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ELECTROCHEMICAL DESTRUCTION OF PHENOXY HERBICIDES ON LEAD DIOXIDE ANODES

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The electrochemical oxidation of substituted phenoxy acetic acids on lead dioxide anodes micromodified by bismuth has been investigated. It has been established that the polarity of the substituents in phenoxyacetic acids does not affect the efficiency of the hydroxylation process. Electron-acceptor substituents as well as electron-donors direct the attack of hydroxyl radicals into para-positions. The conversion time required for the oxidation of the herbicides to the aliphatic compounds in most cases depends on the number of substituents in the aromatic ring and is almost independent of their nature. Oxidation occurs according to the radical mechanism of ipso-substitution in aromatic compounds when attacked by OH radicals and proceeds through the formation of corresponding phenol; subsequent oxidation leads to the formation of corresponding benzoquinones through hydroquinones that has been confirmed by high-performance liquid chromatography. Subsequent hydroxylation of the aromatic ring is accompanied by its cleavage and the formation of aliphatic carboxylic acids, which is further completely mineralized to CO_2 and H_2O.

Keywords: lead dioxide, methanesulfonate electrolyte, advanced oxidation processes, phenoxy herbicides, water treatment.

Introduction

Phenoxyacetic acids with different substituents in the aromatic ring are widely known herbicides and plant growth regulators that are used on a large scale in the agriculture. Most of these compounds easily penetrate into groundwater. It should be noted that phenoxyacetic acids are extremely slowly degraded in the environment [1,2] and are dangerous for humans and animals. They are classified into the 2nd or 3rd Grade of hazard according to the definition of the World Health Organization (WHO). In this regard, the development of methods for effective destruction of herbicides using «green chemistry» technologies based on the synthesis of strong oxidants, such as photochemical [3], phototoxic [4] and electrochemical [5] ones, arouse a considerable interest. The latter methods are quite promising, since they do not require significant costs for their implementation. It is known that the effectiveness of the electrooxidation of organic pollutants depends, first of all, on the anode material, the electrolyte nature and on the structure and composition of the toxicant [5]. The application of anode materials based on lead dioxide presents considerable scientific and practical interest due to the high stability and low cost of the anodes and their high electrocatalytic activity in reactions occurring at high anode potentials with the oxygen-containing radicals participation [6–8].

It appears that there is no systematic information on the effect of phenoxyacetic herbicides structure on their destruction during the electrolysis. The proposed mechanisms of their oxidation are not systematized and often have controversial nature [3,9,10]. In our recent work [11], we have investigated the electrocatalytic activity of micromodified lead dioxide anodes, as well as the nucleation mechanism and kinetics of the electrodeposition of coatings. Having in mind that the challenge in PbO_2 research is to obtain an electrochemically active and durable material, we report and discuss in this work the electrodeposition of PbO_2 from a Bi^{3+}-containing medium. Bearing direct relevance to the electrocatalytic properties, we noted that Bi^{3+}/PbO_2 electrodes feature a significant increase in the amount of labile oxygen intermediates on the electrode surface which are responsible of a high electrocatalytic activity in the advanced oxidation processes of organic compounds [6].

Electrodeposition conditions are known to significantly affect both the physicochemical properties and the electrocatalytic activity of the resulting deposits [6–8,11]. Despite the several dopants, which can be used [6–8], one of the objects of our work was to consider a micromodified system with given electrocatalytic properties in respect to the quantity of surface adsorbed oxygen species. Concerning the last point, we herein report further important details on the mechanism of degradation of substituted phenoxyacetic acids on anodes involved, since the rate of generation of hydroxyl radicals on the Bi^{3+}/PbO_2, is the highest, which coincides with the data of kinetic studies of electrochemical oxidation of organic compounds [6].

Material and methods

Lead dioxide anodes were synthesized according to the method described elsewhere [6–8] by electrochemical deposition of PbO_2 on a platinized titanium substrate. The solution containing 0.1 M $Pb(CH_3SO_3)_2$ and 1 M CH_3SO_3H was used as based electrolyte. $Bi(NO_3)_3$ was used as an additive to the methanesulfonate electrolyte [6].

The electrooxidation of organic compounds was carried out in a thermostated cell with separated electrode compartments at an anode current density of j_a=50 mA cm^{-2}. The volume of anolyte was 160 cm^3. Aqueous solution containing phosphate buffer (0.25 M Na_2HPO_4+0.1 M KH_2PO_4) with the addition of 2×10^{-4} M organic compound (pH 6.55) was used as an electrolyte. Stainless steel was used as a cathode. Lead dioxide electrodes modified by bismuth were used as anodes. The electrode surface area was 2.5 cm^2.

We investigated the oxidation of some herbicides (phenoxyacetic acid (PAA), 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and also several bromo derivatives of PAA as follows: 4-bromophenoxyacetic acid (4-BPA), 2,4-dibromophenoxyacetic acid and 2,4,6-tribromophenoxyacetic acid, 4-chloro-2-methylphenoxyacetic acid (MCPA), 4-nitrophenoxyacetic acid (4-NPA)) with the initial concentration of organic compounds 0.1–0.5 mM. All chemicals were reagent grade.

The change in the concentration of herbicides and aromatic intermediate products during the electrolysis was determined by sampling (volume of 5 cm^3) at regular intervals and measuring the absorbance of the solution in the ultraviolet and visible regions (in a wavelength range of 200–320 nm) using a Kontron Uvikon 940 spectrometer. Solution containing phosphate buffer was used as a reference solution. The analyses of the reaction products were conducted by high-performance liquid chromatography (HPLC) using a Shimadzu RF-10A xL instrument equipped with a Ultraviolet SPD-20AV detector and a 30 cm Discovery® C18 column. Concentration of chloride ions was determined by photometric method using mercuric rhodanide.

Results and discussion

The electronic absorption spectra of 0.1 mM PAA solution at different electrolysis duration on the PbO_2 anode modified by bismuth ions are shown in Fig. 1. According to previously published results [6], this particular anode demonstrates the highest electrocatalytic activity in oxidation of aromatic compounds involved.

As can be seen from the spectral data, after half an hour of electrolysis a plateau appeared at 250–270 nm indicating the formation of a benzoquinone, which continues to be oxidized on the PbO_2–Bi anode. After 1.5 hours of electrolysis, its concentration decreases, and after 2 hours the aromatics disappear completely and the solution becomes uncolored. The conversion of PAA into aliphatic compounds on non-modified lead dioxide anodes ends in 2.5 hours. Later, the time during

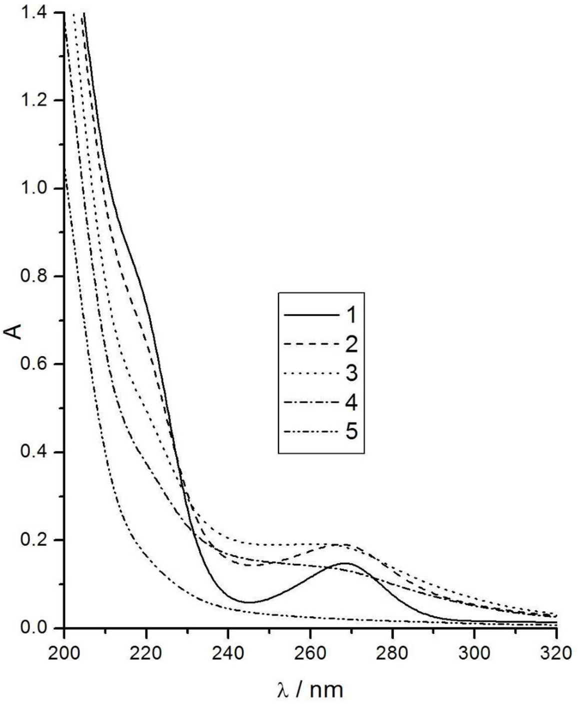

Fig. 1. The absorption spectra of PAA solution (initial concentration 0.1 mM) obtained at different electrolysis duration in a phosphate buffer on PbO_2–Bi anode. Electrolysis duration, h: 1 – 0; 2 – 0.5; 3 – 1; 4 – 1.5; 5 – 2

which the peaks of aromatic compounds disappear on the UV spectra was marked as conversion time.

Semi-quantitative measurements of the influence of the nature of anodic material and organic pollutant on the conversion time of initial compounds into their aliphatic derivatives were carried out. The results of investigations of electrochemical oxidation of a number of phenoxyacetic acids on modified and non-modified PbO_2 anodes are summarized in Table.

The conversion time of phenoxyacetic acid and its derivatives to aliphatic acids (with the initial concentration of 0.1 mM; anode current density is 50 mA cm^2)

Compound formula	Abbreviation	Conversion time, h	
		PbO_2	PbO_2–Bi
$C_6H_5OCH_2COOH$	PAA	2.5	2.0
2,4-$Cl_2C_6H_3OCH_2COOH$	2,4-D	3.0	2.0
4-Cl-2-$CH_3C_6H_3OCH_2COOH$	MCPA	3.0	2.0
2,4,5-$Cl_3C_6H_2OCH_2COOH$	2,4,5-T	4.0	2.5
2,4-$Br_2C_6H_3OCH_2COOH$	–	3.0	2.0
2,4,6-$Br_3C_6H_2OCH_2COOH$	–	4.0	2.5
4-$BrC_6H_4OCH_2COOH$	4-BPA	2.0	1.5
4-$NO_2C_6H_4OCH_2COOH$	4-NPA	4.0	3.0

We followed the disappearance of intermediate aromatic products as a function of electrolysis duration for different concentrations of the initial compound. The mechanism of electrochemical oxidation of the target compound is the same both for non-modified and modified PbO_2 electrodes; this allows comparing electrocatalytic activities in terms of process rates, which depend appreciably on the electrode material. As one can conclude from the obtained results, the modification of the anode material by bismuth ions accelerates the destruction of organic pollutants and reduces the conversion time by approximately 1.5 times. The complete decontamination of pollutants on PbO_2-anodes ends with advanced oxidation of herbicides to CO_2 and H_2O for 4–6 hours and depends on the nature of both anode material and organic substance. Generally, the mineralization of aliphatic acids is slower than that of aromatic ones. It is obvious that the rate of oxidation of herbicides to aliphatic compounds in most cases depends on the number of substituents in the aromatic ring and almost does not depend on their nature, which fully coincides with the concept of a radical mechanism of aromatic substitution when attacked by OH radicals.

The mechanism of the destruction of herbicides in an acidic or neutral medium in the Fenton process and by direct anodic oxidation has been studied in many works [3,5,10], but the information is often contradictory, in particular, with respect to the first stage in the process of oxidation of PAA and its derivatives. A number of papers [3,5,12–14] reported that the cleavage of phenoxy herbicides begins with the electrophilic attachment of hydroxyl radical to the aromatic ring to form a cyclohexadienyl radical, which can then enter into the reactions of dimerization, disproportionation, oxidation, and some others depending on the nature of reaction medium. Under the oxidation conditions, the products of hydroxylation predominate both in the aromatic nucleus and in the α-position of the side chain, which is accompanied by its cleavage and the formation of 2,4-dichlororezorcin or 2,4-dichlorophenol, respectively. It should be noted that derivatives of resorcinol in our case are not formed. The mechanism of phenoxyacetic acid degradation proposed by Ren et al. [15] is most consistent with our experiment. Above mentioned authors analyzed previously obtained experimental data and, using quantum-chemical calculations, showed that the most energy-efficient are ipso-attacks of hydroxyl radicals at the positions of C_1–O, para–C_4 or ortho–C_2 leading to the cleavage of the corresponding groups (if present) and the hydroxylation of the aromatic nucleus in substituted phenoxyacetic acids.

Thus, the most energy-efficient stage for all phenoxy herbicides is the electrophilic ipso-substitution of the side chain by OH-radicals with C_1–O splitting according to the addition-splitting mechanism and the formation of corresponding phenols. Ren et al. [15] noted that a bulky substituent in the ortho-position may create steric interference in the substitution reaction, but if the group has a donor character, then there is a slight activating effect of the ortho-substituent. The presence of electron-acceptor groups in the aromatic nucleus may inhibit in a small extent the process of hydroxylation of the aromatic nucleus. After the completion of the first stage, the process of substituting the groups in the para-position of the aromatic nucleus onto the hydroxyl radicals, with the subsequent oxidation of the corresponding hydroquinones to the benzoquinones, becomes energetically beneficial. Both electron-donors and electron-acceptor substitutions almost do not affect the rate of replacement process. The intermediate σ-complex formed after the OH-radical attack is equally stabilized by the substituents irrespective of their polarity, which leads to a slight acceleration of the substitution reaction as compared to the compound without substituents.

Substituted hydroquinones are further oxidized to benzoquinones, whose destruction takes the basic time of reaction. Simultaneously, a further accumulation of hydroxyl groups in a molecule occurs, initially in the ortho-position, and then elsewhere in the herbicide, which provokes the cleavage of the aromatic nucleus and the formation of a number of aliphatic acids, in particular glycolic, glyoxime, maleic, fumaric and oxalate [6,9,11,15]. According to data of work [15], the formation of aliphatic acids is possible only after the ipso-replacement of the side chain, the complete replacement of the substituents, if they exist, in the para- and ortho-positions of the aromatic nucleus to the hydroxyl groups and subsequent hydroxylation.

Based on the results of photometric investigations on the concentration of chloride ions (Fig. 2) and UV spectra (Fig. 3) during electrolysis, we have experimentally confirmed this scheme of degradation of phenoxyacetic acids by oxidation on PbO_2-anodes. It was established that in the case of oxidation of 2,4-D and 2,4,5-T, the accumulation of chloride ions in the solution occurs and at the moment of disappearance of absorption maxima on UV spectra, the concentration of Cl^- reaches a maximum value. Thus, the concentration of chloride ions in 2–2.5 hours of electrolysis is equal to $(7.6\pm0.2)\times10^{-4}$ mol dm^{-3} (for 2,4-D) and $(1.1\pm0,1)\times10^{-3}$ mol dm^{-3} for 2,4,5-T, respectively, which is 93% and 95%, according to the theoretically calculated concentration of chlorides for the following reactions of incineration of 2,4-D (1) and 2,4,5-T (2) herbicides:

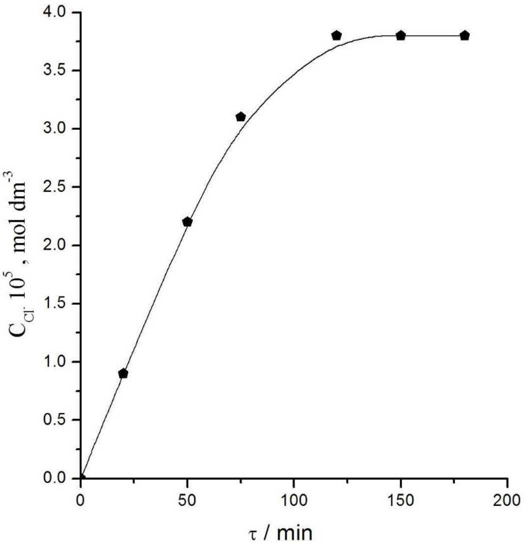

Fig. 2. Change in the concentration of chloride ions as a function of electrolysis time for 0.1 mM 2,4-D solution on PbO_2–Bi anode

$$C_8H_6Cl_2O_3+13H_2O=8CO_2+2Cl^-+32H^++30\bar{e}; \quad (1)$$

$$C_8H_5Cl_3O_3+13H_2O=8CO_2+3Cl^-+31H^++28\bar{e}. \quad (2)$$

It is noteworthy that at the moment from which the slower process of the destruction of aliphatic acids to CO_2 and H_2O begins; the dechlorination process is already completed, which coincides with the results of the calculations given in the paper [15]. Further, the concentration of Cl^- ions remains constant which indicates the stability of chloride ions in the solution under the experimental conditions and the absence of their oxidation to form Cl_2 or oxygen-containing compounds of chlorine.

Spectral data (see Fig. 3) indicate that a complete conversion of 2,4-D to aliphatic products occurs on unmodified anodes in 3 hours. The use of bismuth-modified lead dioxide anode leads to a reduction in the conversion time of the herbicide, which ends in 2 hours. The initial solution of 2,4-D is characterized by the absorption maxima at 230 and 280 nm. At the beginning of electrolysis, a decrease in the absorbance at 230 nm is seen, and the formation of an intermediate oxidation product, benzoquinone, is observed as evidenced by the appearance of the plateau at 250–270 nm. Benzoquinone is the main intermediate compound formed by the oxidation of phenoxyacetic acids, regardless of the nature of the substituents in the aromatic nucleus, however the time required for its accumulation depends on the nature of anode material. Thus, in the case of oxidation of 2,4-D on the PbO_2-anode (Fig. 3,a), benzoquinone appears after 1.5 hours, and it appears after 0.5 hours in the case of PbO_2–Bi-anodes (Fig. 3,b). A further oxidation of the herbicide leads to the disappearance of peaks at 230 and 280 nm and the absence of absorption in the region of 250–270 nm, which indicates a complete conversion of 2,4-D and aromatic products of its oxidation to aliphatic acids after 2–3 hours of electrolysis.

The comparison of the data on oxidation of 2,4-D and PAA shows that in both cases, benzoquinone is the main intermediate product, the formation of which consumes most of the conversion time.

The conversion of the trihalogensubstituted aryloxycarboxylic acids (2,4,5-T and 2,4,6-tribromophenoxyacetic acid) on PbO_2–anodes ends in 4 hours, regardless of the nature of the halogen

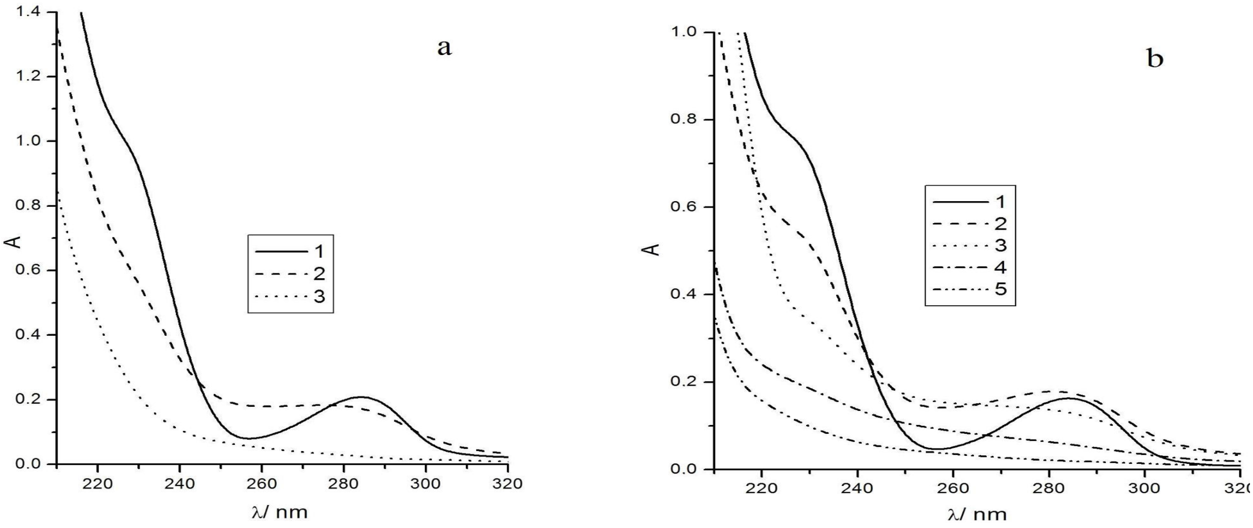

Fig. 3. The electronic absorption spectra of 0.1 mM 2,4-D solution at different electrolysis duration on the non-modified PbO$_2$ anode (a) and PbO$_2$ anode modified by bismuth ions (b), where electrolysis duration is (in hours): 1 – 0; 2 – 1,5; 3 – 3 (a) and 1 – 0; 2 – 0.5; 3 – 1; 4 – 1.5; 5 – 2 (b)

and its location in the aromatic ring (Fig. 4).

As one can see, the destruction of these compounds requires the most time compared to other herbicides, which obviously depends on the number of substituents in the ring. In the UV spectra of 2,4,5-T, we observed a decrease in the absorption maxima of the herbicide and aromatic fragments in the region of 220–230 nm and 280–300 nm (Fig. 4,b). The formation of a halogen-substituted benzoquinone is accompanied by the formation of a plateau in the region of 250–270 nm on the UV spectra. For 2,4,6-tribromophenoxyacetic acid characteristic peaks are located at 310 and 250 nm (Fig. 4,a). After an hour of electrolysis, a peak displacement of 310 nm occurs at a peak of 280 nm, indicating an accumulation in the solution of intermediate benzoquinone, whose concentration decreases over time. The complete destruction of aromatic derivatives of 2,4,6-tribromophenoxyacetic acid occurs in 4 hours of electrolysis.

The electrochemical oxidation of 2,4,6-tribromophenoxyacetic acid and 2,4,5-T on modified lead dioxide anodes does not change the nature of UV spectra, but the time spent on the destruction is much smaller (2.5 hours). Consequently, in the case of direct anodic oxidation on the PbO$_2$ anodes, both

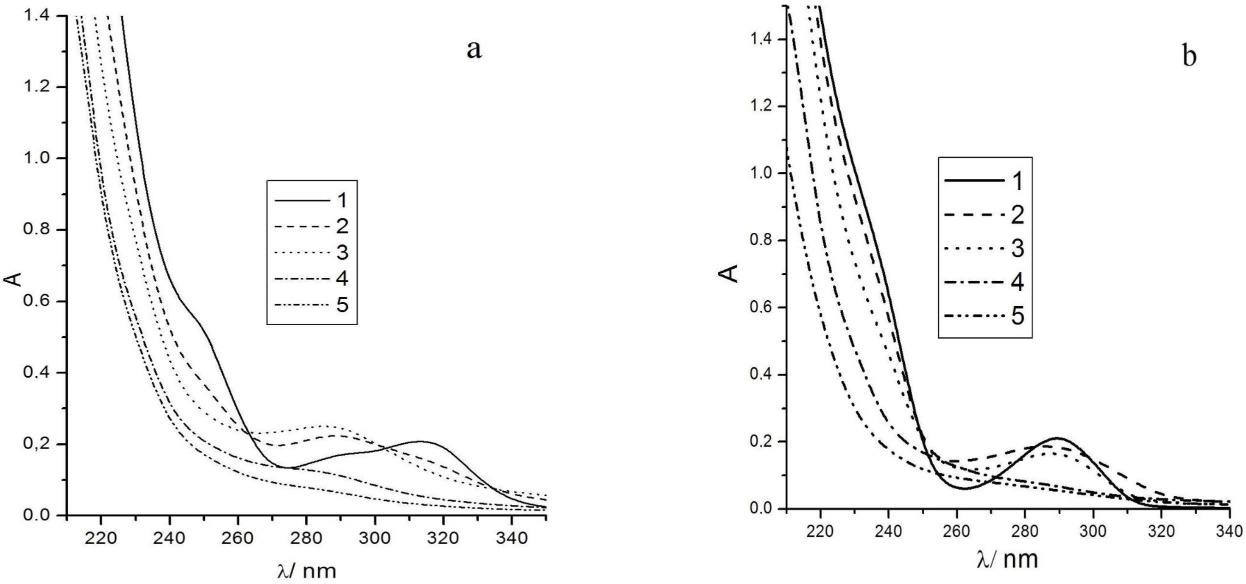

Fig. 4. The electronic absorption spectra of 0.1 M 2,4,6-tribromophenoxyacetic acid solution (a) and 2,4,5-T solution (b) on the PbO$_2$ anode, where electrolysis duration is (in hours): 1 – 0; 2 – 1; 3 – 2; 4 – 3; 5 – 4

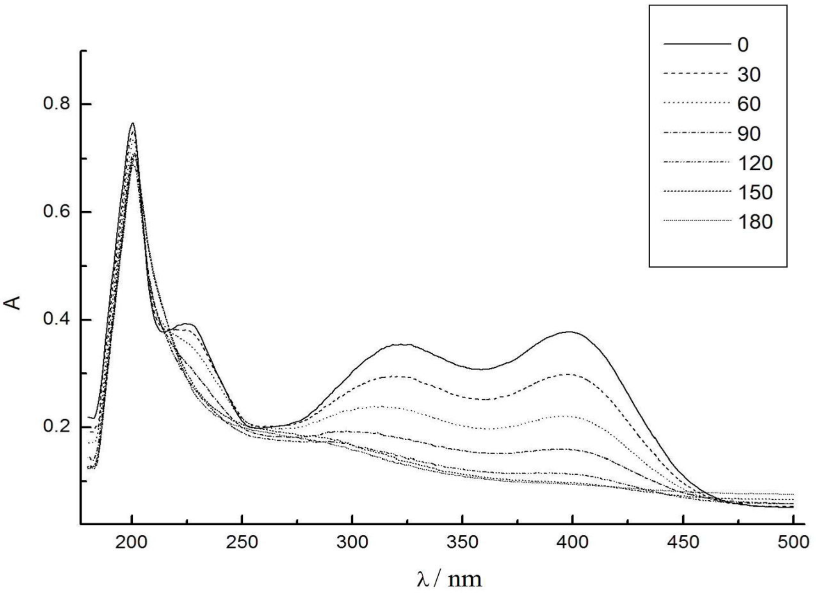

Fig. 5. The electronic absorption spectra of 2×10^{-4} M 4-NPA solution at different electrolysis duration (in hours) on the PbO_2–Bi anode

modified and unmodified, there is a conversion of halogen derivatives of phenoxyacetic acids into non-toxic aliphatic acids that are easily degraded by biological methods, which makes it possible to effectively use this method as a preliminary step in the degradation of toxic halogenated organic compounds in combination followed by biological treatment of wastewater.

The degradation of MCPA on bismuth-doped anodes occurs in 2 hours, which we observed in the case of 2,4-dichloro-and 2,4-dibromo-phenoxyacetic acids. As a result of the ipso-substitution of the side chain in the MCPA, we detected the formation of 4-chloro-o-cresol and glycolic acid, which coincides with the literature data [9]. Further attack of the OH radical on the C_4-position of 4-chloro-o-cresol leads to the formation of methylhydroquinone, which is rapidly oxidized to methyl-p-benzoquinone, as evidenced by the appearance of a plateau at 260–280 nm on the UV spectra.

The electrochemical oxidation of 4-BPA and 4-NPA is also accompanied by the formation of corresponding phenols, but the time required for their destruction is somewhat different from the general scheme (see Table). Thus, 4-BPA on both PbO_2 and PbO_2–Bi anodes is converted into aliphatic compounds faster than PAA, and for the destruction of the 4-NPA it takes much longer. Obviously, the slow oxidation of the 4-NPA is due to the peculiarities of its structure. It is known that p-nitrophenols in solutions are strongly associated with intermolecular hydrogen bonds formed between hydroxyl groups and nitro groups. Consequently, the destruction of these bonds requires an additional time in contrast to the 4-BPA (Fig. 5).

It is noteworthy that a quite rapid conversion in this case is accompanied by the appearance of an intense brown coloration of the solution due to the formation of stable intermediate products, but an increase in electrolysis time leads to the decoloration of the solution. Maleic acid and stoichiometric NO_3^- were identified in the solution by high-performance liquid chromatography. The main aromatic intermediate product in this case was also 1,4-benzoquinone.

Conclusions

Destruction of phenoxy herbicides in aqueous solutions by the electrochemical oxidation on lead dioxide anodes is the safe, ecological and efficient process of water purification and does not require additional use of chemical reagents for oxidation. The oxidant is constantly restored in the reaction medium by electrooxidation of water. PbO_2–Bi anodes deposited from methanesulfonate electrolyte show the highest electrocatalytic activity in advanced oxidation of various phenoxyacetic acids. The use of the electrocatalysts involved allows reducing the incineration time of herbicides by 25–50% compared to unmodified anodes.

It has been established that the polarity of the substituents in phenoxyacetic acids does not affect the efficiency of the hydroxylation process, and electron-acceptor substituents, as well as electron-donors, direct the attack of hydroxyl radicals into para-positions. The conversion time required for the oxidation of the herbicides to the aliphatic compounds in most cases depends on the number of substituents in the aromatic ring and is almost independent of their nature. These facts satisfactorily correlate with the concept of a radical mechanism of ipso-substitution in aromatic compounds when attacked by OH radicals. The first stable product formed by the reaction of addition-splitting of the side chain with the OH radical is the corresponding phenol. Subsequent oxidation with hydroxyl radicals leads to the formation of the corresponding benzoquinones through hydroquinones. Based on UV-spectroscopy, photometric studies and high-performance liquid chromatography, the stoichiometric amounts of Cl^-, NO_3^- ions, which pass into the solution and then do not oxidize, have been identified, the formation of the corresponding benzoquinones has been confirmed. Subsequent hydroxylation of the aromatic ring is accompanied by its cleavage and the formation of aliphatic carboxylic acids, which is further completely mineralized to CO_2 and H_2O.

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ЕЛЕКТРОХІМІЧНЕ ОКИСНЕННЯ ФЕНОКСИГЕРБІЦИДІВ НА ДІОКСИДНОСВИНЦЕВИХ АНОДАХ

Л. Дмітрікова, О. Шмичкова, Т. Лук'яненко, С. Загорулько, О. Веліченко

Досліджено електрохімічне окислення різнозаміщених феноксиоцтових кислот на мікромодифікованих бісмутом діоксидносвинцевих анодах. Встановлено, що полярність замісників у феноксиоцтових кислотах не впливає на ефективність процесу гідроксилювання; електронно-акцепторні замісники, як і донори електронів спрямовують атаку гідроксильних радикалів в пара-положення. Час конверсії, необхідний для окиснення гербіцидів до аліфатичних сполук, в більшості випадків залежить від кількості заступників в ароматичному кільці та майже не залежить від їх природи. Окиснення відбувається згідно з радикальним механізмом іпсо-заміщення в ароматичних сполуках за атаки ОН-радикалів і протікає через утворення відповідного фенолу, подальше окиснення приводить до утворення відповідних бензохінонів через гідрохінони, що було підтверджено методом високо ефективної рідинної хроматографії. Подальше гідроксилювання ароматичного кільця супроводжується його розщепленням і утворенням аліфатичних карбонових кислот, які далі повністю мінералізуються до CO_2 і H_2O.

Ключові слова: плюмбум діоксид, метансульфонатний електроліт, процеси поглибленого окиснення, феноксигербіциди, очистка води.

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The electrochemical oxidation of substituted phenoxy acetic acids on lead dioxide anodes micromodified by bismuth has been investigated. It has been established that the polarity of the substituents in phenoxyacetic acids does not affect the efficiency of the hydroxylation process. Electron-acceptor substituents as well as electron-donors direct the attack of hydroxyl radicals into para-positions. The conversion time required for the oxidation of the herbicides to the aliphatic compounds in most cases depends on the number of substituents in the aromatic ring and is almost independent of their nature. Oxidation occurs according to the radical mechanism of ipso-substitution in aromatic compounds when attacked by OH radicals and proceeds through the formation of corresponding phenol; subsequent oxidation leads to the formation of corresponding benzoquinones through hydroquinones that has been confirmed by high-performance liquid chromatography. Subsequent hydroxylation of the aromatic ring is accompanied by its cleavage and the formation of aliphatic carboxylic acids, which is further completely mineralized to CO_2 and H_2O.

Keywords: lead dioxide; methanesulfonate electrolyte; advanced oxidation processes; phenoxy herbicides; water treatment.

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