 46–44121 Феррара, Италия*

Аннотация

Исследовано электрохимическое окисление п-нитроанилина и *n*-нитрофенола на диоксидносвинцовых анодах, модифицированных различными ионными добавками. Общий механизм окисления органических соединений ароматической природы включает окисление до промежуточных соединений с хиноидным строением, реакции ароматического размыкания кольца и формирования алифатических продуктов (главным образом, кислот) и в идеальном случае – полная минерализация до CO_2 и H_2O. Результаты исследований показали, что обе реакции протекают через образование *n*-бензохинона. Расчеты, основанные на кинетических исследованиях, показали, что константы скорости разрушения исследуемых органических соединений зависят от состава электрода и варьируются в зависимости от природы и количества модифицирующих добавок в диоксиде свинца. Наибольший интерес для электрохимического разрушения органических соединений представляют модифицированные висмутом диоксидносвинцовые аноды, для которых константа скорости окисления *n*-нитроанилина увеличивается в 1.6 раз по сравнению с немодифицированным покрытием. Максимальная электроактивность катализатора достигается при увеличении доли α-фазы, с одной стороны, и увеличении количества лабильных кислородсодержащих частиц на поверхности электрода, которые участвуют в электрохимическом окислении ароматических соединений, с другой стороны.

Ключевые слова: электрохимическое окисление, гидроксил-радикалы, диоксид свинца, метансульфонатный электролит.

Introduction

The line of research involved in the manuscript belongs to the world's key development priorities of modern chemistry and attracted considerable attention of researchers as indicated by the large number of publications. The results on the use of advanced catalytic oxidation method (advanced oxidation process – AOP) achieved over the last 5 years for the destruction of chemical and biological toxins and pollutants listed in review [1]. Based on the information provided in the publications [2–4], clearing of the aquatic environment from pollution by anthropogenic organic chemicals are known to be a very difficult problem even in industrial enterprises, which are widely used chemical reagent methods. Attempts to transfer this experience in agriculture in general has not been successful because the traditional methods and technologies are not adapted to the conditions of agriculture require huge capital costs for associated infrastructure and industrial engineering of the necessary reagents of shipping them over long distances to the place of use.

An alternative to traditional methods of water purification from toxic aromatics are electrochemical technologies that should be attributed to relatively reagent less, as latter are formed at the time of use. Other advantages include their efficiency, ease of use, ease of automation, modularity structures and the flexibility to scale based on the needs in use [5]. These techniques are promising for the treatment of water from a wide range of organic compounds of different types [6], for example, phenolic compounds [7; 8] and pesticides [9]. The electrochemical degradation of toxic pollutants is achieved both through direct transfer of electric charge between the electrode and the organic compounds and secondary chemical reactions, the oxidant in which are oxygen-containing radicals formed during electrolysis of water molecules. In both cases the optimal choice of anode material is critical, not only ratio, and direction of oxidation depends on it. For example, some electrodes in the oxidation of organic compounds may form polymers due to the nucleophilic attack of neutral molecules by radicals [10]. In recent years, a large number of materials have been used for the selective and non-selective anodic oxidation of resistant organic compounds, but the problem of choosing the optimal and chemically stable material still remains an open question requiring further study.

Experimental and Methods

All chemicals were reagent grade. Platinized titanium was used as substrate. Titanium sheet was treated as described in [11] before platinum layer depositing. Lead dioxide coatings were electrodeposited at anodic current density 10 mA · cm^{-2} from methanesulfonate electrolytes that contained 1M CH_3SO_3H, 0.1 M $Pb(CH_3SO_3)_2$ and 0.1 M $Bi(NO_3)_3$, $Ce(NO_3)_3$, $(CH_3COO)_4Sn$, $K_2(NiF_6)$, $K_2(SnF_6)$ as dopants. The determination of modifying additive in anodic materials was carried out with Graphite furnace atomic adsorption spectroscope [GF-AAS] model Analyst 800.

Having in mind that the challenge in PbO_2 research is to obtain an electrochemically active and durable material, in this work we electrodeposited PbO_2 from $CH_3SO_3^-$-containing medium.

Since methanesulfonate is becoming the most popular electrolyte for PbO_2 electrosynthesis due to probability of the deposition of coatings up to 2 mm thick with low internal stresses [12], we chose these electrolytes because they are easy to prepare and work with; and PbO_2 obtained in this medium has satisfactory mechanical properties and significantly different electrocatalytical activity in respect to coatings, obtained in traditional nitrare baths.

X-ray powder diffraction data were collected on a STOE STADI P automatic diffractometer [13] equipped with linear PSD detector (transmission mode, 2θ/ω-scan; Cu $K\alpha_1$ radiation, curved germanium (1 1 1) monochromator; 2θ-range $6.000 \leq 2\theta \leq 102.945$ 2θ with step 0.015 2θ; PSD step 0.480 °2θ, scan time 50 s/step).

Qualitative and quantitative phase analysis was performed using the PowderCell program [14]. For selected samples with relatively high degree of crystallinity the Rietveld refinement was carried out using FullProf.2k (version 5.40) program [15].

XPS studies were carried out on a PHI 5000 spectrometer using monochromatic Al$K\alpha$ radiation for excitation. The BE value of C(1s), due to adventtious carbon and residual solvent, is 284.8 [±0.3] eV.

The electrooxidation of organic compounds was carried out in undivided cell at j_a = 50mA cm^{-2}. The volume of anolyte was 50 cm^3. Solution, containing phosphate buffer (0.25 M Na_2HPO_4 + 0.1 M KH_2PO_4) + $2 \cdot 10^{-4}$ M organic compound, (pH = 6.55) was used as electrolyte. Stainless steel was used as cathode. Modified lead dioxide electrodes were used as anodes. Electrode surface area was 1 cm^2.

Analyses of the reaction products were conducted by HPLC using a Shimadzu RF-10A xL instrument equipped with a Ultraviolet SPD-20AV detector and a 30 cm Discovery® C18 column. Ozone analysis was carried out mostly by iodometric titration [16]. In some cases the results were checked by the spectrophotometric method. The formation of colored compounds during electrolysis was followed by UV-visible spectroscopy. The changing of the concentration of the organic substance during the electrolysis was measured by sampling (volume of 5 cm^3) at regular intervals and measuring the optical density of the solution in the ultraviolet and visible region (wavelength range 200–570 nm) using a Kontron Uvikon 940 spectrometer. Solution, containing phosphate buffer, was used as reference solution.

Results and Discussion

Electrochemical degradation of organics in the wastewater is known to be a very important task. The development of electrode materials used for wastewater treatment is recognized as the subject of many investigations. Synthetic diamond electrodes modified with boron (BDD), for example, commonly used as electrocatalysts [17], as well as anodes based on PbO_2 [18]. It should be noted that in the first case the basic problem is the high power consumption due to the low conductivity of modified synthetic diamond, which makes them unsuitable for use as anodes in industry. Thus, more promising are materials based on lead dioxide, the more so because of their electrocatalytic activity, which can be significantly increased by the modification.

The process of oxidation of organic substances is not necessarily a direct electrochemical process. Quite likely, it occurs via oxidants generated in the primary electrochemical reaction, for example, the formation of hydroxyl radicals and ozone. So this process is a secondary chemical process. It should also be noted, that it is not always taken into account the fact that the oxygen evolution reaction on the electrode can occur in conjunction with other reactions with the transfer of oxygen, such as oxidation of organic [17; 19] or inorganic compounds [18], which are not necessarily implemented independently of other.

The effectiveness of such processes depends on the ratio of the rates of reactions both of the formation and the disappearance of OH-radicals. The accumulation of a sufficient amount of radicals on the electrode surface and the near electrode layer facilitates their interaction with inorganic and organic compounds, causing partial or complete destruction of these compounds [12].

The synthesis of strong oxidants such as ozone can be assigned to another group of anodic reactions occurring at high anodic potentials with oxygen-containing particles participation. Since ozone formation occurs simultaneously with the oxidation processes of organic compounds [20; 21], its synthesis in the electrolysis process can contribute to the destruction of toxic organic substances. As one can conclude from the obtained results, the current efficiencies of ozone evolution on electrodes deposited from methanesulfonate electrolytes are approximately three times lower than on the materials obtained from nitrate bath [22]. Modification by ionic additives increases the current efficiency of ozone, but the latter is characterized by the values in the range of a few percent [12].

An observed phenomenon is caused by differences in the chemical and phase composition of deposits obtained from nitrate and methanesulfonate electrolytes, namely, in the degree of surface hydroxylation. As the oxygen species strongly bounded with the electrode surface are involved in the process of ozone evolution [23], the decrease in their number would lead to a decrease in current efficiencies of ozone evolution, which is observed in the case of coatings obtained from the methanesulfonate electrolytes [22; 24; 25].

In order to determine the influence of deposition conditions and the composition of the anode materials, based on lead dioxide, on their electrocatalytic activity in respect to the oxidation of organic toxicants 4-nitroaniline and 4-nitrophenol were selected as model aromatics. This choice was due to the fact that the electrochemical incineration of phenolic compounds on the different electrodes is well studied process, so the attention can be focused only on the clarifying of the role of the anode material.

Thus, in particular, a considerable number of publications are devoted to aromatic compounds electrooxidation, in which PbO_2 and other oxides of noble metals are used as anode materials [2; 12; 26]. The anodic oxidation of phenols may occur in two pathways, depending on the acid-base properties of the system [27–31].

Oxidation of *p*-nitroaniline. As it is noted in [32], the general mechanism of the oxidation of organic compounds of aromatic nature will include oxidizing of compounds to the intermediates with quinoid structure, reactions of aromatic ring opening and formation of aliphatic products [mainly acids] and in ideal case – the complete mineralization to CO_2 and H_2O. According to [33], quite a number of intermediates are produced during anodic oxidation of *p*-nitroaniline. The primary intermediates include maleic acid and benzoquinone.

The mechanism of *p*-nitroaniline electrooxidation on modified lead dioxide electrodes was considered in detail in our previous publications [12]. The HPLC investigation has shown 1,4-benzoquinone as the major aromatic intermediate. Only aliphatic acids can be detected in a solution after long-term electrolysis.

Electronic absorption spectra of solutions at different electrolysis time were taken in order to determine the time of the disappearance of intermediate aromatic products and a change in the concentration of the initial compound.

Fig. 1 shows the absorption spectra in the visible and UV regions obtained at different times of electrolysis in a phosphate buffer on nonmodified lead dioxide anode.

It should be noted that electrocatalytic activity of lead dioxide anodes in respect to the oxidation of *p*-nitroaniline depends on the concentration of methanesulfonate ions in the deposition electrolyte.

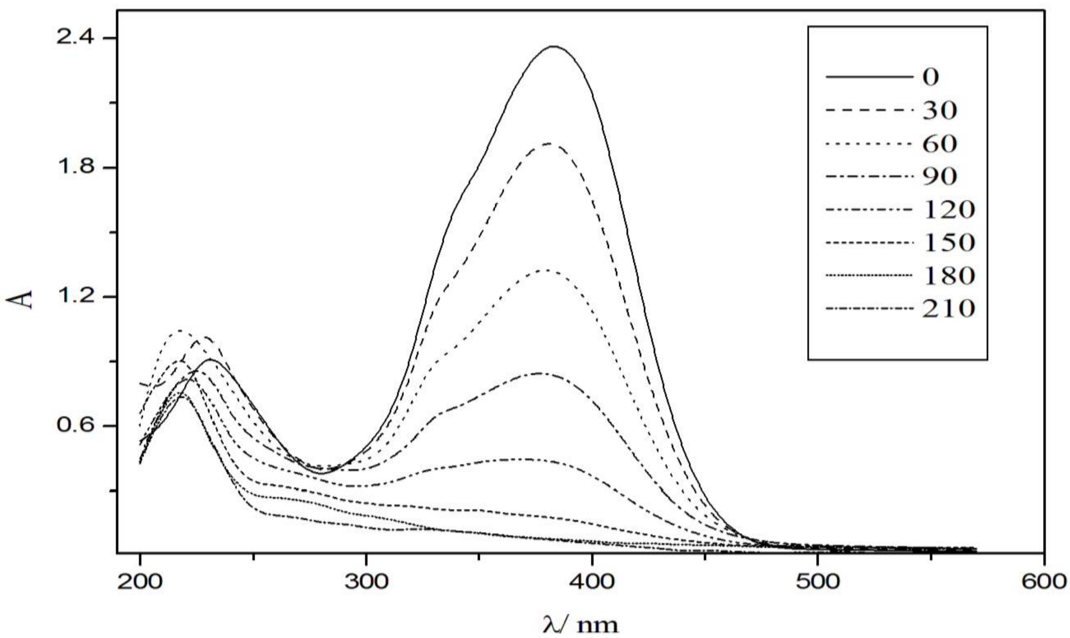

Fig. 1. The absorption spectra of *p*-nitroanilline solution (initial concentration $2 \cdot 10^{-4}$M) obtained at different time of electrolysis in a phosphate buffer on lead dioxide anode

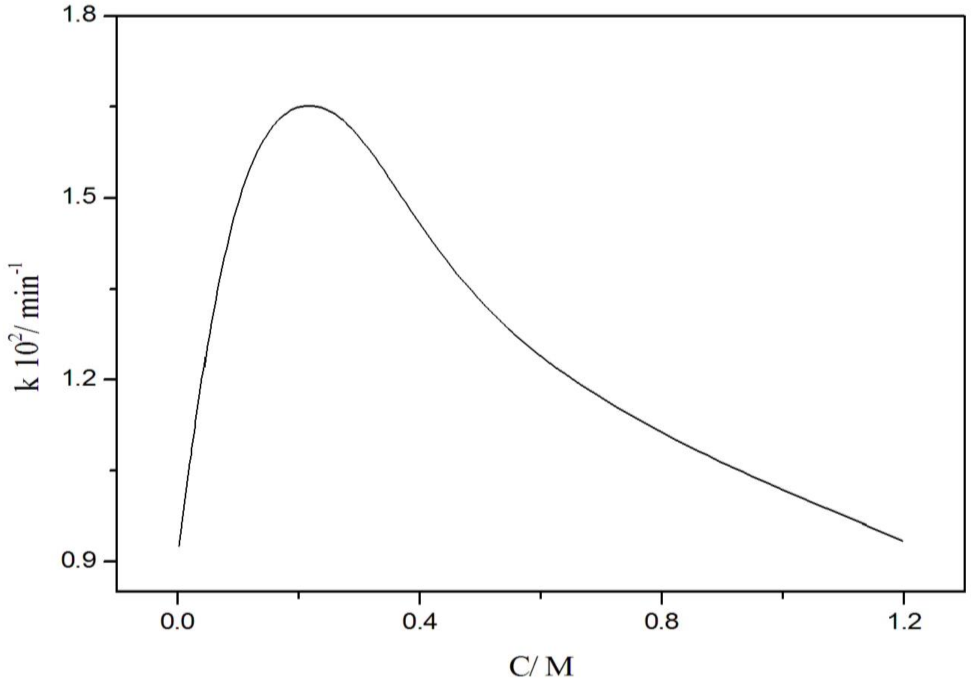

Fig. 2. The plot of apparent heterogeneous rate constant of *p*-nitroanilline oxidation on PbO_2-anodes versus the concentration of CH_3SO_3Na in the deposition solution

The dependence has extreme character with a maximum at 0.1–0.3 M concentrations of CH_3SO_3Na (Fig. 2). As follows from the obtained results (Table 1), the chemical composition of lead dioxide is practically no changed. In this case, structural factors play a significant role. Maximum electrocatalytic activity is achieved by increasing the proportion of α-phase, on the one hand, and increase the crystalline zone of oxide on the other, which leads to increased amounts of oxygen containing particles strongly bounded to the electrode surface that participate in the electrochemical oxidation of aromatic compounds [12].

Table 1

The phase composition of lead dioxide coatings depending on deposition conditions

Deposit	T/K	Content /wt.%/ α-PbO_2/β-PbO_2
PbO_2	282	59/41
PbO_2	298	90/10
PbO_2–1.81 wt.% Bi	282	5/95
PbO_2–0.019 wt.% Ce	298	83/17
PbO_2–1.81 wt.% Sn	298	44/56
PbO_2–0.042 wt.% Ni; 0.043 wt.% F	298	0/100
PbO_2–1.56 wt.% Sn; 0.04 wt.% F	298	38/62

Obtained results can be satisfactorily described in the framework of the mechanism [12], wherein the primary intermediate is benzoquinone. Since the electrochemical destruction of *p*-nitroaniline occurs via the formation of benzoquinone, electrochemical destruction of this compound was investigated further. Fig. 3 shows the absorption spectra of *p*-benzoquinone solution obtained at different time of electrolysis in a phosphate buffer on lead dioxide anode. Kinetic parameters of the electrochemical oxidation of *p*-benzoquinone were commented in [12].

The processes of *p*-nitroaniline electrochemical oxidation on unmodified and modified lead dioxide electrodes occur qualitatively the same and differ only in the rate. This suggests the invariability of the mechanism of *p*-nitroaniline oxidation on different materials that allows one for a correct comparison of their electrocatalytic activity.

According to calculations (Table 2), based on kinetic studies of the reaction rate constant of *p*-nitroaniline degradation depends on the composition of the electrode material and varies due to the nature and content of ionic additives in lead dioxide.

The maximum interest for the electrochemical destruction of organic substances represents lead dioxide electrodes modified by bismuth to which a rate constant of *p*-nitroaniline oxidation increases in 1.6 times compared with nonmodified electrodes (see Table 2). In other cases, the rate constants are comparable.

Oxidation of *p*-nitrophenol. Since mechanism of electrooxidation of *p*-nitrophenol was considered in detail previously, let's concentrate only of the effect of dopants on the reaction rate. Fig. 4 shows the absorption spectra of *p*-nitrophenol solution obtained at different time of electrolysis in a phosphate buffer on lead dioxide anode.

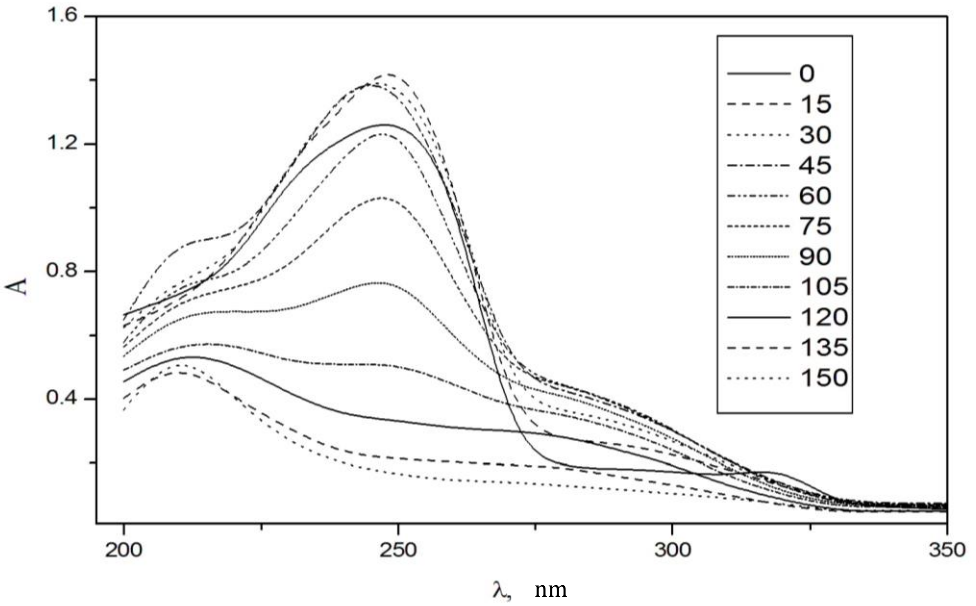

Fig. 3. The absorption spectra of *p*-benzoquinone solution (initial concentration 10^{-4}M) obtained at different time of electrolysis in a phosphate buffer on lead dioxide anode

As was suggested in [12], maleic acid and a stoichiometric amount of NO_3^- were detected as electrolysis products by high performance liquid chromatography. The primary aromatic intermediate in this case was also a 1,4-benzoquinone, but its concentration was an order of magnitude higher than in the oxidation of *p*-nitroaniline [12]. The latter indicates a more effective destruction of the aromatic ring in the case of *p*-nitroaniline.

As one can conclude from obtained results (Table 3) rate constants of *p*-nitrophenol oxidation on modified lead dioxide electrodes somewhat lower than those for *p*-nitroaniline [12].

Table 2

Kinetic parameters of the electrochemical oxidation of *p*-nitroaniline ($2\cdot10^{-4}$ M) on modified PbO_2-anodes

Anode	Apparent heterogeneous rate constant, $k\cdot10^2$, min^{-1}
PbO_2	1.68
PbO_2–1.81 wt.% Bi	2.76
PbO_2–0.019 wt.% Ce	1.36
PbO_2–1.81 wt.% Sn	1.38
PbO_2–0.042 wt.% Ni; 0.043 wt.% F	1.66
PbO_2–1.56 wt.% Sn; 0.04 wt.% F	1.38

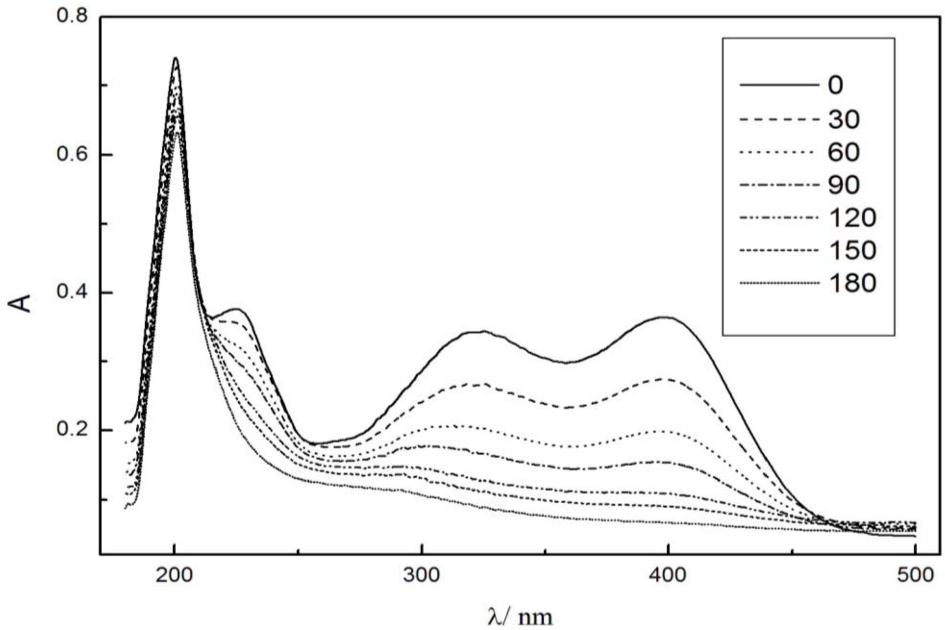

Fig. 4. The absorption spectra of *p*-nitrophenol solution (initial concentration $2\cdot10^{-4}$M) obtained at different time of electrolysis in a phosphate buffer on lead dioxide anode

Table 3

Kinetic parameters of the electrochemical oxidation of *p*-nitrophenol ($2\cdot10^{-4}$ M) on modified PbO_2-anodes

Anode	Apparent heterogeneous rate constant, $k\cdot10^2$, min^{-1}
PbO_2	0.84
PbO_2–1.81 wt.% Bi	0.88
PbO_2–0.019 wt.% Ce	0.52
PbO_2–1.87 wt.% Sn	0.54
PbO_2–0.042 wt.% Ni; 0.043 wt.% F	0.82
PbO_2–1.56 wt.% Sn; 0.04 wt.% F	0.52

Conclusions

The processes of electrochemical oxidation of investigated organic compound on unmodified and modified lead dioxide electrodes occur qualitatively the same and differ only in the rate. This suggests the invariability of the mechanism of their oxidation on different materials that allows one for a correct comparison of their electrocatalytic activity.

According to calculations, based on kinetic studies of the reaction rate constant of organic compounds degradation depends on the composition of the electrode material and varies due to the nature and content of ionic additives in lead dioxide.

The maximum interest for the electrochemical destruction of organic substances represents lead dioxide electrodes modified by bismuth to which a rate constant of *p*-nitroaniline oxidation increases in 1.6 times compared with nonmodified electrodes. In other cases, the rate constants are comparable.

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