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Valorisation of original nanostructured lead oxides thin films issued from an innovating electrochemical depollution process: Application to the total electro-mineralisation of glyphosate

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ABSTRACT

Glyphosate is a very problematic pollutant in the world. This study presents a simple treatment to degrade it until total mineralisation with no production of AMPA (aminomethylphosphonic acid), its main by-product more toxic and persistent, by using original nanostructured lead oxides thin films. The synthesis conditions of these materials were determined previously in relation to an innovating electrochemical depollution process of water polluted by soluble lead. Different parameters were evaluated such as pH, initial concentration, lead oxide type and consequently its particular morphology. The solutions were systematically analysed by ion chromatography to determine the concentrations of organic pollutants and ionic species produced, and by UV-visible spectroscopy to quantify released lead during process. The thin films were characterized by XRD, SEM and EDS, before and after interaction. The Pb-04 sample type (pure β - PbO_2 with cubic needles nanostructures) seems particularly efficient to obtain a total mineralisation with a mineralisation capacity equal to (1127 ± 56) mg of glyphosate/g of material. Moreover, lead was not released in solution due to a total regeneration with the similar crystalline structure. These results are very promising for potential valorisation of heavy metals wastes for future applications at room temperature and very low electrical inputs.

1. Introduction

Glyphosate (N-(phosphonomethyl) glycine, $\text{C}_3\text{H}_8\text{NO}_5\text{P}$) is one of the most used herbicides for agricultural, forestry, and urban setting in the world, that is why this molecule is largely found in environment and particularly in surface and ground waters [1,2]. Moreover, glyphosate can be accumulated in soils, with a long half-life due to its strong adsorption on minerals [3], but it can be also degraded. Indeed, Aminomethylphosphonic acid (AMPA), which is more toxic and persistent than glyphosate, is commonly found in soils as a metabolite of microbial degradation of this widely used herbicide. Most studies that have analysed both glyphosate and AMPA in environmental water samples have assumed that the AMPA is derived (at least mainly) from degradation of glyphosate [4,5]. A study performed by Struger and Byer between 2009 and 2011 on 219 sites on the world shows that 77.2 % among them are contaminated by glyphosate and 76.7 % by AMPA [5].

In 2015, the International Agency for Research on Cancer classified glyphosate as “probably carcinogenic to humans”. Due to its suspected

toxicity, this molecule is controlled and regulated in water. For instance, the concentration of glyphosate found in surface or ground water is in the range of 2–430 $\mu\text{g L}^{-1}$ in the USA, higher than in Europe: 0.59–165 $\mu\text{g L}^{-1}$. These values exceed the maximum contaminant level goal of 0.7 $\mu\text{g L}^{-1}$ for drinking water [1]. Therefore, it is always necessary to improve and/or to develop processes able to degrade glyphosate contained in wastewaters coming from urban, industrial or agricultural, and ideally with no production of AMPA (total mineralisation).

Several review papers have compiled the main treatment technologies applied for the elimination of glyphosate [3,6]. The most conventional methods are (i) adsorption [7–9], (ii) biological treatment [10,11], (iii) Advanced Oxidation Processes (AOPs) [12,13], and (iv) (electro)-chemical oxidation process of glyphosate or AMPA by different types of materials [14–17].

This latter method appears very promising for future applications. For example, pure birnessite (a manganese oxide) as electrodeposited thin films, used as material electrodes, is an eco-friendly and efficient technique for the degradation of glyphosate and AMPA, until mineralisation of 80 %, in very soft conditions (room temperature) and at low

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Table 1

Lead oxides films obtained as a function of pH and potential, in pure water or in the presence of ions in solution, for an electric charge equal to 0.9C: Crystalline structure and morphologies.

Samples	pH	E (V)	electrodeposition medium	time (min)	Mass (10 ⁻³ g)	Precipitation yield (%)	Crystalline structure	Morphology Q = 0.9C
Pb-01	4.2	0.7	Milli-Q water	183	0.9	81	β -PbO ₂ + Pb ₃ O ₄	Irregular
Pb-02	2	1.0	Milli-Q water	166	0.6	54	β -PbO ₂	Irregular
Pb-03	2	1.2	Milli-Q water	75	0.8	72	β -PbO ₂	Branch
Pb-04	4.2	0.7	NaCl (1 M)	100	0.6	54	β -PbO ₂	Cubic needles
Pb-05	4.2	0.7	NaNO ₃ (1 M)	210	0.5	45	β -PbO ₂ + Pb ₃ O ₄	Irregular
Pb-06	4.2	0.7	Na ₂ SO ₄ (1 M)	110	0.5	45	β -PbO ₂	Irregular

costs (very low electric inputs, no production of radicals). Although long interaction durations may be required for concentrated solutions, this material can self-regenerating, which is a real asset for applications [14]. This low electric input is a very easy way to improve the spontaneous degradation capacities of the thin films of manganese oxides (e.g. oxidation processes via spontaneous electronic transfers), and their self-regenerating capacities [14].

In the literature, other materials used as electrodes are reported to degrade glyphosate, with more or less complex compositions (i.e. Ti/Ru_{0.30}Sn_{0.70}O₂; Ti/(RuO₂)₂(Ta₂O₅)_{0.30}; Ti/Ru_{0.30}Pb_{0.70}O₂; ...), [15]. For example, Neto and De Andrade [15] have studied glyphosate oxidation by using complexes anodes in chloride medium. After 4 h of electrolysis with an anode Ti/Ru_{0.30}Sn_{0.70}O₂, a complete glyphosate removal from the electrolysed solution was achieved. In the chloride matrix, the application of 50 mA cm⁻² allowed to reach nearly total mineralisation (release of phosphate ions close to 91 %). However, chlorination can be inappropriate, notably from the associated risk of forming toxic by-products such as organochlorinated compounds.

As far as we know, only two studies in the literature have investigated the electro-degradation of glyphosate by pure PbO₂, one on 3D anodes boron-doped diamond (BDD) electrodes [16] and the other one on Ti [17]. The degradation performed by electro-oxidation following the application of current with high intensities, seems efficient to degrade glyphosate with high mineralisation rates. Nam Tran et al. [17] provide by measurement of Total Organic Carbon (TOC) a degradation of 95 % of glyphosate by using Ti/PbO₂ anode in sulphate medium with a current intensity equal to 4.77 A and a treatment time fixed to 173 min. However, it is important to mention that lead released in solution was not measured during the degradation, while this point could be essential for applications.

Therefore, it appears that the degradation was performed only by electro-oxidation following the application of current with high intensities. In contrary, no study has yet investigated the possible spontaneous degradation of PbO₂ by oxidation processes, as far as we know. In the present article, we studied different thin films of pure lead oxides with original nanostructures for testing their (electro)-chemical oxidation capacities towards glyphosate. The synthesis conditions of these materials were determined previously in relation with an innovating electrochemical process of water depollution containing soluble lead [18,19]. They were electrodeposited by varying the potential, the pH and the medium containing soluble lead. The crystalline structures of these films, never reported in the literature, appear originals for such oxides and could be very interesting for these semiconductor materials, which can be used in numerous applications (catalysis, energy, photovoltaic...), and particularly for (electro)catalytic reactions towards organic pollutants. Indeed, PbO₂ is known in the literature for having good properties to degrade pharmaceuticals pollutants for example [20].

The first part of this paper describes the synthesis of these films and their particular crystalline structures, and the second part is devoted to the study of their degradation capacities towards glyphosate, in first by spontaneous interaction and in second one by coupling with electrochemistry. We have chosen to study the behaviour of these materials to-

wards the degradation of glyphosate because we have already developed its very efficient (electro)-degradation by thin films of manganese oxides with very low energy inputs. In this context, we have developed a systematic and rigorous experimental procedure based on analyses of solution in addition to the characterisation of materials [14,21], which was similarly applied in the present paper. Finally, some information about possible applications are given and discussed.

2. Experimental

2.1. Chemicals

Reagents, glyphosate (1000 µg.mL⁻¹ PESTANAL® analytical standard Sigma Aldrich ≥100 %), NaOH (1 M, Fluka ≥97 %), NaCl (ACS Reagent Sigma Aldrich ≥99.0 %), NaNO₃ (ACS Reagent Sigma Aldrich ≥99.0 %), and Na₂SO₄.10 H₂O (ACS Reagent Sigma Aldrich ≥99.0 %), a standard solution of Pb(II) (1002 ± 4 mg.L⁻¹, 5 % HNO₃, Alfa Aesar) intended for use as certified reference materials or calibration standard for inductively coupled plasma optical emission spectroscopy (ICP-OES), were used as received. All solutions were prepared by using Milli-Q water.

2.2. Electrochemical synthesis of lead oxides thin films

The electrodeposition of lead oxide thin films were done by using 50 ml of Pb(II) solution prepared at 27 mg L⁻¹ in different media such as pure water (Milli-Q), or in the presence of NaCl (1 M) or NaNO₃ (1 M) or Na₂SO₄ (1 M). The pH of the solution was adjusted by NaOH (1 M) if necessary. Chronoamperometry method was used for the electrodeposition of lead oxide thin film by imposing a constant potential with a fixed electrical charge Q (Coulomb, C). The choice of the synthesis potential according to the chemical medium for each thin film was made according to the depollution process already patented and published [18,19]. A classical electrochemical cell with three electrodes was used: a reference electrode of mercurous sulphate type, a platinum wire as a counter electrode, and a glass plate covered with tin dioxide SnO₂:F (FTO Fluorine-doped Tin Oxide, Solems, noted SnO₂), with a surface delimited by an adhesive (3cm²) as a working electrode. All electrodeposition was performed at room temperature with gentle stirring of solution by a magnetic stirrer (250 rpm).

2.3. (Electro)-chemical oxidation experiments

Degradation studies were performed with one sample of electrodeposited lead oxide introduced into a cell containing 20 ml of milli-Q water with glyphosate (no electrolyte) at different concentrations, from 25 µM (4.2 mg L⁻¹) to 200 µM (33.8 mg L⁻¹). Different parameters were studied and optimised for an efficient degradation of glyphosate until mineralisation: initial pH of solution, lead oxide sample type, value of the imposed potential. At the end of the interactions, the pH was systematically measured and no change was noted whatever the conditions.

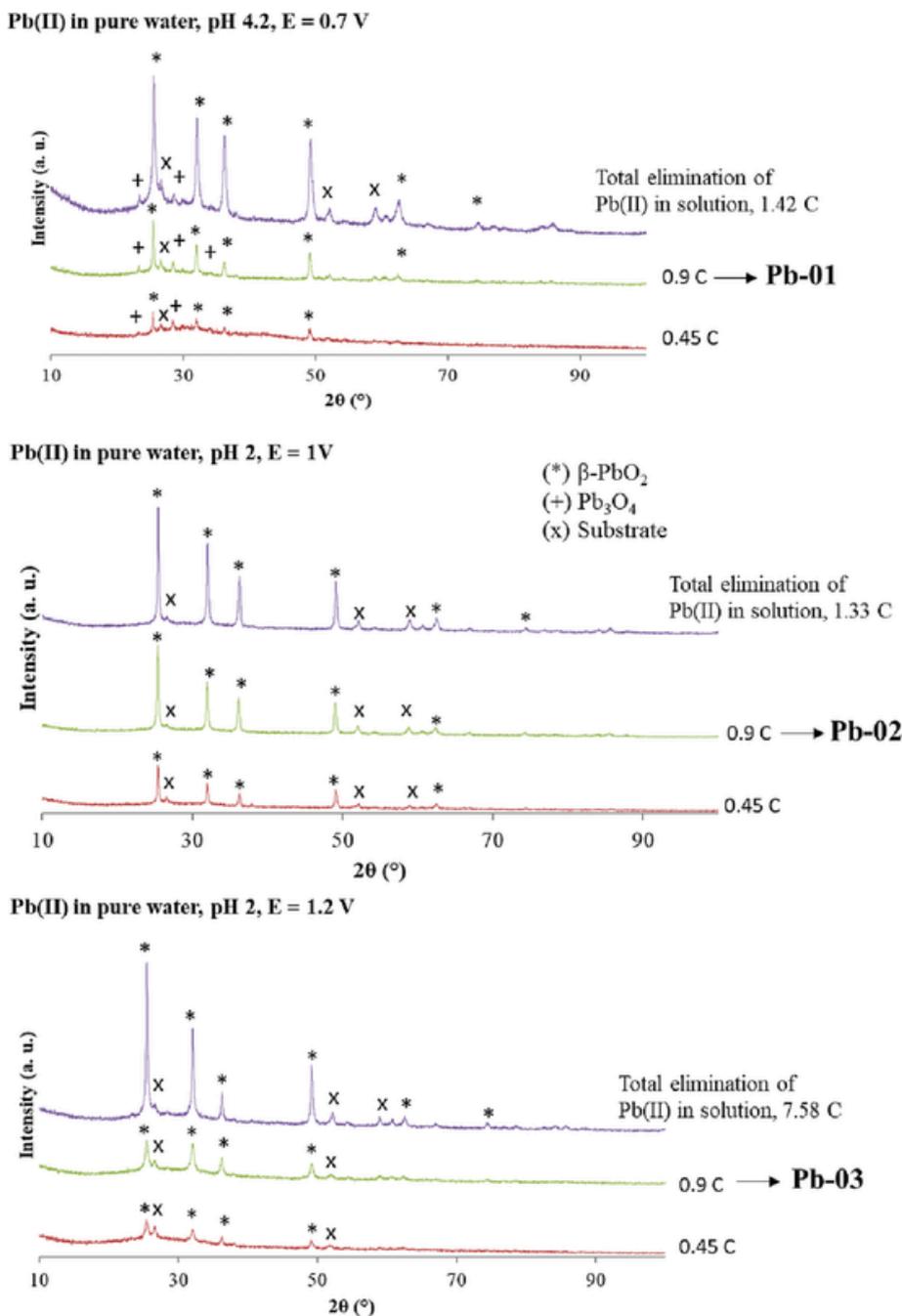


Fig. 1. X-ray diffractograms of electrodeposited lead oxides thin films onto SnO₂ substrate (S = 3 cm²), with different electrodeposition conditions, from a Pb(II) solution at 27 mg L⁻¹ in pure water for different electrical charges.

2.4. Analyses of solution

The solutions being always clear whatever the conditions, the analyses were performed directly without filtration. To determine the concentrations of glyphosate and AMPA, nitrate and phosphate ions, the solutions were analysed by ion chromatography (Thermo Fisher Scientific, Dionex integrion HPIC) before and after interaction. The column type is "Dionex IonPac AS19-4 μ m IC Columns", and hydroxide was the eluent used with a gradient method.

Nevertheless, it is well known that orthophosphate ions, generated by C—P bond cleavage, are the better indicator of mineralisation rates of glyphosate [14,21,22]. That is why, for determining the degradation and/or mineralisation of glyphosate, we based on the determination of the remained concentrations of glyphosate, in addition to the concen-

trations of AMPA and phosphate ions produced. Therefore, after interaction of lead oxide thin film with a solution of glyphosate, the degradation rates were calculated according to the Eq. (1), and the mineralisation rates according to the Eq. (2), [14,21]:

$$\% \text{Degradation} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

With C₀, the initial concentration of glyphosate (mol L⁻¹), and C_t (mol L⁻¹) the remaining concentration of glyphosate determined at t (h).

$$\% \text{Mineralisation} = \left(\frac{C_{\text{Ions phosphate produced}}}{C_0 \text{ glyphosate}} \right) \times 100 \quad (2)$$

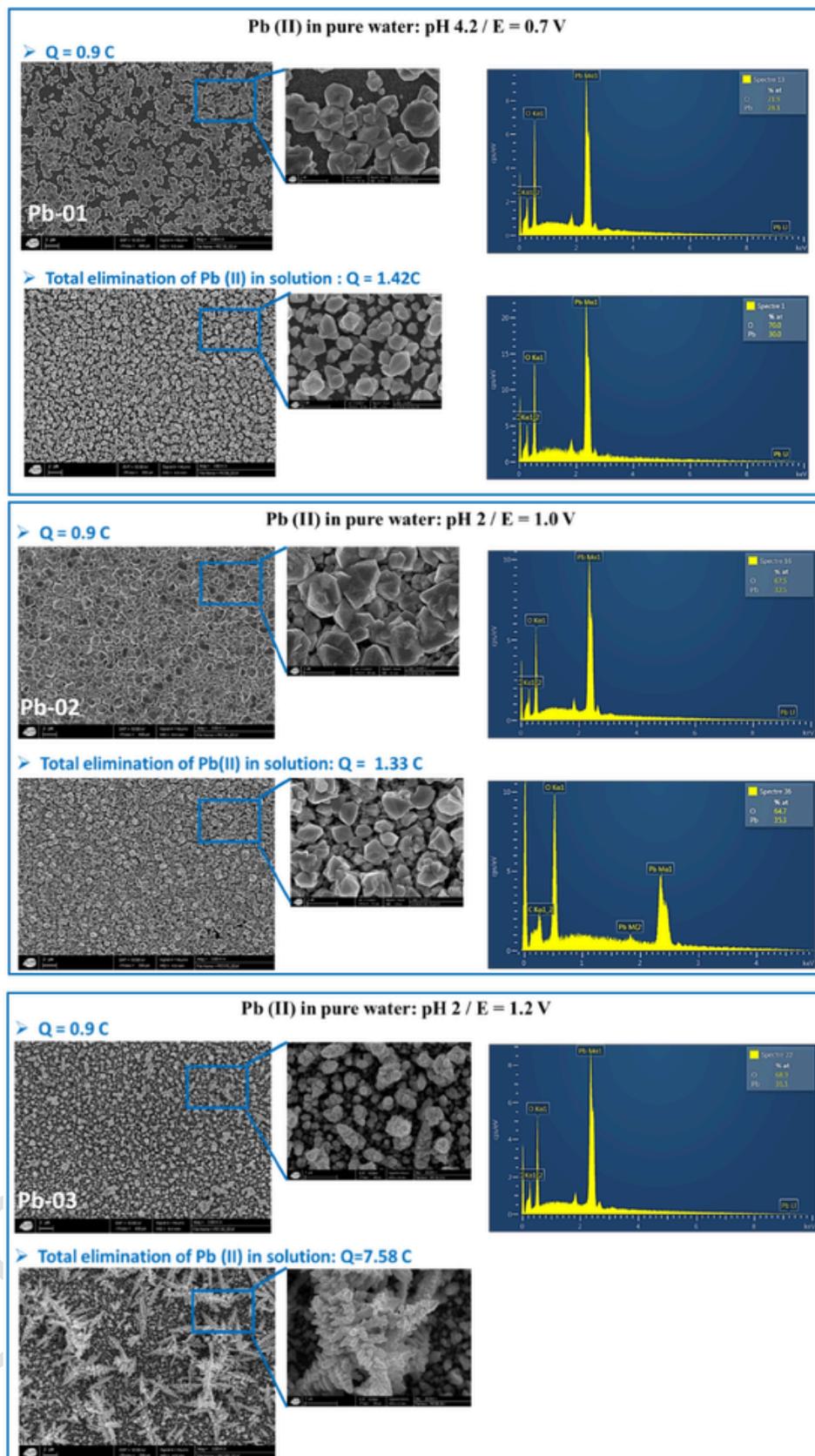


Fig. 2. SEM observations ($\times 3000$ and $\times 20,000$) and associated analyses by EDS of electrodeposited lead oxides thin films onto SnO_2 substrate ($S = 3 \text{ cm}^2$), with different synthesis conditions, from a Pb(II) solution at 27 mg L^{-1} in pure water for $Q = 0.9 \text{ C}$ and the electrical charges for the total elimination of Pb (II).

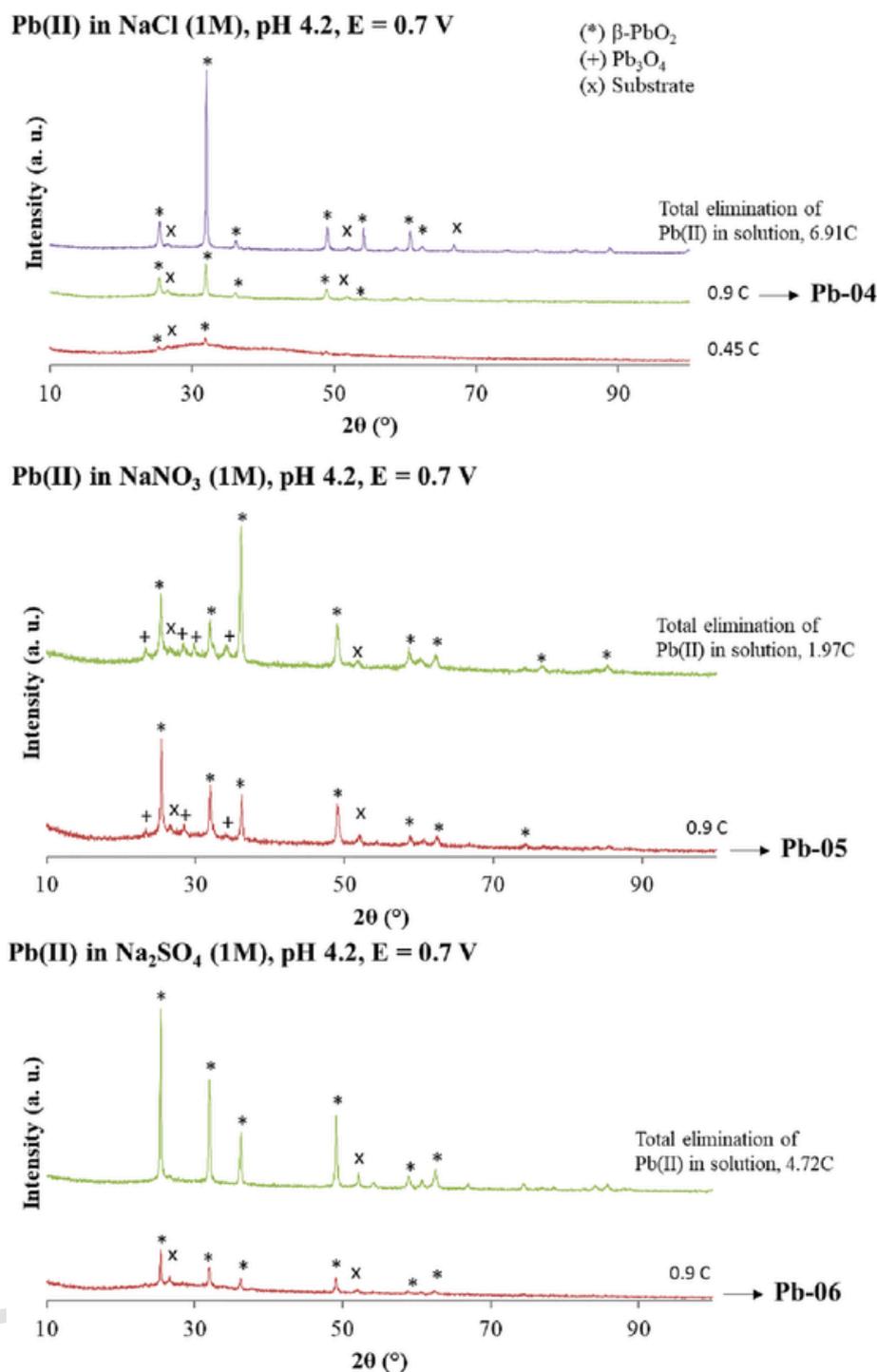


Fig. 3. X-ray diffractograms of electrodeposited lead oxide thin films onto SnO₂ substrate ($S = 3 \text{ cm}^2$) obtained from a Pb(II) solution at 27 mg L^{-1} in the presence of ionic species in aqueous solution for different electrical charges.

With $C_{\text{ions phosphate produced}}$ the concentration of phosphate ions (mol L^{-1}) determined in solution after t (h), and C_0 , the initial concentration of glyphosate (mol L^{-1}).

In addition, released lead in solution was checked after each interaction experiment by UV-visible measurements using the appropriate Pb Spectroquant® test (1.09717.0001; 0.1 mg L^{-1} to 5.00 mg L^{-1} corresponding to $0.483 \text{ }\mu\text{M}$ to $24.1 \text{ }\mu\text{M}$ respectively). Absorbance measurements were performed at wavelength $\lambda = 520 \text{ nm}$ by a spectrophotometer (Varian Cary® 50 UV-visible Agilent) in an optical cell (1 cm) [19].

2.5. Characterisation of thin films

All characterisations were carried out before and after interactions, directly without any preparation step since the thin films were sufficient conductive and adherent. The crystal structure of the recovered films was determined by X-Ray Diffraction (XRD) with classical measurements ($\theta/2\theta$) by a BRUKER θ - θ diffractometer equipped with a copper anode ($\lambda_{\text{Cu}} = 1.540600 \text{ \AA}$) and a LYNXEYE detector.

The texture of the thin films was observed by a MEB-FEG MERLIN Zeiss Scanning Electron Microscopy (SEM). These observations were

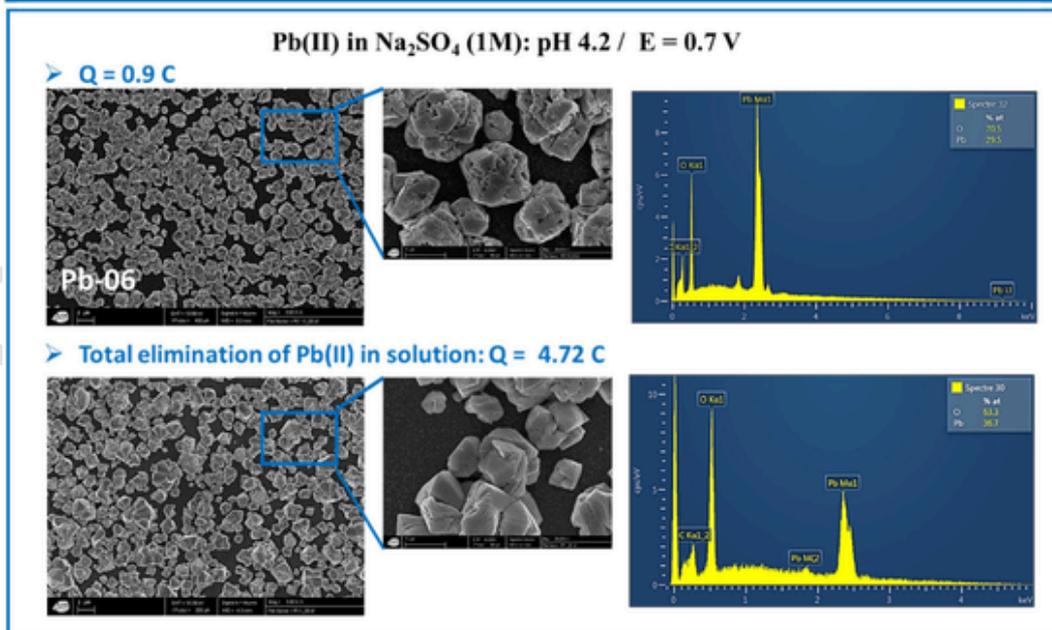
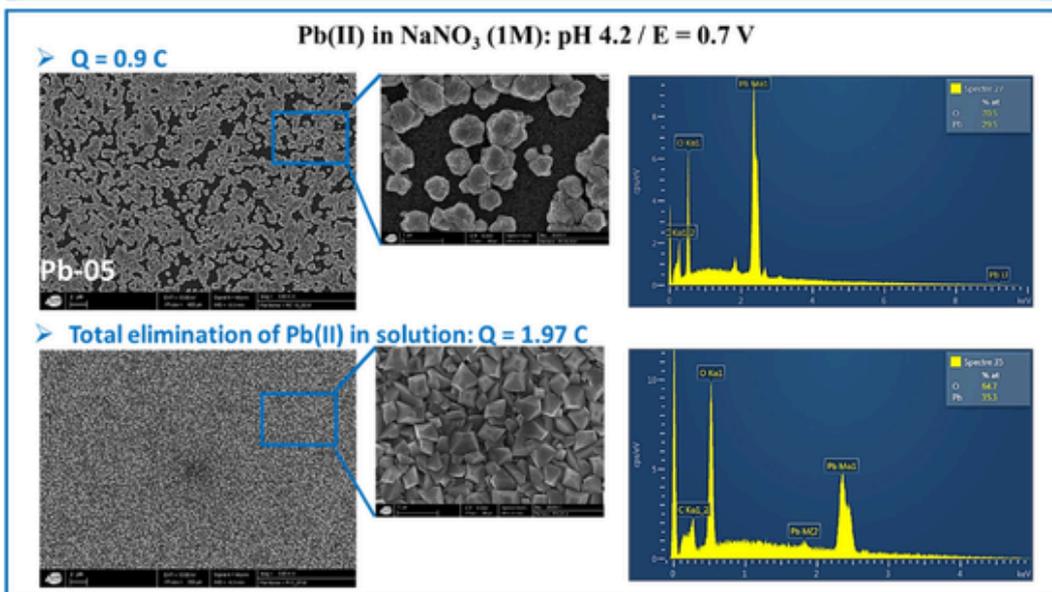
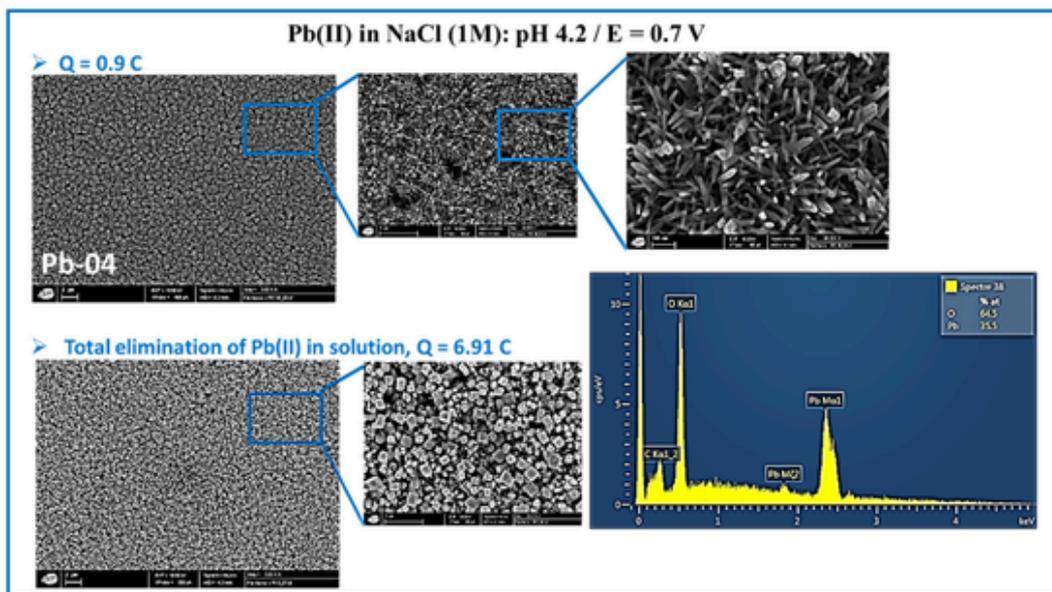


Fig. 4. SEM observations ($\times 3000$, $\times 20,000$ and $\times 100,000$) and the associated EDS analyses of electrodeposited lead oxide thin films onto SnO_2 substrate obtained from a Pb(II) aqueous solution at 27 mg L^{-1} in the presence of ionic species for $Q = 0.9\text{C}$ and the electrical charges for the total elimination of Pb(II) .

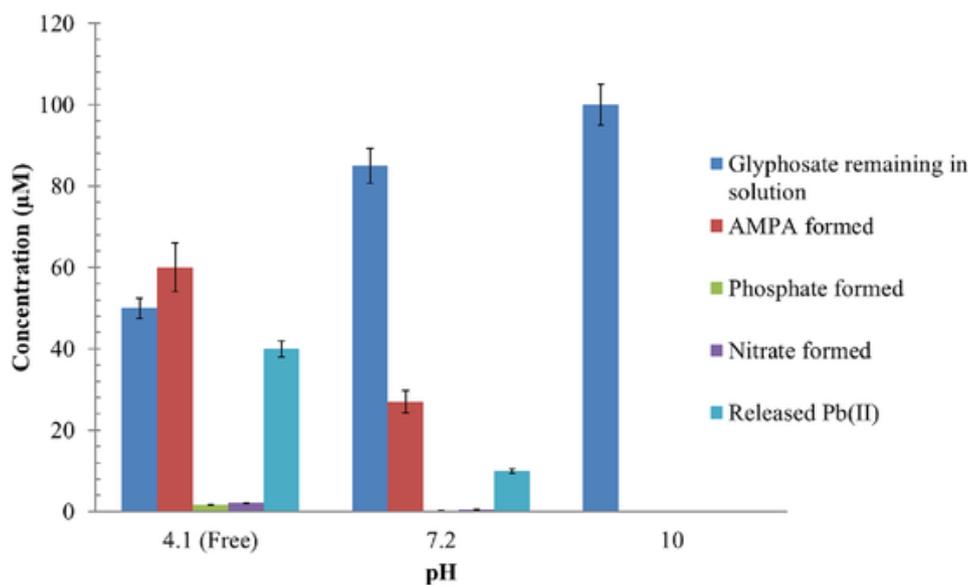


Fig. 5. Concentrations of species present in solution after interaction of an aqueous solution with initially $100 \mu\text{M}$ of glyphosate at different pH in a thermostatically controlled oven at $25 \text{ }^\circ\text{C}$ during 24 h under stirring at 250 rpm, with Pb-01 lead oxide sample.

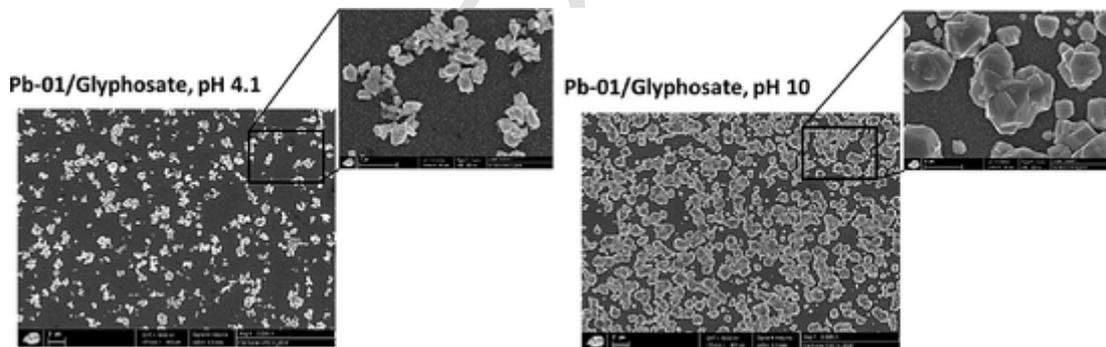


Fig. 6. SEM observations of Pb-01 lead oxide samples ($\times 3000$ and $\times 20,000$) after interaction and degradation of glyphosate (initial concentration equal to $100 \mu\text{M}$ in aqueous solution) with different initial pH in a thermostatically controlled oven at $25 \text{ }^\circ\text{C}$ during 24 h under stirring at 250 rpm.

supplemented by Energy Dispersive Spectroscopy analyses (EDS) to determine the chemical composition.

3. Results and discussion

3.1. Electrodeposition of lead oxide thin films: influence of the medium

The electrodeposition of lead oxides thin films was performed from a Pb(II) solution under different conditions depending of the pH and the medium, either in pure Milli-Q water, either in the presence of ionic species, and based to our previous study focused on the total depollution of aqueous solutions containing soluble lead [18,19]. The experimental conditions of the six different types of samples are regrouped in Table 1. In the aim to study its eventual effect on the nanostructure, different values of electric charges were imposed during the electrodeposition (0.45C and 0.9C), in complement to the free electric charge Q corresponding to the total removal of lead containing in the starting solution (27 mg L^{-1}), this latter value varying in function of the experimental conditions. For each case, the adherent films electrodeposited on the conductive substrate (SnO_2) were characterized by XRD, SEM and EDS.

3.1.1. In pure milli-Q water

Fig. 1 reports the three diffractograms of the films electrodeposited in pure Milli-Q water for the different values of pH and potentials as indicated in Table 1. In all cases, the solids are well crystallized with the presence of many peaks, and the crystallinity increases with the electric charge, in link to an increase of the electrodeposited amount (Faraday's law, Eq. (3)). The main diffraction peaks observed for the three diffractograms at 25.4° , 32.0° , 36.2° , 49.1° , 52.2° , 62.5° and 74.5° belong to the $\beta\text{-PbO}_2$ planes (110), (101), (200), (211), (220), (301) and (321) respectively, by comparison with the standard diffraction peaks (JCPDS 89-2805). But, for an electrodeposition performed at $\text{pH} = 4.2$ and a potential of 0.7 V, Pb_3O_4 is also detected according to JCPDS 85-0859 card, however as a few amount due to the very low intensity of the characteristic peaks observed at 23.2° and 30.8° (planes (100) and (110) respectively). These results are in good coherence with the diagram of Pourbaix [23].

Fig. 2 presents the SEM observations of the deposits obtained for $Q = 0.9\text{C}$ and the free electrical charges corresponding to the total elimination of soluble lead, with the associated analyses by EDS. In all cases, lead and oxygen are detected with percentages in good agreement with the XRD measurements, which report the formation of pure

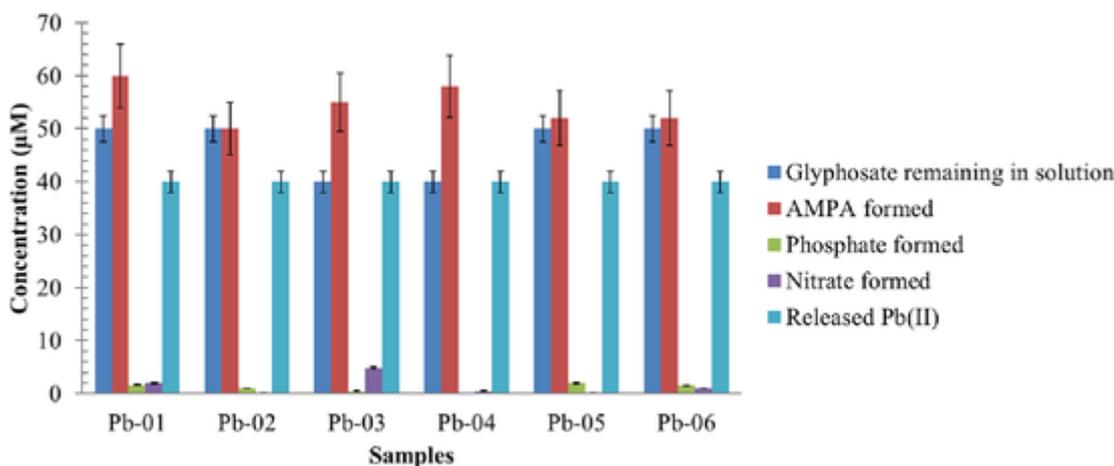


Fig. 7. Concentrations of species present in solution after interaction of an aqueous solution with initially 100 μM of glyphosate and a pH equal to 4.1 (free) in a thermostatically controlled oven at 25 $^{\circ}\text{C}$ during 24 h under stirring at 250 rpm, with different types of electrodeposited lead oxide samples.

oxides. The presence of Sn, corresponding to the substrate (i.e. SnO_2) was not detected for these values of electric charges indicating that the amount and/or covering of the surface were important. It appears also that the morphology of the crystals varies considerably in function of the conditions (potential and pH).

For a solution at pH 4.2, and under a potential of 0.7 V, crystals present irregular morphologies (no defined shape), which is the most common morphology found in the literature [24,25]. By increasing the electric charge Q, the morphology was preserved as well as the size of the crystals, but the covered surface becomes more important. When the electrodeposition occurred at 1.0 V at pH = 2, the crystals present the same irregular morphology, and when the electric charge Q increases, the surface coverage stayed identical with the preservation of such morphology. In contrary, under a potential of 1.2 V at pH = 2, the crystals have the appearance of branches, which become more and more dendritic with the increase of the electric charge Q.

While the irregular morphology is the most common found in the literature [24,25], conversely no study in the literature mentions the electrodeposition of lead oxide as $\beta\text{-PbO}_2$ under other morphologies, such as branches or dendritic branches as reported in this study.

3.1.2. In presence of ionic species

The electrodeposition of lead oxide films was performed by imposing a potential of 0.7 V at pH = 4.2 in the presence of NaCl (1 M), or NaNO_3 (1 M), or Na_2SO_4 (1 M) for different values of electrical charges. As previously, the adherent films obtained were characterized by XRD, observed by SEM, and analysed by EDS.

The X-ray diffractograms of these films show that the solids are well crystallized and that their crystallinity increases with the electric charge Q, Fig. 3. In the presence of NaCl (1 M) or Na_2SO_4 (1 M), an adherent film of pure $\beta\text{-PbO}_2$ is obtained while in the presence of NaNO_3 (1 M), the deposit is composed of a mixture of lead oxides, similarly as in pure water for this value of pH ($\beta\text{-PbO}_2$ as a main compound with a small amount of Pb_3O_4). Furthermore, a significant preferential orientation was observed in the case of NaCl and NaNO_3 according to the plane (101) at 32.0° and (200) at 36.2° respectively.

The deposits obtained for $Q = 0.9\text{C}$ and the free electrical charges corresponding to the total elimination of soluble lead were also observed by SEM and analysed by EDS, Fig. 4. According to the EDS analyses, lead and oxygen are detected in all cases with the percentages of oxygen and lead in good agreement with XRD results confirming the formation of pure lead oxides. As previously, the presence of Sn, corresponding to the substrate (i.e. SnO_2) was not detected for these values of electric charges, indicating that the amount and/or covering of the surface were important. Moreover, it also appears on Fig. 4 that the

morphology of the crystals varies considerably depending of the ions present in solution and also according to the electric charge Q, proportionally related to the amount of material electrodeposited according to Faraday's law (Eq. (3)).

For example, in the presence of NaCl (1 M), crystals of pure $\beta\text{-PbO}_2$ are in the form of needles, for an electric charge equal to 0.9C, and when the electric charge raises, the needles growth as cubic form. In the presence of NaNO_3 (1 M), lead was electrodeposited as a mixture of $\beta\text{-PbO}_2$ and Pb_3O_4 , according to XRD measurements, and the morphology of the crystals is irregular for an electric charge fixed to 0.9C. However, for a quantity of electricity equal to 1.97C corresponding to a total elimination of lead, one obtains a morphology in the shape of pyramid, which is in good coherence with the preferential orientation observed on diffractogram for this specific value of electric charge. In contrary, in presence of Na_2SO_4 (1 M), lead oxide electrodeposited as pure $\beta\text{-PbO}_2$ presents always an irregular and classical morphology for both amounts of electricity (0.9C and 1.25C). These different morphologies can be due to that following the nucleation phase, some ions in solution (NaCl or Na_2SO_4 or NaNO_3) can poison certain surfaces and then induce the growth of particles in specific directions. Indeed, some molecules can be adsorbed and modified the growth process even blocking the active sites inhibiting [26].

Table 1 summarizes the conditions of the six electrodeposited lead oxide samples, with the duration and the mass for an electric charge fixed to 0.9C, and the associated composition and morphology. The choice of this electric charge value allows having the minimum possible mass of PbO_2 electrodeposited with a good repeatability of synthesis. Furthermore, in all cases, thin films were well adherent and visually very homogeneous. It appears also that in all cases, the synthesis of the films is performed by the formation of 3D islands during the electrochemical process. This observation is relatively classical for electrodeposition process that begins generally from surface or nucleation site defects [18,19,26].

According to Faraday's law, Eq. (3), the theoretical mass of the electrodeposited lead oxide as PbO_2 for an electrical charge fixed to $Q = 0.9\text{C}$ is equal to $1.11 \times 10^{-3}\text{ g}$ (with $n = 2$ and $M = 239.2\text{ g}\cdot\text{mol}^{-1}$).

$$m_{\text{theo}} = \frac{Q}{n \cdot F} \cdot M \quad (3)$$

With Q, the electrical charge; n, the number of electrons required for the formation of one mole of the studied chemical compound; F: Faraday's constant (96,485C mol⁻¹); M: molecular weight of the studied chemical compound.

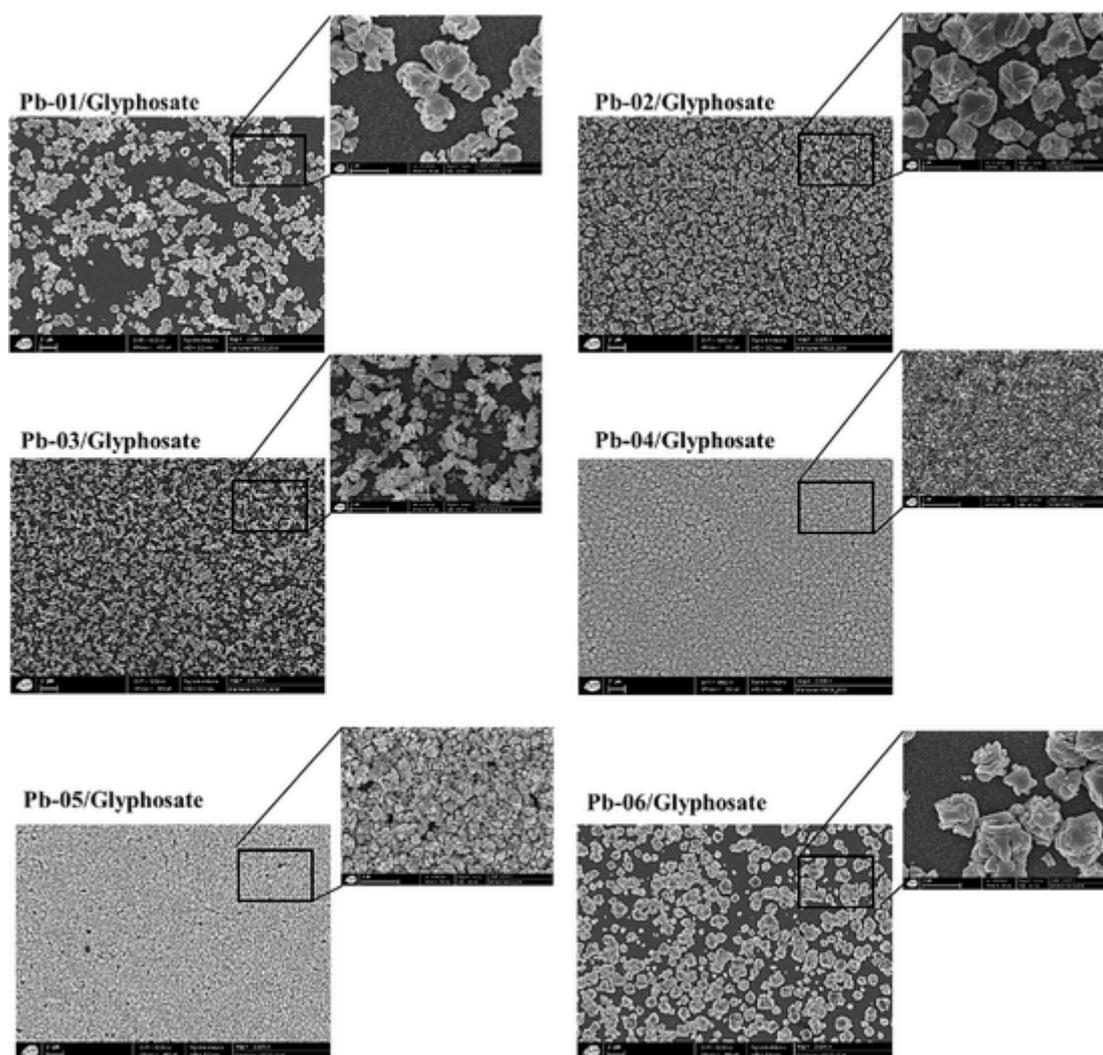


Fig. 8. SEM observations of the different lead oxide films ($\times 3000$ and $\times 20,000$) after interaction and degradation of an aqueous solution with initially $100 \mu\text{M}$ of glyphosate and a pH equal to 4.1 (free) in a thermostatically controlled oven at 25°C during 24 h under stirring at 250 rpm.

It appears that the faradic and precipitation yields vary for each electrodeposition condition, which is not surprising due to the difference of morphologies, Table 1.

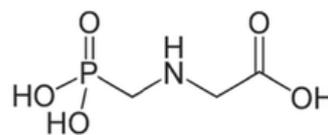
Few studies in the literature describe the mechanism of lead oxide formation and all these studies have the objective of synthesizing this compound for various applications, and not in the aim to depollute aqueous solutions [27–29]. That is why these original morphologies, in the form of branches, needles, pyramids and cubes are not classical and were never reported in the literature, as far as we know. Hence, knowing if these samples are interesting for applications and particularly for (electro)-catalytic applications seemed pertinent. For that, we have studied their degradation capacity towards glyphosate as organic pollutant by spontaneous and electrochemical ways.

3.2. Degradation of glyphosate and expected by-products

The mineralisation of glyphosate has been largely studied in the literature by different processes, such as via microbial degradation [30], birnessite powder [22] or as electrodeposited thin films [14,21] or by advanced oxidation process [3].

Two main degradation pathways for glyphosate are reported in the literature: one by C—N bond cleavage in first via the production of AMPA, which can be also degraded into phosphate ions, Eqs. (4.1) and

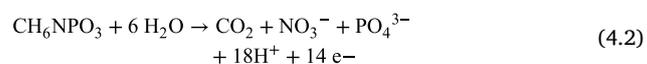
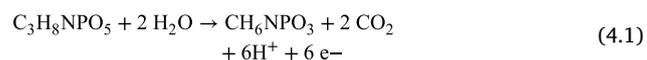
(4.2) respectively, and the other one by a direct mineralisation into phosphate ions by C—P bond cleavage, Eq. (5).



Glyphosate, $\text{C}_3\text{H}_8\text{NPO}_5$

AMPA,

- Glyphosate degradation via AMPA production (C—N bond cleavage):



- Direct mineralisation of glyphosate (C—P bond cleavage):

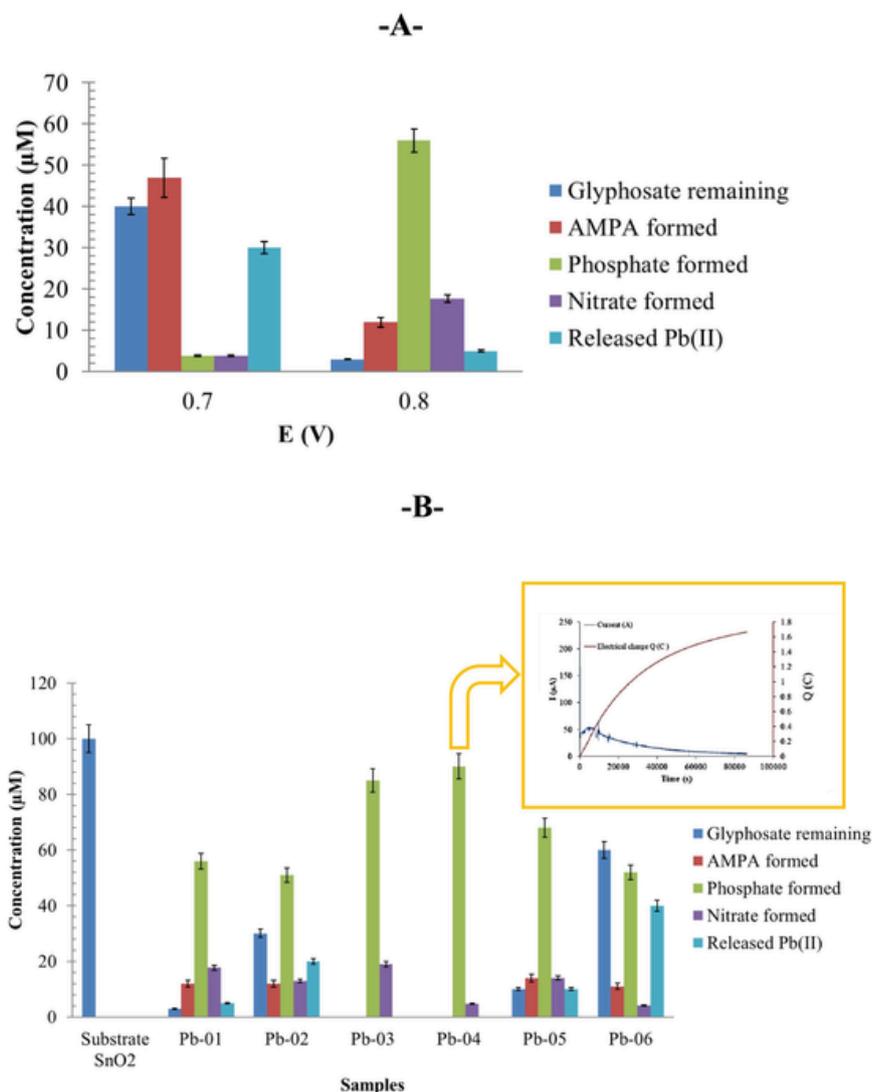
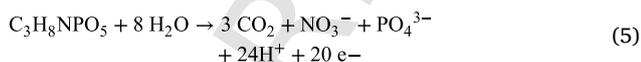


Fig. 9. Concentrations of species present in solution after interaction of glyphosate aqueous solution with an initial concentration of 100 μM and a pH equal to 4.1 (free) during 24 h under stirring at 250 rpm with -A- Pb-01 sample with different imposed potential values; -B- Different types of samples with a potential fixed at 0.8 V. Insert: Variation of the current and the electrical charge as a function of time during the degradation of glyphosate by using Pb-04 sample.



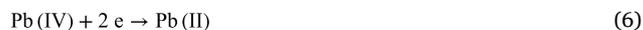
As far as we know, only two studies in the literature report the degradation of glyphosate by pure lead oxide, and only under the effect of high applied currents, and not by a simple direct contact (e.g. spontaneous reaction) or with very few electrical inputs like performed with thin films of manganese oxides [14,21]. According to these two studies, the degradation was done through the generation of physically adsorbed hydroxyl radicals and the oxidation of glyphosate may be total. It is important to mention also that no studies in the literature have measured the release of lead in solution during the degradation, while this point could be essential for applications.

In this study, the option of direct electronic transfers was supposed due to the strong oxidant properties of lead oxides. For that, the degradation of glyphosate could be similar to that observed in the case of manganese oxide thin films [14,21] either in spontaneous way either coupled to electrochemistry. However, in this latter case, the formation

of radicals can be excluded since the intensity of currents will be very low (only few $\mu\text{A cm}^{-2}$).

If glyphosate is partially degraded into AMPA, or totally mineralised, then in parallel lead oxide must be reduced with the production of Pb(III) and/or Pb(II) species by spontaneous electronic transfers. However, Pb(III) being very unstable [31], it is more likely that Pb(IV) will be reduced into soluble Pb(II), Eq. (6):

■ Reduction of lead Pb(IV) contained in lead oxide:



For proving that glyphosate was degraded and/or mineralised with lead oxides thin films by spontaneous reactions and/or with a low electrical inputs, the concentrations of glyphosate and by-products, such as AMPA, nitrate and phosphate ions were systematically quantified by ion chromatography, and the release of lead in solution was measured after each interaction by UV-visible measurements using the Spectroquant® kit, in complement to the characterisation of the solids by XRD, SEM and EDS after interaction experiments.

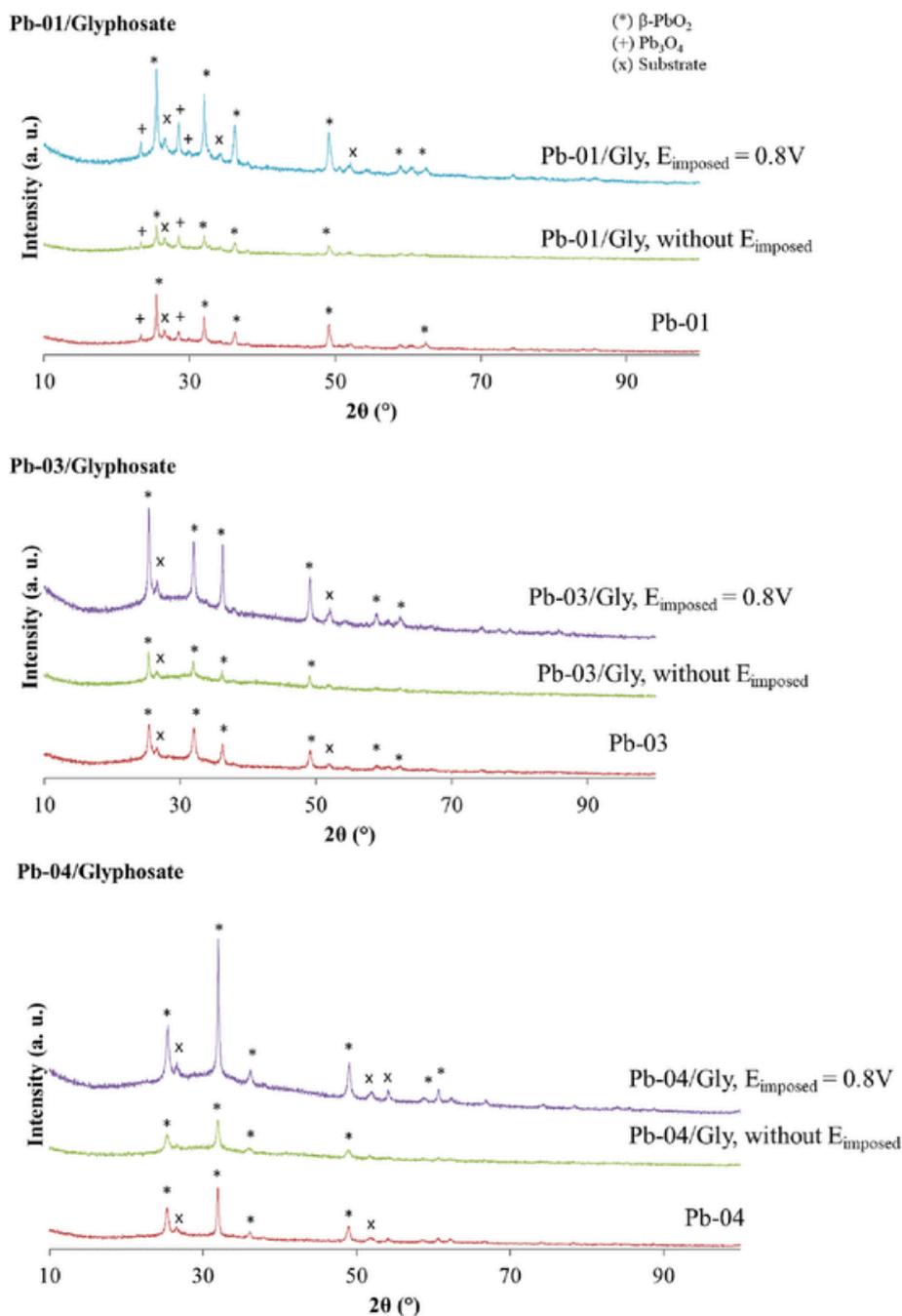


Fig. 10. X-ray diffractograms of different types of samples before use, after interaction with an aqueous solution of glyphosate with initially 100 μM and a pH equal to 4.1 (free) during 24 h under stirring at 250 rpm, without and with applied potential ($E = 0.8 \text{ V}$).

3.3. Studies of the degradation ability of these electrodeposited lead oxide thin films towards glyphosate by spontaneous interaction

The influence of different parameters such as the initial pH of the solution, the initial concentration of glyphosate, the type of sample, was studied. Nevertheless, in a first step, for studying the optimal parameters of degradation, the conditions were researched with the sample Pb-01 electrodeposited with an electrical charge fixed to 0.9C, which corresponds to a classical morphology for a mixture of lead oxides (a majority of $\beta\text{-PbO}_2$ with small amount of Pb_3O_4), Table 1.

3.3.1. Effect of pH

The effect of pH was studied for a solution containing glyphosate with a concentration of 100 μM (16.9 mg L^{-1}). The pH of the solution

was adjusted by the addition of NaOH (1 M) ranging from 4.1 (free) to 10. One sample of lead oxide Pb-01 ($S = 3 \text{ cm}^2$) was introduced into 20 ml of this solution. The interactions were carried out in a thermostatically controlled oven at 25 $^\circ\text{C}$ for 24 h under stirring at 250 rpm.

Fig. 5 shows that after 24 h for a pH equal to 4.1, 50 μM of glyphosate were detected in solution corresponding to 50 % of degradation, calculated according to Eq. (1). In contrary, for pH = 7.2 and pH = 10, glyphosate was largely detected in solution, with 90 μM and 100 μM respectively, corresponding only to 10 % of degradation and no degradation. Moreover, the degradation of glyphosate occurred via the C—N bond cleavage with the formation of AMPA as the major product, in addition to the formation of a small amount of phosphate and nitrate ions. In parallel, a significant release of lead in solu-

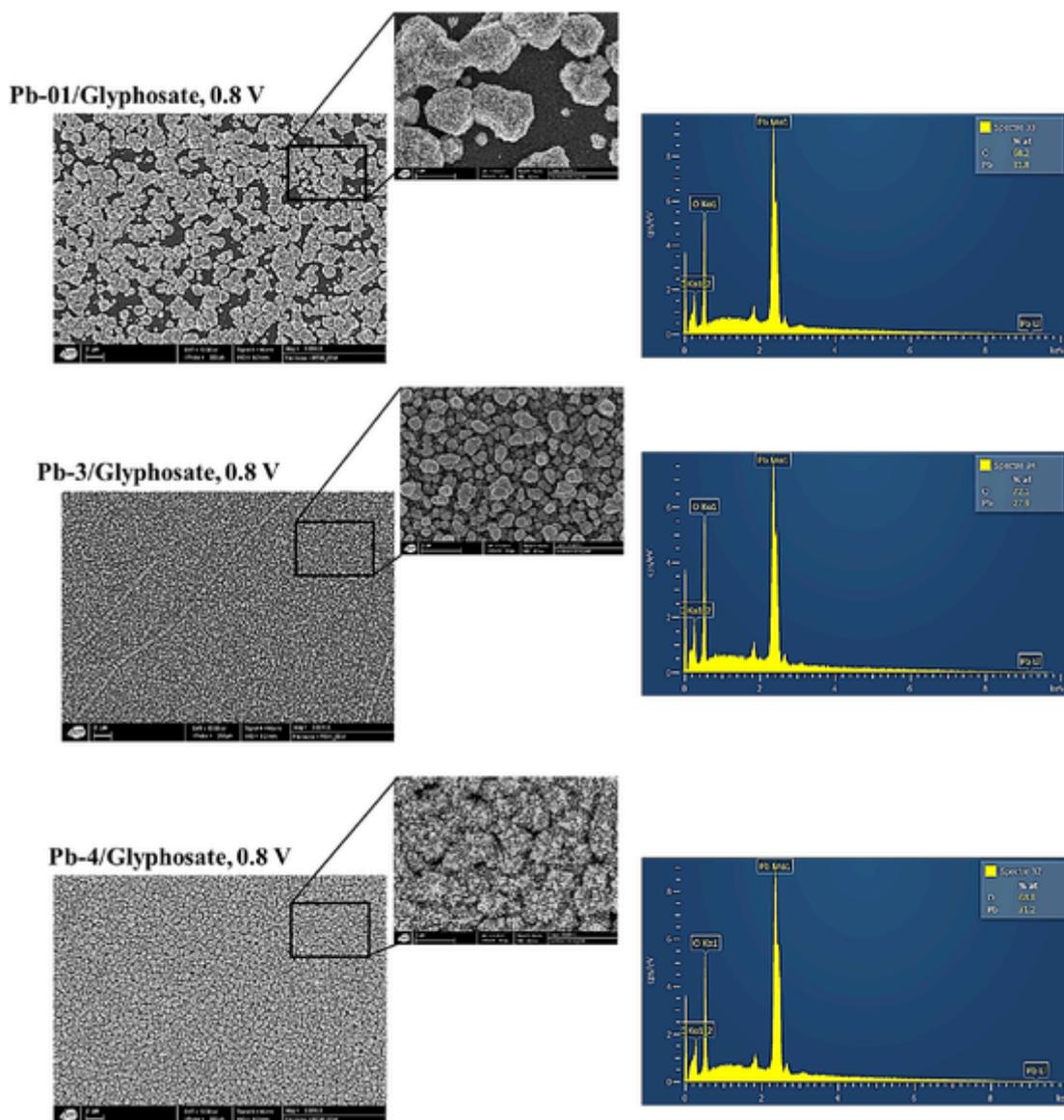


Fig. 11. SEM observations and the associated EDS analyses of the different types of samples after interaction with an aqueous solution with initially 100 μM of glyphosate and a pH of the solution equal to 4.1 (free) during 24 h under stirring at 250 rpm, with an applied potential ($E = 0.8$ V).

tion was observed (~ 40 μM), particularly at $\text{pH} = 4.1$ when the most amount of glyphosate was degraded.

According to the literature, lead oxide $\beta\text{-PbO}_2$ has a zero charge point $\approx 4.8\text{--}7.4$ [31]. The zero charge point corresponds to the pH for which the lead oxide surface has a neutral charge. Below this pH value, the lead oxide surface is positively charged and above the pH value, the surface charge is negative. On the other hand, glyphosate has three functions: a carboxylic acid function, a phosphoric acid function and an amine function. It can exist in five different ionisation states depending on pH with pK_a values equal to 0.8, 2.6, 5.6 and 10.6 [21,32]. The pK_a values of 0.8 and 5.6 are attributed to the phosphoric acid function, the pK_a value of 2.6 to the carboxylic acid function and the pK_a value of 10.6 to the amine function. With increasing pH, the acid functions release their hydrogens leading to a negatively charged molecule [33]. In the pH range, when the maximum degradation was obtained, the solid (PbO_2) is positively charged while the overall charge of the glyphosate is negative, which explains an optimal attraction between the two allowing to promote the degradation, and in good coherence with the presence of soluble lead.

The observations of Pb-01 thin film by SEM after the interaction at pH 4.1 and 10 are reported on Fig. 6. The sample with the degradation performed at pH 4.1 has a much less covered surface in amount of material compared to the sample before interaction (Fig. 2), which is consistent with the glyphosate degradation rate and the release of lead in solution. Conversely, the sample that did not allow degradation (interaction at pH 10) appears intact in good coherence with the absence of lead in solution. According to these results, the free pH of solution containing glyphosate ($\text{pH} \approx 4.1$) was chosen for further studies.

3.3.2. Effect of sample type

The effect of sample type was studied for a solution containing glyphosate at a concentration of 100 μM (16.9 mg L^{-1}) in a volume of 20 ml, the pH of the solution was 4.1 (free). One sample of each type of lead oxide electrodeposited with an electrical charge of 0.9C ($S = 3$ cm^2) was introduced into the solution. As previously, the interactions were carried out in a thermostatically controlled oven at 25 $^\circ\text{C}$ for 24 h with stirring at 250 rpm.

In all cases, glyphosate was degraded with the main formation of AMPA, and some phosphate and nitrate ions, in addition to a significant

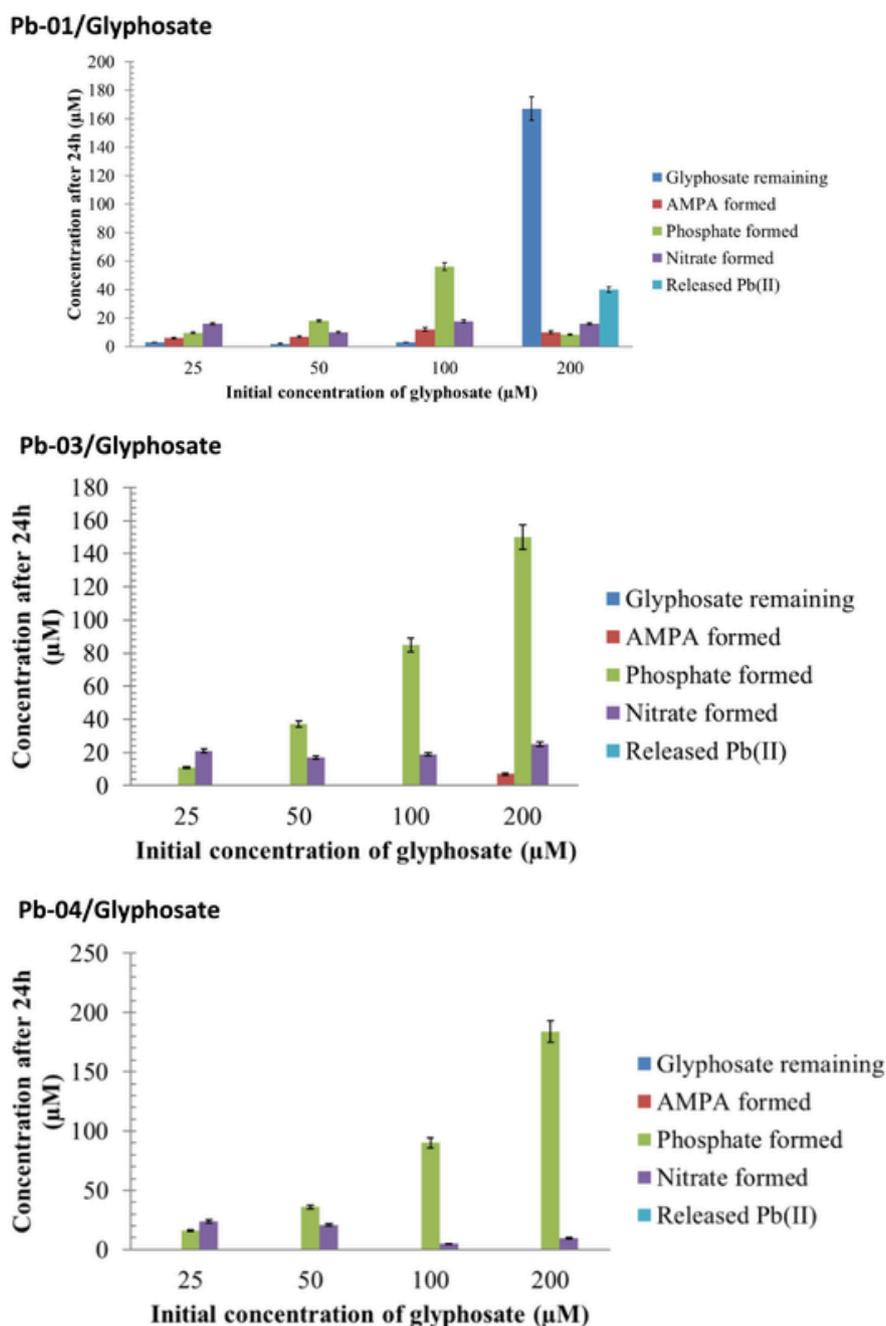


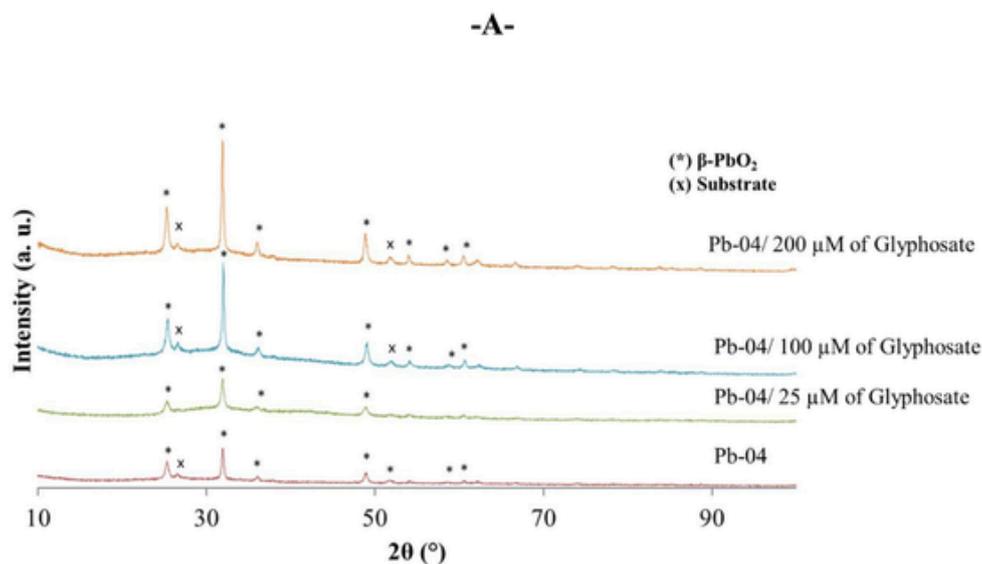
Fig. 12. Concentrations of species present in solution after interaction of glyphosate solution during 24 h with Pb-01, Pb-03 or Pb-04 samples with a potential fixed at 0.8 V as function of different initial concentration of glyphosate.

and equivalent release of lead in solution independently of the sample type, Fig. 7. However, the most important spontaneous degradations were obtained with samples of type Pb-03 and Pb-04 whose morphologies of pure β - PbO_2 are branches and cubic needles respectively. SEM observations of these six samples after their interaction and degradation of glyphosate show little modifications, Fig. 8, compared to samples before interaction (Figs. 2 and 4). Indeed, any change in the morphology of the materials was observed, but only a less covered surface following a loss of the amount of electrodeposited material in good coherence with the presence of lead in solution.

In all cases, after 24 h, the concentrations of glyphosate detected in solution, comprised between 40 and 50 μM according to the type of samples, were significantly decreased compared to the initial concentration (100 μM) (Fig. 7), indicating degradation rates close to 50 %. In

these experimental conditions, glyphosate was mainly degraded into AMPA via spontaneous electronic transfers that occurs at the surface of lead oxide thin film. This degradation was accompanied by a release of lead in solution ($\sim 40 \mu\text{M}$), but the quantity found in solution is largely lower than the expected amount ($\sim 10 \%$ experimental vs 50 % theoretical expected), considering the experimental degradation rates of glyphosate into AMPA according to these equations (Eqs. (4.1), (4.2) and (6)). This result supposes a possible adsorption of Pb(II) onto lead oxides surfaces as already observed for spontaneous degradation of organic compounds with manganese oxides thin films [21,34,35].

However, even if the amount of soluble lead is lower than expected, this release can be problematic. For resolving this problem, we thought to couple the spontaneous degradation under the effect of applied of fixed potential. Indeed, in our previous studies, performed with man-



-B-

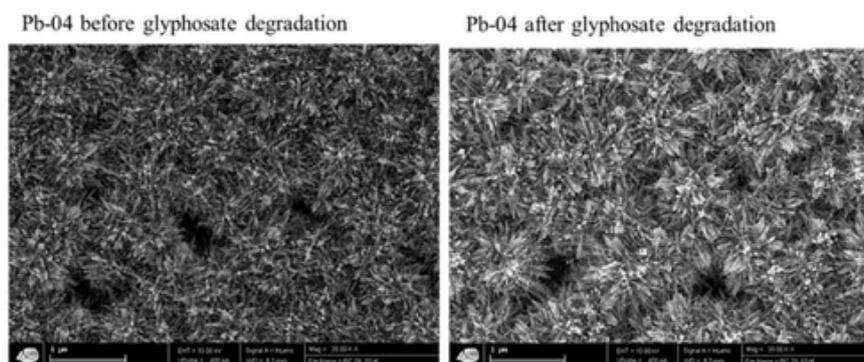


Fig. 13. -A- X-ray diffractograms of Pb-04 lead oxide before and after degradation of glyphosate as function of different initial concentrations with a potential fixed at 0.8 V during 24 h —B— SEM observations of Pb-04 lead oxide film before and after interaction with an aqueous solution containing initially 200 μM of glyphosate and a pH equal to 4.1 (free) with a potential fixed at 0.8 V during 24 h.

ganese oxide thin films [14], the imposition of a potential leads to a significant increase of the degradation capacity, but also to a total regeneration of the materials via electrodeposition in continuous [14]. In a similar way, the imposition of a potential in the case of lead oxides thin films could increase the degradation rates but also the electrodeposition of Pb(II) released in continuous, according the same principle than reported in our innovating depollution process [18,19].

3.4. Effect of electrochemical coupling on degradation ability and release of lead in solution

For these electrochemistry experiments, lead oxide thin films electrodeposited onto the SnO₂ were used as working electrodes in a classical electrochemical set-up, with the same electrodes used previously for the synthesis (i.e. a platinum wire and a mercurous sulphate electrode as the counter electrode and reference electrode respectively). The other interaction conditions were the same that during spontaneous interactions for better comparison (i.e. volume of 20 ml, free pH 4.1, under fixed stirring at 250 rpm).

The influence of different parameters such as the value of the applied potential, the type of sample studied, and the concentration of the pollutant in solution were studied. As previously, the concentrations of glyphosate and the main by-products were determined by ion chromatography, the release of lead in solution was measured after each interaction by UV-visible measurements using the Spectroquant® kit, and the solids were characterized by XRD, SEM and EDS after interaction experiments.

3.4.1. Choice of the value of potential applied during interaction

It was important that the value of applied potential did not modify the materials during interaction and that no parasite electrochemical reactions occurred (e.g. oxidation of water). For that, two potentials were chosen in order to study the influence of electrochemistry: 0.7 V, which is the value used for the electrodeposition of lead oxide at this pH, and 0.8 V, which is slightly more oxidising value. This preliminary study was carried out using one sample of Pb-01 as a reference.

After 24 h, and under a potential of 0.7 V, the concentration of glyphosate determined was equal to 40 μM corresponding to a degrada-

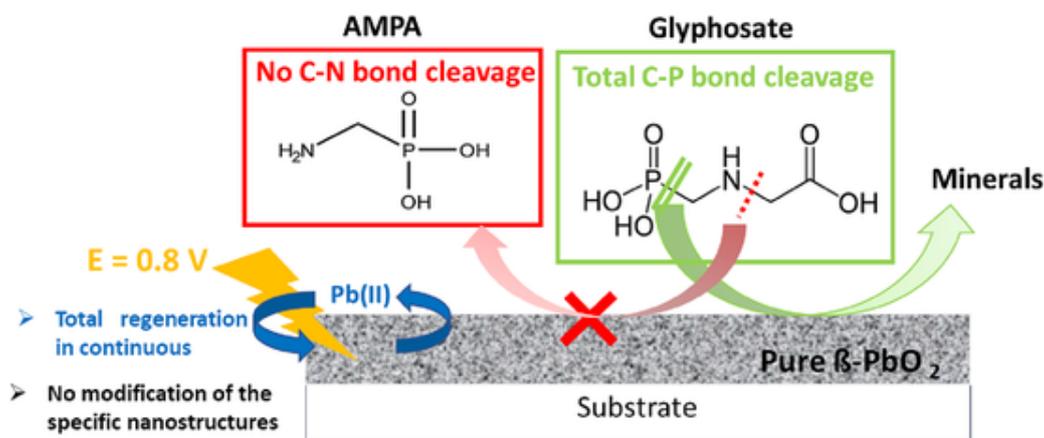


Fig. 14. Schematic degradation and mineralisation of glyphosate in the best conditions with pure β - PbO_2 (Pb-03 and Pb-04 type samples) by spontaneous electronic transfers and the total regeneration in continuous of their specific nanostructures (as branch or cubic needles) by coupling to electrochemistry ($E = 0.8 \text{ V}$).

tion rate of 60 %, with the formation of AMPA as the major compound ($45 \mu\text{M}$) (C—N bond cleavage), Fig. 9-A, with a slight amount of nitrate and phosphate ions ($\sim 5 \mu\text{M}$ for each specie respectively), whereas under a potential of 0.8 V , glyphosate was mainly mineralised by forming phosphate ions as the major product (C—P bond cleavage), with a concentration equal to $55 \mu\text{M}$, accompanied by a significant amount of nitrate ions ($\sim 18 \mu\text{M}$), and a low amount of AMPA ($\sim 10 \mu\text{M}$). In both cases, the amount of lead released in solution compared to spontaneous reactions is reduced and more particularly for 0.8 V ($30 \mu\text{M}$ and $5 \mu\text{M}$ for 0.7 V and 0.8 V respectively). As discussed previously and for comparison, glyphosate was degraded into AMPA after 24 h without electrochemistry, with a degradation rate equal to 50 %, and a significant release of lead in solution ($40 \mu\text{M}$), Fig. 7.

The effect of the electrochemistry being particularly significant for $E = 0.8 \text{ V}$ with a significant mineralisation by C—P bond cleavage (high production of phosphate ions), that is why the interaction experiments were only performed by fixing this value. Moreover, it is important to mention that the maximal current intensity measured was $6.6 \mu\text{A cm}^{-2}$, (graph not shown), which is very low and largely inferior to the intensities values reported in the literature for the degradation of glyphosate by pure PbO_2 electrode (50 mA cm^{-2} for example) [15,17].

3.4.2. Effect of the sample type

The same study was performed during 24 h in similar conditions (0.8 V) with the different types of samples in comparison to the substrate alone (SnO_2). In absence of lead oxide films (SnO_2 alone), glyphosate was not degraded in comparison to the all other samples, Fig. 9-B. Moreover, the results obtained show clearly that after 24 h the glyphosate was completely mineralised without any production of AMPA (only phosphate ions) by using the Pb-03 and Pb-04 samples, Fig. 9-B, the two types of samples with particular morphologies compared to the literature (branch and cubic needles respectively).

In addition, Pb(II) was not detected in solution according to the analyses performed by the Spectroquant® kit. This result is in good agreement with the hypothesis that the applied potential can allow in continuous the electrodeposition of Pb(II) released in solution, due to the reduction of Pb(IV) to Pb(II) during the degradation of glyphosate. Indeed, the total mineralisation of glyphosate at $100 \mu\text{M}$ in 20 ml of solution at free pH 4.1 occurred after 24 h under an imposed potential of 0.8 V using a lead oxide sample Pb-03 or Pb-04. However, based on equations Eqs. (5) and (6), in order to degrade one mole of glyphosate, 10 mol of lead were needed for the production of 20 mol of electrons. Therefore, to degrade spontaneous $100 \mu\text{M}$ into 20 ml (2.10^{-6} mol), 2.10^{-5} mol of lead are needed to have sufficient electrons, and then in consequent the release of soluble lead should be equal to $2 \times 10^{-5} \text{ mol}$, corresponding to 4.14 mg L^{-1} . However, the amount of lead released in

solution after 24 h was not detected by the Spectroquant® kit ($< 0.1 \text{ mg L}^{-1}$) with the electrochemical coupling confirming an efficient re-electrodeposition as lead oxide.

In complement, a typical example of the current variation during the degradation of glyphosate by Pb-04 sample, as a function of time with the electrical charge recorded during the degradation, is presented Insert Fig. 9-B. By applying the Faraday's law (Eq. (3)), the theoretical electric charge should be equal to $Q_{\text{theo}} = 3.85\text{C}$, for this initial concentration of glyphosate, if the total degradation was carried out only under the effect of the electrochemistry according to Eq. (5). However, the experimental electric charge was equal to $Q_{\text{exp}} = 1.66\text{C}$. This difference can be explained probably by the fact that the electrochemistry is mainly used for the regeneration of lead oxide, and that the degradation of glyphosate would be spontaneous, i.e. by direct interaction with lead oxide thin film as reported previously.

The X-ray diffractograms of the three types of samples, Pb-01, Pb-03 and Pb-04, show that the crystallinity of the lead oxide thin films increases after their use for the degradation of glyphosate, under the effect of the potential fixed at 0.8 V , compared to the samples after spontaneous interactions, Fig. 10. These results confirm that the regeneration of the lead oxide by electrodeposition was performed by keeping the same crystal structure. In addition, the characterisation of these three samples by SEM and their analysis by EDS, after the degradation of glyphosate under the effect of the potential, show clearly that no modification was observed (texture and covering of the substrate surface). Moreover, the percentages of O and Pb remain identical without any other chemical species, Fig. 11.

3.4.3. Effect of the initial concentration of glyphosate

The effect of glyphosate concentration on the degradation ability of the samples was studied using the three types of samples: Pb-01, Pb-03 and Pb-04. The solutions contained different concentrations of glyphosate ($25, 50, 100$ and $200 \mu\text{M}$ corresponding to $4.2, 8.4, 16.9$ and 33.8 mg L^{-1} respectively) in a volume of 20 ml with free pH. These concentrations are high compared to those found in polluted waters but can correspond to real cases of polluted solutions [36]. The interactions were carried out at room temperature during 24 h under stirring of 250 rpm with an applied potential equal to 0.8 V .

From these results presented on Fig. 12, we can conclude clearly that the lead oxide thin film Pb-04 keeps its remarkable degradation capacities whatever the quantity of glyphosate present in solution (from $25 \mu\text{M}$ to $200 \mu\text{M}$), by forming only mineral products. The lead oxide thin film Pb-03 also keeps the same degradation capacities towards glyphosate in solution by forming mineral products for initial concentrations ranging from 25 to $100 \mu\text{M}$, nevertheless, for a higher concen-

tration, 200 μM , although glyphosate is completely degraded, a small amount of AMPA was produced (7 μM).

Therefore, Pb-03 and Pb-04 samples, which present original nanostructures, are largely more efficient for the degradation of glyphosate compared to the sample Pb-01, which presents the classical morphology. However, for the three types of sample, it is important to highlight that we did not encounter the problem of lead release in solution, regardless of the initial concentration of glyphosate to be degraded confirming the real interest of coupling spontaneous reaction with electrochemistry.

The X-ray diffractograms of Pb-04 sample, before and after glyphosate degradation with different initial concentrations, confirm that the thin film is still in the form of pure $\beta\text{-PbO}_2$, with in addition of a significant gain in crystallinity, Fig. 13-A. These results support our hypothesis that the lead released in solution, during the spontaneous degradation of glyphosate, is then re-electrodeposited under the effect of the imposed potential. Moreover, the crystallinity can be improved because this value of potential is slightly higher than the value of the synthesis potential (0.7 V). Thus the more glyphosate is degraded in solution, the more lead released is re-electrodeposited with a higher crystallinity. The observation of the sample Pb-04 by SEM (Fig. 13-B) after the total degradation of 200 μM of glyphosate under a potential of 0.8 V shows no change in the texture of the material; it keeps its very particular morphology in the form of cubic needles.

Fig. 14 resumes schematically the global mechanism of glyphosate degradation in the best conditions by coupling to electrochemistry with the specific nanostructured Pb-03 and Pb-04 type samples.

3.4.4. Calculation of efficacy and energy costs for the best Pb-04 sample

Based on these experimental results, and as already reported in our previous studies concerning the degradation of glyphosate and AMPA by electrodeposited thin films of manganese oxides [14], we can calculate for the highest concentration studied (200 μM) the Mineralisation Capacity (MC), corresponding to the mass of glyphosate which can be mineralised by 1 g of studied material (mg of glyphosate / g of studied material), of the best Pb-04 sample according to Eq. (7):

$$MC = \left([\text{Gly}]_{\text{initial}} \times V \times M_{\text{gly}} \right) / m_{\text{Pb-04}} \quad (7)$$

With $[\text{Gly}]_{\text{initial}} = 200 \mu\text{M}$; $V = 20 \cdot 10^{-3} \text{ L}$; $M_{\text{gly}} = 169.07 \text{ g mol}^{-1}$; $m_{\text{Pb-04}} = 0.6 \cdot 10^{-3} \text{ g}$.

In these conditions, the mineralisation capacity of Pb-04 sample is equal to 1127 mg of glyphosate /g of Pb-04, which is very high and without detection of lead released in solution. This capacity is probably not the maximum since higher concentrations have not been studied. Nevertheless, this value of mineralisation capacity is widely superior to the values reported in the literature for glyphosate removed for either sorption or degradation [3]. Moreover, the degradation was performed in very soft conditions (at room temperature and ambient pressure), in a classical electrochemical set-up, without adding reagents and/or production of wastes, and requiring no regeneration of the material.

In complement, the maximum energy consumption for the degradation reaction was estimated for the best Pb-04 sample based on laboratory experiments and on registered current (Insert Fig. 9-B) by using the following equation, Eq. (8):

$$E_{\text{consumed}} = (I \cdot V \cdot t) / 1000 \quad (8)$$

With E, the energy consumed (kWh), I, the maximal intensity of the measured current (A), V, the imposed potential (V), t, the duration applied to have a total degradation of glyphosate into mineral species (h).

Taking into consideration the maximum recorded current, a power consumption of $1.07 \cdot 10^{-6} \text{ kWh}$ was required to degrade 100 μM (16.9 mg L^{-1}) of glyphosate until the total mineralisation. This energy consumption is much lower than that reported in the literature for electrochemical oxidation of glyphosate based on the production of radicals

[16,37], while the mineralisation rates obtained in this study are also very high. Consequently, such samples with original nanostructures could certainly resolve one of the disadvantages reported generally for the electrochemical oxidations techniques based on the production of radicals [3].

4. Conclusions

There are several effective techniques for the degradation of glyphosate, but it is important to improve continuously their capabilities by avoiding and/or limiting undesirable effects. In this study, we have reported a simple electrochemical oxidation process for the degradation and mineralisation of glyphosate performed at room temperature, with very low energy inputs, without the addition of electrolyte, by using lead oxide thin films with particular morphologies, in relation to our innovating electrochemical process of water depollution containing soluble lead.

The sample Pb-04, a pure $\beta\text{-PbO}_2$ with an original cubic needles morphology seems particularly interesting when a potential equal to 0.8 V was applied. Indeed, it allowed a total (electro)-degradation of glyphosate without the production of AMPA (aminomethylphosphonic acid), with a mineralisation capacity worth to 1127 mg of glyphosate/g of Pb-04, without Pb(II) released in solution, due to a very efficient re-electrodeposition with the same crystalline structure. These results are particularly encouraging for future applications performed at low costs for the efficient degradation until mineralisation of organic pollutants such as glyphosate, with no production of AMPA, the main by-product more toxic and persistent than glyphosate. Moreover, it is a very interesting way for valorisation of heavy metal wastes coming from our innovating electrochemical depollution process for a very efficient circular economy.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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