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Development of an efficient electrochemical process for removing and separating soluble Pb (II) in aqueous solutions in presence of other heavy metals: Studies of key parameters.

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Abstract

A very simple electrochemical process was developed for a high efficient elimination of Pb (II) from wastewaters. The principle is to remove soluble Pb (II) as oxide(s) adherent thin films only on the effect of an imposed specific potential by chronoamperometric method and an adequate pH, without adding reagents, at room temperature and in a conventional container. This treatment is very efficient for removing 99.99 % of Pb (II) and directly reaching acceptable concentrations for the environment and drinking water standards, with low energy input. Firstly, the key parameters that could influence the efficiency of lead removal, such as the pH and the adequate values of potential, the initial concentration and the duration, were studied in pure water. Systematically, the solution was analyzed to quantify the concentration of Pb (II), and the recovered solid as an adherent thin film was characterized by XRD, SEM and EDS to determine its nature according to the experimental conditions. In a second part, the same treatment was applied with the optimized conditions in the presence of chemical ionic species and other heavy metals such as Cd(II), Ni(II) or Cu(II) to confirm the possibility to have a total elimination and separation of lead from these other heavy metals. To conclude, this electrochemical process was applied with success on an effluent coming from a WWTP confirming the real interest of this easy electrochemical process for an efficient separation and purification of wastewaters containing soluble lead.

KEY WORDS: Depollution; Electrodeposition; Heavy metal; Thin film; Separation; Oxides

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1 Introduction

The preservation of the environment, and particularly the problem of water pollution, is a major preoccupation, shared by all, public, industrials, scientists, researchers and decision-makers (at national, European and international levels) due to the crucial consequences on the human health. In this context, developing efficient and eco-compatible treatments is always a challenge for wastewater treatment.

In recent years, treatments of polluted waters by electrochemical processes have aroused a lot of interest, mainly due to their low costs, their simplicity of implementation, the limited production of waste, but mainly for their high efficiency [1-7]. Different electrochemical processes were already developed such as electrolytic processes (electrolysis, electrodialysis, electrocoagulation, electrofloculation, electroflotation), and different advanced oxidation processes, which can be coupled with electrochemistry (photocatalysis, photolysis of water, Fenton reaction, irradiation in the presence of an oxidant) [3-12]. For example, these electrochemical processes are known to be effective for the treatment of leachate coming from hazardous waste landfills [5] or wastewater [3,4,6,7,10-14], or to remove organic compounds [1,3,12-16] and/or inorganic species such as heavy metals [17-21].

Today, numerous scientific researches focus on the elimination of emerging organic pollutants, however the pollution of aquatic environments by heavy metals is also very worrying because of their toxicity and persistence. In fact, these chemical compounds do not degrade causing them to accumulate in the environment and then in the food chain with very harmful effects on aquatic life, animals, plants and ecology, and finally on human health [22].

According to the literature studies, two main electrolytic processes can remove heavy metals contained in wastewater: electrocoagulation [23] and electrolysis by reduction of soluble ions into metals [17]. However, the electrocoagulation, even if it requires little maintenance, must still prove itself on the scale of an industrial site [7]. Heavy metals can be also removed by advanced oxidation processes, coupled or not with electrochemistry. For example, (electro)Fenton treatment is able to effectively destroy sludge flocs and solubilize extracellular polymeric substances fractions. However, heavy metals may be possible released at the same time since they can form metal organic complex compounds in presence of organic matter, which can be separated from sludge system under mechanical dewatering [24,25]. These advanced oxidation processes offer many advantages: technically simple processes, which can be operated generally without particular supervision, the absence of secondary wastes production, and capacities to treat variable flows. For these many reasons, advanced oxidation processes, coupled or not to electrochemistry, seem to be the techniques of tomorrow due to their excellent results [26].

In this context, this article presents a simple electrochemical process to remove soluble Pb (II) dissolved in aqueous solutions even in presence of other chemical species. This novel method removes lead in the form of a pure electrodeposited lead oxide(s) thin film adhering to a conductive support at room temperature without addition of reagents and / or complexing agents, and only based on the effect of a specific applied potential for a pH, that is why an international patent was deposited [27]. Indeed, even if the electrodeposition of pure oxides thin films of various materials [2, 28-30] and lead in particular [31, 32] is already largely reported in the literature for synthesis and/or for various applications (e.g. (electro)catalysis [13, 33, 34]), no study focusses on the depollution of aqueous solutions as reported today in this article.

The present paper focuses in the first part on the study of the main parameters, which can influence the efficiency of this treatment, such as the value of pH, the applied potential, the duration and the initial concentrations of Pb (II) in pure water. In a second part, the influence of the main common chemical inorganic species (e.g. Na_2SO_4, $NaNO_3$, and NaCl) present at high concentration (1M) in synthetic aqueous solutions was studied to evaluate their possible effect on the efficiency to remove Pb (II). The presence of one organic specie (CH_3COONa) at high concentration (1M) was also studied to test the effect of such organic compound on the lead removal efficiency. According to the same way, experiments were performed in presence of other heavy metals, such as Cd (II) or Ni (II) or Cu (II) at an equivalent concentration than that soluble lead, to study their effect on the removal efficiency of lead and their possible separation. Indeed, this point is particularly important because the separation of lead with other heavy metals is generally complicated and required complex chemical and/or physical processes [35-37]. Finally, a test was carried out at laboratory scale on an effluent coming from a WWTP to evaluate the real interests of this very simple process for purification of wastewaters containing soluble lead.

2 Experimental

2.1 Chemicals

Reagents, NaOH (1M), HNO_3 (1M) (ACS Reagent Sigma Aldrich), $Na_2SO_4.10H_2O$, $NaNO_3$, NaCl and CH_3COONa (VWR ProLABO chemicals), standard solutions of Pb (II), Cd (II), Ni (II), and Cu (II) (1002 ± 4 $mg.L^{-1}$, 5% HNO_3) (Alfa Aesar), intended for use as certified reference materials or calibration standard for inductively coupled plasma optical emission spectroscopy (ICP-OES), were used without further purification. All solutions were prepared by using Milli-Q water.

2.2 Electrochemical experiments

Electrochemical experiments were performed in a conventional electrochemical setup with three electrodes: a Mercurous Sulfate Electrode (MSE, E = 0.6513 V/ENH) as reference electrode, a platinum wire wound spirally for having a surface equal to the working electrode as counter electrode, and a glass plate covered with tin dioxide SnO_2:F (Fluorine-doped Tin Oxide, Solems, noted SnO_2) as working electrode. Some tests were performed with 316 L

Stainless Steel. All electrochemical measurements were carried out at room temperature, in air with an atmospheric pressure, using a microautolab potentiostat piloted by its associated software GPES (*General Purpose for Electrochemical System*) with a computer.

For determining the adequate values of potential according to pH, classical electrochemical measurements were performed by cyclic voltammetry ($v = 10$ mV.s^{-1}) with a solution of Pb (II) containing 6.5 µmol into 50 mL of pure water (corresponding to a concentration of 27 mg.L^{-1}), at different pH (free pH ≈ 2 and others pH adjusted by adding NaOH (1 M)). **Figures S1, S2 and S3 in supplementary data** present measurements obtained for free pH, pH = 4.2, and pH = 6. The determined ranges of potential corresponding to the anodic peaks in these conditions are regrouped in **Table 1**.

The electrochemical treatment for removing soluble lead was carried out in the same conventional electrochemical setup with the electrodes that cited previously; the surface of the working electrode (SnO_2 or 316 L Stainless Steel for few tests) was always limited to 3 cm^2. The treatment was performed for different durations by imposing the adequate potential determined previously by cyclic voltammetry (chronoamperometry method) for each pH, and with always a gentle stirring of the solution (250 rpm).

Experiments were firstly performed on 50 mL of pure water containing Pb (II) at free pH (pH ≈2) and pH =4.2, adjusted by the addition of NaOH (1M)). At the end of the treatment, the solutions stayed always clear that is why they can be analyzed directly without any preparation to quantify the concentration of soluble lead. Each measurement was repeated several times for confirming the good repeatability and reproducibility of the treatment according to the value of pH. Some experiments were also performed at pH = 6, but a weak precipitation was observed in the solution for this value of concentration that is why these experimental conditions were less scrutinized and performed only for one value of potential (e.g. 0.7 V).

The effect of the presence of chemical species on the efficiency of the treatment was performed for E = 0.7V on aqueous solutions containing soluble lead (6.5 µm in 50 mL) and Na_2SO_4 (1M) or $NaNO_3$ (1M) or NaCl (1M) at pH = 4.2, or at pH = 6 (free pH) for one organic specie (CH_3COONa (1M)). The efficiency of the electrochemical treatment was also studied for E = 0.7V at pH = 4.2 in the presence of another heavy metal such as Cd (II) or Cu (II) or Ni (II), present in an equivalent concentration than of lead (6.5 µmol in 50 mL). The aim of these latter experiments was also to determine their possible separation. For that, systematic analyses of the solutions were performed at the end of this electrochemical treatment to quantify also Cd(II) or Cu(II) or Ni(II) in supplement to the concentration of soluble lead. Whatever the chemical species, no precipitate was formed in solution. Each measurement was repeated several times to estimate the repeatability and the reproducibility of the treatment.

2.3 Analyses of solution

The concentration of Pb (II) present in the solution was determined by using the specific Pb Spectroquant® test (1.09717.0001; 0.1 mg. L^{-1} to 5.00 mg. L^{-1}). Absorbance measurements were performed at 520 nm by a spectrophotometer (Varian Cary® 50 UV-visible Agilent). The amount of removed Pb (II) was calculated by the difference between the initial amount and the equilibrium one using **Eq. 1,** and the percentage of Pb (II) removed from the solution after the electrochemical treatment by using **Eq.2**:

$$n_{\text{Pb(II) removed}} = n_{\text{Pb(II) initial}} - n_{\text{Pb(II) at t}} \qquad \textbf{Eq.1}$$

$$\text{Pb (II)removed (\%)} = \frac{n\,Pb(II)initial - n\,Pb(II)\ at\ t}{n\,Pb\,(II)\ initial} * 100 \qquad \textbf{Eq.2}$$

With n in mol, and t, corresponding to a fixed duration in hour (h)

Some complementary measurements were performed by using screen-printed electrodes specifically developed in our laboratory and dedicated in particular to the detection of lead in the trace state solution [38, 39].

The analyses of the other heavy metals present in solution were performed with specific Spectroquant® tests for Cd (II) (Spectroquant® 1.01745.0001; 0.01 mg. L^{-1} to 0.50 mg. L^{-1} Cd(II)), Cu (II) (Spectroquant® 1.14767.0001; 0.10 mg. L^{-1} to 6.00 mg. L^{-1} Cu(II)), and Ni (II) (Spectroquant® 1.14785.0001; 0.10 mg. L^{-1} to 5.00 mg. L^{-1} Ni(II)). Absorbance measurements were performed at the adequate wavelength: 520 nm for Cd (II), 600 nm for Cu (II), and 450 nm for Ni (II) respectively.

2.4 Characterization of recovered thin films by XRD, SEM and EDS analyses

All characterizations were carried out directly without any preparation step since the thin films were sufficient conductive and adherent. The crystal structure of the recovered films was characterized by X-Ray Diffraction (XRD) with classical measurements ($\theta/2\theta$) by a BRUKER θ- θ diffractometer equipped with a copper anode (λ_{Cu}=1.540600 Å) and an LYNXEYE detector.

The morphology of the thin films was observed by a MEB-FEG MERLIN Zeiss Scanning Electron Microscopy (SEM). These observations were supplemented by Energy Dispersive Spectroscopy analyzes (EDS) to determine the chemical composition.

3 Results and discussion

3.1 Effect of the potential according to pH on the removal efficiency of soluble Pb (II) present alone in pure water

3.1.1 Determination of the adequate potentials by cyclic voltammetry measurements

The Pourbaix diagram of lead in absence of complexing agent shows a complex chemistry due to numerous oxidation states with the possibility of forming several oxides according to pH and potential: PbO, Pb_3O_4 and PbO_2 [40]. However, this diagram corresponds to thermodynamic data, and does not take account of kinetic phenomenon, that is why experimental measurements are necessary. Moreover, even if many studies in the literature have already reported electrochemical measurements for lead in various aqueous solutions with different values of pH for syntheses and/or applications [1, 13], the main objectives were not the same. Therefore, it was important to determine first the behavior of lead in pure water without adding electrolyte in function of pH for finding the adequate values of anodic potentials in the aim to develop this electrochemical depollution treatment based on the formation of adherent thin films of lead oxide(s).

For that, cyclic voltammetry measurements were performed without stirring on model solutions of Pb (II) present alone (6.5 µmol in 50 mL corresponding to 27 $mg.L^{-1}$) in pure Milli-Q water without addition of electrolyte at free pH (≈2), pH = 4.2, and pH = 6. Figures S1, S2 and S3 in the supplementary data present these measurements respectively. A weak precipitation was observed for this concentration at pH = 6 that is why this experimental case was less scrutinized. From these measurements, the anodic potential ranges, corresponding to the oxidation and formation of a solid on the working electrode in link to the presence of a light brown deposit visible on the working electrode, were determined for the three pH, **Table 1**. As expected, these values are in good coherence with the Pourbaix diagram [40].

For confirming the possibility to remove soluble lead quantitatively as adherent thin films, chronoamperometry measurements were carried out.

3.1.2 Determination of the optimal conditions by chronoamperometry measurements

Chronoamperometry measurements were carried out on model solutions containing only Pb (II) at 27 mg. L^{-1} in pure water with gentle agitation (250 rpm) in the same conventional electrochemical setup with the three electrodes cited above (SnO_2 as working electrode).

First, measurements were done at free pH ≈ 2 for two values included in the potential range: 1.0 V and 1.2 V (**Table 1)**. After 24 h, in both cases, an adherent deposit was formed onto the SnO_2 substrate without any precipitation in solution. The limpid solutions were analyzed by using the specific Pb (II) Spectroquant® test (limit detection equal to 0.1 mg. L^{-1}), and in both cases, lead was not detected, which signifying that the adherent deposits onto the SnO_2 substrate correspond to the total elimination of Pb (II) initially present in the solutions. **Figure 1** reports as a histogram the percentages of lead removed from the solutions determined after 24 h for these two values of potentials at this pH**.** For confirming these results, different experiments were carried out by imposing values of potential outside the potential range of the anodic peaks determined previously. In these conditions, no film was formed onto the SnO_2 substrate, and Pb (II) remained quantitatively in the solutions as soluble specie (no precipitate).

Similar experiments were carried out for an equivalent solution of Pb (II) (27 mg. L^{-1}), with a pH adjusted to 4.2 by addition of NaOH (1M), for different potentials inside the determined range for this pH: 0.5 V; 0.6 V; 0.7 V and 1.0 V (**Table 1)**. For these four values of potentials, an adherent deposit was formed systematically onto the SnO_2 substrate without precipitate in solution. The percentages of lead removed from the solutions after 24 h was reported on **Figure 1.** After 24h, a significant elimination of lead comprised between 40 % for 0.5 V and 100 % for 0.7 V was obtained respectively. It was noteworthy that a slight decrease in pH was observed in the case of the total elimination obtained at E = 0.7 V (final pH ≈ 3.9). This value of potential being also included in the anodic range observed for a pH equal 6 (**Table 1)**, that is why a treatment was carried out in these conditions, although there is a slight precipitate in the solution at this value of pH and for this concentration. After 24 hours, an adherent deposit was formed onto the SnO_2 substrate with a total elimination of Pb (II) from the solution (**Figure 1).**

These all results confirm that the imposition of a potential included in the range of anodic peak detected by cyclic voltammetry measurements allows the partial or total removal of soluble Pb (II) from aqueous solutions as an adherent thin film.

3.1.3 Characterization of the adherent thin films obtained in the case of a total lead removal

To understand the total lead elimination phenomenon from aqueous solution into the form of an adherent film, it was essential to characterize precisely the solids obtained according to the experimental conditions (e.g. pH and imposed potential). Only the cases with limpid solutions (no precipitate) were studied.

3.1.3.1 Identification of the crystal structures and the crystallite sizes by X-Ray Diffraction (XRD)

The nature of the deposits formed during the electrochemical treatment of Pb (II) solution allowing the total elimination of Pb (II) in solution after 24 h was determined by XRD. **Figure 2** shows the obtained X-ray diffractograms for three adherent thin films obtained for different potential and pH values. The three diffractograms present numerous peaks with significant intensities meaning that the electrodeposited compounds are very well crystallized whatever the experimental conditions.

When the electrochemical treatment of a Pb (II) solution were performed at pH ≈ 2, under a fixed potential equal to E = 1.0 V or E = 1.2 V, soluble lead was electrodeposited as an adherent film of pure ß-PbO_2 according to JCPDS 00-035-1222 (**Figure 2**, red and green curves respectively). The common name of this compound is Plattnerite, which has a tetragonal crystal structure [41, 42]. The diffractogram of the thin film, obtained after the treatment of a Pb (II) solution at pH = 4.2 and under a potential E = 0.7 V is presented on **Figure 2**, blue curve. The peaks show that Pb (II) was electrodeposited onto SnO_2 substrate in the form of a mixture composed of ß-PbO_2 and Pb_3O_4 according to JCPDS 00-041-1493. The common name of Pb_3O_4, which possesses a tetragonal crystal structure, is Minium [42, 43]. The nature of the obtained compounds according to pH and potential is in good agreement with the Pourbaix diagram. In addition, a preferential orientation of ß-PbO_2 according to the hkl (200) plane (peak at 36.19^0) was observed for the treatments performed at pH = 4.2 under 0.7 V, and at pH ≈ 2 under 1.0 V, in contrary to the case of the electrochemical treatment performed at pH ≈ 2 under 1.2 V. All results about nature and orientation are regrouped in **Table 2.**

From these diffractograms, it was possible to determine also the size of the crystallites using the Scherrer formula, **Eq.3:**

$$L = \frac{0,9\,\lambda}{ß\,cos\,\theta} \qquad \textbf{Eq.3}$$

With L: Size of crystallites (nm)
λ: Wavelength of X-ray source for copper (0.1540600 nm)
ß: Width of the peak at mid-height (radian)
Θ: Diffraction angle of the line considered (radian)

Only the crystallites sizes of ß-PbO_2 were determined because this compound is present in all films with a very intense peak situated at 25.4 °, which is not the case of the characteristic peaks of Pb_3O_4 (very low intensity). It appears that the crystallite sizes seems vary mostly according to the pH value and not to the value of potential, **Table 2**.

3.1.3.2 Observation of the nanostructures by SEM and analyses by EDS

The morphologies of the films obtained after each treatment were observed by SEM because in all cases the films were well adherent. According to the pictures, the shape and the size of the crystals are clearly depending on the experimental conditions, **Figure 3**. However, the absence of a uniform film whatever the conditions signifies that the removal process of lead from solution 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.

Figure 3-A shows the film recovered after a treatment carried out at pH = 4.2 at 0.7 V, Pb (II) being eliminated in the form of a mixture of ß-PbO_2 and Pb_3O_4, and **Figure 3-B** after a treatment performed at 1.0 V at pH ≈ 2, when Pb (II) was electrodeposited as pure ß-PbO_2. In the two cases, the deposits consist of crystals with similar shape and size, which varies approximately between 0.5 and 1 µm. This shape of crystal is the classic form generally found in the literature for lead oxide [44,45]. In contrary, when the treatment was carried out in the same acidic medium (pH ≈ 2) but under a potential of 1.2 V, the deposition of pure ß-PbO_2 is in the form of branches (dendrites), whose length varies between 2 and 4 µm, **Figure 3-C**. This very specific and original structure has never been reported for this type of lead oxide in the literature, as far as we known. These different forms of crystals observed in function of the experimental conditions are consistent with XRD results, which report a preferential orientation for the crystals shown in **Figures 3-A and 3-B**, and the absence of a preferential orientation in the case of the branches (**Figure 3-C**).

In addition, whatever the experimental conditions, the crystals are in all cases pure and systematically consisting only of lead and oxygen according to EDS spectra with percentages coherent with the determined compounds by XRD.

3.1.4 Discussion about the general principle for removal soluble Pb (II) as adherent oxide(s) thin films

According to these results, the principle of this electrochemical treatment is based on the change of the oxidation state of lead by imposing an oxidant potential. Initially, lead is soluble in solution (State 1, e.g. Pb (II)) and under the effect of the potential, it can be more or less oxidized (State 2), and precipitated onto the electrode as adherent thin films of oxide(s) with various compositions depending on the conditions.

According to studies in the literature, Velichenko et al. have proposed the following mechanism for the formation of PbO_2 deposited onto a gold substrate from 1 mM Pb (II) present in a solution of $HClO_4$ (1M), (**Eq.4 to Eq.6**) [46]:

$$OH^- \longrightarrow OH_{ads} + e^- \qquad \textbf{Eq.4}$$

$$Pb^{2+} + OH_{ads} + OH^- \longrightarrow Pb(OH)_2^{2+} + e^- \qquad \textbf{Eq.5}$$

$$Pb(OH)_2^{2+} \longrightarrow PbO_2 + 2H^+ \qquad \textbf{Eq.6}$$

The authors suggested that the product of the reaction (**Eq.5**) could be adsorbed, and accumulated on the surface of the electrode leading to the crystallization of PbO_2 according to the reaction (**Eq.6**). According to other studies in the literature, PbO_2 can also decompose slowly into Pb_3O_4 according to reaction (**Eq.7**) [47,48]:

$$3\,PbO_2 \longrightarrow Pb_3O_4 + O_2 \qquad \textbf{Eq.7}$$

In our case, it was found that for higher values of potential (1.0 V and 1.2 V) in acidic solutions (pH ≈2), only the formation of β-PbO_2 is obtained in good agreement with the Pourbaix diagram [40]. For lower potential (0.7 V) and higher pH (pH = 4.2), a mixture of oxides is obtained (β-PbO_2 and Pb_3O_4), also in good agreement with the Pourbaix Diagram.

3.2 Effects of duration and initial concentration on the elimination of soluble Pb (II) present alone in pure water

For these studies, only aqueous solutions of Pb (II) with a pH fixed to 4.2 were chosen because (**i**) these experimental conditions correspond to a more complex case due to the formation of a mixture of lead oxides, and (**ii**) this value of pH is low acid and near the neutrality, which is the more case of wastewaters.

The electrochemical treatment was carried out by chronoamperometry under a potential of 0.7 V at room temperature and using SnO_2 as substrate (an area limited to 3 cm^2) in 50 mL of solution.

3.2.1 Effect of duration

Studies were carried out for determining the effect of durations **(i)** on the efficiency of the electrochemical treatment to remove lead, and **(ii)** on the obtained solids. For that, a solution of Pb (II) with an initial concentration equal to 27 $mg.L^{-1}$ was chosen.

Figure 4 reports the current densities measured in continuous during the electrochemical treatment for 24 hours of this solution (blue curve) in comparison to the other one without Pb (II) (red curve). When Pb (II) is in solution, the current density is high and reaches 0.035 $mA.cm^{-2}$ after approximately 3200 s. Then, the intensity gradually decreases over time to become almost zero after ≈ 40000 s (approximately 12 hours). In contrary, when Pb (II) is not present in the solution (red curve), the current density stays very low during all the experiment confirming the total absence of a significant electrochemical reaction at this value of potential in these experimental conditions (e.g. substrate alone).

To study more precisely the elimination of lead, several experiments were carried out in the same conditions but with different durations: 1 h, 2 h, 4 h and 6 hours. For each duration, the solution was analyzed by using the Spectroquant® lead test followed by UV-visible spectroscopy measurements at the appropriate wavelength. The insertion in **Figure 4** reports all analyzes in the form of a histogram. After one hour, when the maximum value of the current density was reached, it is found that already 27 % of the initial amount of Pb (II) was eliminated in link to the formation of a visible deposit onto the SnO_2 substrate. After 6 hours, the film formed on the substrate is clearly visually thicker and well adherent in connection to the elimination of 86 % of the initial amount of soluble lead. After 24 hours, Pb (II) is quantitatively eliminated, and the current density becomes very low (in order of 10^{-7} $A.cm^{-2}$) **Figure 4.** This low value of current is due to the absence of electroactive species in solution, as already observed for a solution without lead (red curve), and not to the eventual passivation of the working electrode by the electrodeposited thin film**.**

In parallel, the obtained thin films were observed by SEM after one hour (**A**), two hours (**B**) and 24 hours (**C**), **Figure 5**. From the first hour (**Figure 5A**), it can be observed the presence of small crystals with a mean size close to 20-50 nm and well homogenously distributed onto the surface of the SnO_2 substrate. This observation is in good agreement with the elimination of 27 % of Pb (II). With time, the surface of the substrate becomes more and more covered by crystals, with an increase of their size and number, in link to the amount of eliminated Pb (II) (**Figures 5B and 5C)**. From these SEM observations, it is possible to conclude that the removal soluble Pb (II) by this electrochemical treatment is directly performed by a nucleation process with formation of 3D islands growth according to the model of Volmer-Weber [49] that is relatively classical for electrodeposition processes.

To complete the SEM observations, some XRD measurements were performed on the thin films obtained after one hour and 24 hours (not shown). In each case, the same compounds are present (Pb_3O_4 and β-PbO_2) for these experimental conditions (pH and E), confirming that the mixture is independent of the duration.

3.2.2 Effect of the initial concentration of Pb (II)

In order to assess the capacities of this electrochemical treatment for removing soluble lead, studies were carried out using Pb (II) solutions at different initial concentrations ranging from 0.5 mg. L^{-1} to 100 mg. L^{-1}. This wide range of concentrations is representative of real cases of contaminated solutions of various origins. The solutions were prepared from Pb (II) standard solution and Milli-Q water, with a pH adjusted to 4.2 by the addition of NaOH (1M) if necessary; no precipitate was formed whatever the initial concentration. As previously, the treatment was carried out by imposing a constant potential equal to 0.7 V on 50 mL of solution with stirring at room temperature for 24 h.

Current densities recorded during chronoamperometry experiments are presented in **Figure 6**. Firstly, it is noted that the values vary greatly with the concentration of Pb (II) initially present in solution. When the solutions are concentrated in Pb (II) (e.g. concentrations equal or greater than 27 mg. L^{-1}), the current densities are significant on over long periods, with an increase of the intensity in link to the initial concentration, compared to those measured for less concentrated solutions (<5 mg. L^{-1}) whose intensities remain very low (order of µA. cm^{-2}).

As previously, the concentrations of Pb (II) were measured after 24 h for all solutions by using the Spectroquant® lead test. A total elimination of Pb (II) was obtained for all solutions after this duration excepted for that containing initially 100 mg. L^{-1}, **Inset Figure 6.** Indeed, after 24 hours, 80% of the initial amount of Pb (II) were eliminated, however the concentration in solution stays still high (around 20 mg. L^{-1}) that is why the current density is always significant (≈ 0.020 $mA.cm^{-2}$), **Figure 6**. Although this result is already very encouraging in view of the initial concentration, it was important to check whether it was possible to increase this elimination yield with a longer duration. A 48-hours treatment allowed a total elimination of Pb (II) from this concentrated solution, **Inset Figure 6.** In each case, an adherent deposit was obtained systematically regardless of the initial concentration and duration.

In parallel, SEM observations were carried out for deposits obtained from solutions initially containing 1 $mg.L^{-1}$, 5 $mg.L^{-1}$ and 27 $mg.L^{-1}$ of Pb (II) after a treatment during 24 h, and 100 $mg.L^{-1}$ of Pb (II) after 48 h, to study the influence of the initial concentration of Pb (II) in solution on the nanostructures of the thin films. The photographs presented in **Figure 7** show that the sizes of the lead oxides crystal increases significantly with the initial concentration of Pb (II) in the solution to be treated. In addition, the surface of the SnO_2 substrate becomes more and more covered as the concentration increases, but never as a uniform thin film. Indeed, whatever the concentrations, the growth of the electrodeposited thin films was made with the formation of 3D islands.

From these SEM observations, it is possible to estimate the crystal sizes of these deposits for the different initial Pb (II) concentrations. Their size varies between 0.5 and 1 µm (1 $mg.L^{-1}$), 1 and 2 µm (5 $mg.L^{-1}$), 1 and 4 µm (27 $mg.L^{-1}$) respectively. For the deposition obtained from a solution of 100 $mg.L^{-1}$, the surface of the substrate is completely covered and the crystals are entangled with each other making it difficult to estimate their size. However, the fact that it is possible to eliminate very high concentrations of Pb (II) while the substrate is totally covered signifies also that the adherent thin film presents a good electronic conductivity without any passivation of the surface of the working electrode.

To complete the SEM observations, some XRD measurements were done on thin films obtained with solutions containing initially 27 mg. L^{-1} and 100 mg. L^{-1} after a total elimination of Pb (II) (24 h and 48 h respectively) (not shown). In each case, the same compounds are present (Pb_3O_4 and β-PbO_2) in these experimental conditions (pH and E), with peaks more intense for the higher concentration due certainly to a more important amount of matter.

3.3 Presence of chemical species or heavy metals in the aqueous solution: effect on efficiency and their possible separation?

The influence of various chemical species present in the aqueous solution, such as classical inorganic ionic salts (NaCl or $NaNO_3$ or Na_2SO_4), or one organic specie (CH_3COONa), or another heavy metal, such as Cd (II) or Cu (II) or Ni (II), was studied to evaluate the effect on the efficiency of the electrochemical treatment. In supplement, it was interesting to study the possible separation of soluble lead with other heavy metals. Whatever the conditions, no precipitate was formed in the solution

3.3.1 Presence of ionic species

First, the influence of ionic species was studied during the electrochemical treatment of Pb (II) solutions with an initial concentration of 27 mg. L^{-1} prepared from a standard solution, with the presence of NaCl (1M), or $NaNO_3$ (1M), or Na_2SO_4 (1M) or CH_3COONa (1M). These ionic species were selected because they are largely present in wastewaters and often at high concentration. That is why, a concentration of 1 M was chosen.

In all cases, the pH was adjusted to 4.2 by adding NaOH (1M) excepted for CH_3COONa (free pH =6). The treatment was carried out under an imposed potential of 0.7 V based on the results obtained in pure water. After 24 h, a total elimination of Pb (II) was obtained for all solutions, accompanied by the formation of adherent deposits onto SnO_2, **Figure 8A.** These results mean that this treatment is also effective for removal soluble lead in presence of these species, and even at high concentration (1M), which is extremely interesting for future applications.

3.3.2 Presence of other heavy metals

It seemed very important to study the influence of the presence of other heavy metals in solution, and their possible effect on the elimination of soluble Pb (II). The most common heavy metals were chosen such as Cd (II), Cu (II) and Ni (II), because these chemical species can be largely present with lead in real effluents, and often at high concentrations. For that, these studies were carried out with Pb (II) solutions (6.5 µmol into 50 mL) prepared with Milli-Q water from standard solution in the presence of 6.5 µmol of another heavy metal (Cd (II) or Cu (II) or Ni (II)).

The electrochemical treatment of each solution was carried out during 24 h by chronoamperometry, under an imposed potential of 0.7 V, at room temperature, with gentle stirring. The pH was systematically adjusted to 4.2 by the addition of NaOH (1M). These experimental parameters correspond to the optimized conditions for the total elimination of lead present alone in pure water. In each case, an adherent thin film was deposited onto the SnO_2 substrate with a total elimination of Pb (II), **Figure 8B,** while Cd (II) or Cu (II) or Ni (II) remained quantitatively in solution according to systematic analyses performed with the specific Spectroquant® kits. An equivalent treatment with a longer duration (48h) had no effect on the elimination of these heavy metals, which always remains quantitatively in solution.

These results are extremely interesting for future applications to obtain a quantitative removal of lead from aqueous solution with a total separation of other heavy metals such as Cd (II), Ni (II) or Cu (II).

3.4 *Real interests of this electrochemical treatment for potential applications?*

3.4.1 Comparison to environmental and drinking water standards

Until now, the amount of Pb (II) in solution were measured using the Spectroquant® lead test with a detection limit equal to 0.1 mg. L^{-1} (4.8 10^{-7} mol. L^{-1}). This limit remains high for precisely determining the removal efficiency of this treatment, and particularly in comparison to the WHO norms for drinking water and the environment standards (10 µg. L^{-1} and 7.2 µg. L^{-1} respectively) [50]. For that, supplementary measurements were performed by using screen-printed electrodes specifically developed in our laboratory and dedicated to the detection of heavy metals, and lead in particular in the trace state in solution (order of 10^{-8} mol. L^{-1}, i.e. 2.07 µg.L^{-1}) [38,39].

For these complementary measurements, the electrochemical treatment was tested according to previous results by applying two different experimental conditions: the first one at pH = 4.2 under 0.7 V, and the second one at free pH (≈ 2) under 1.0 V. The two treatments were performed at room temperature during 24 h on 50 mL of a Pb (II) solution containing initially 27 mg. L^{-1} with gentle stirring. After 24 h, the concentrations of Pb (II) remaining in the solutions determined by the screen-printed electrodes are equal to 4 µg. L^{-1} (2.10^{-8} mol. L^{-1}) for the first conditions, and 8 µg. L^{-1} (4.10^{-8} mol. L^{-1}) for the second ones respectively.

These results mean that this innovative treatment allows the decontamination of the lead-loaded solutions (27 mg. L^{-1} initially), for these two experimental conditions with a depollution percentage in order of 99.99%. In addition, the concentrations reached are in the good respect to the environment standards and the WHO norms for drinking water [50]. These results are remarkable and very promising for future applications.

3.4.2 Determination of the energy costs

It was important to estimate the energy costs for the implementation of this electrochemical process. The energy consumed can be estimated using the **Eq. 8**:

$$E_{\text{consumed}} = I.V.t \qquad \textbf{Eq.8}$$

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 elimination of the metal present in soluble form in the solution (h).

The evaluation was estimated for the standard case corresponding to the treatment at laboratory scale of 50 mL of a solution containing 27 mg.L^{-1} of Pb (II) with SnO_2 as substrate (S = 3 cm^2). The estimation was performed using the maximal current intensity and not the average value over the entire period of treatment meaning that the energy costs are greatly overestimated. The maximal intensity of current measured in this case reaches 10^{-4} A, corresponding to an energy equal to 8.4 .10^{-4} kWh. For the year 2020, the price of 1 kWh in France being equal to 0.17 €, the estimated energy cost corresponds to 1.4 10^{-4} €. According to these calculations, the price for removal 1kg of Pb (II) recovered as oxide(s) thin films is largely inferior to 100 € at the laboratory scale. This result shows that this decontamination process is not only efficient and easy to implement (conventional reactor, no chemicals used, in air and at room temperature) but also required low energy costs.

3.4.3 ***Influence of the substrate nature***

Until now, only SnO_2 was used as a conductive substrate for this treatment. However, while this substrate is interesting for fundamental studies, its application in industrial or environmental processes could be limited. That is why, it was important to test and validate the possibility to use another substrate more usual. Our choice was fixed to 316 L Stainless Steel, which is largely used in different industries [51].

For that, the same two experimental conditions detailed previously were tested with 316 L Stainless Steel as working electrode with a similar surface (S = 3 cm²): the first one at pH = 4.2 under 0.7 V, and the second one at free pH (≈ 2) under 1.0 V. The two treatments were performed during 24 h with gentle stirring at room temperature with a Pb (II) solution containing initially 27 mg.L^{-1}. In the two cases, a total elimination of Pb (II) was obtained after 24 h with the formation of adherent thin films onto 316 L Stainless Steel, exactly like to those obtained onto SnO_2. These results signify that it will be possible to develop this process with this substrate largely used in industries.

3.4.4 Application to a real wastewater sample

Until now, studies were fundamental and focused on different parameters that could affect the efficiency of Pb (II) removal from model solutions by the electrochemical process. After optimizing of all the conditions, this treatment was applied to an effluent coming from a WWTP to test its capacities.

Before applying the electrochemical treatment on such sample, chemical steps were carried out in the conventional way. Firstly, the pH of the sample was measured, and then an acidification by the addition of nitric acid was carried out to reach a pH ≈ 2, in the aim to dissociate all complexes formed between heavy metals and organic micro pollutants [52]. The filtration of the sample was then carried out using filters (0.2 µm; IC certified with hydrophilic PTFE membrane) to remove suspended solids. After this pre-treatment step, the sample was analyzed by UV-visible measurements using the adequate Spectroquant® test to identify the presence of heavy metals that have been studied previously. Two heavy metals were detected, Pb (II) and Cd (II) with a concentration equal to 0.8 mg.L^{-1} and 1.2 mg.L^{-1} respectively.

The electrochemical treatment of this sample was carried out on a volume of 50 mL in a conventional electrochemical cell with the three usual electrodes (SnO_2 as working electrode). The pH was adjusted to 4.2 by the addition of NaOH (1M), and a potential of 0.7 V was imposed by chronoamperometry for 24 h under stirring at room temperature. After 24 h, a very thin and adherent deposit was recovered onto the SnO_2 substrate, and lead was not detected in the solution by Spectroquant® test, while cadmium was still detected with the same concentration of 1.2 mg.L^{-1}.

This test therefore confirms that this treatment is effective even on a real sample for the total removal of dissolved Pb (II), with the total separation of Cd (II), at room temperature without addition of reagents and / or complexing agents, and only under the effect of an applied potential and at a given pH. This result is very encouraging for future applications.

4 Conclusions

This study reports the development of an innovative and effective electrochemical treatment, performed at room temperature and without adding reactants and/or complexing agents, for decontaminating aqueous solutions loaded with soluble Pb (II), based on the formation of lead oxide(s) as adherent thin films. It is a very efficient and simple process to implement up for eliminating 99.99 % of Pb (II) even for high contents in solution, and which allows reaching directly acceptable concentrations in the good respect with the environment standards (10 µg. L^{-1}) and the WHO norms for drinking water (7.2 µg. L^{-1}). Moreover, the fact that soluble Pb (II) was eliminated as an adherent deposit onto a solid substrate appears very interesting for applications because no filtration is required, which is generally an energy consuming step.

In this paper, many parameters such as pH, imposed potential, durations and initial concentrations of Pb (II) were studied first on model solutions to determine the efficiency of this innovative treatment. Then in view of these encouraging results, complementary studies were performed to determine the effect of the presence of other chemical species in solution. It appears that this treatment stays efficient for eliminating lead whatever the presence of chemical species. Moreover, it is possible to have a total separation from other heavy metals such as Cd (II), Ni (II) or Cu (II), and even in a real sample, which is very promising for future applications.

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Tables:

Table 1: Potential ranges of the anodic peaks observed following cyclic voltamperometric measurements with SnO_2 as substrate in a solution of Pb (II) at 27 mg. L^{-1} for different pH adjusted by adding NaOH (1M), if necessary.

pH of solution	Potential range of anodic peak (V)
2	1.0 – 1.3
4.2	0.5 – 1.1
6	0.3 – 1.1

Table 2: Nature, orientation, and crystallite sizes of ß-PbO_2 calculated from the most intense peak at 25.4°, for the films obtained after the total elimination of Pb (II) present in the solution by electrochemical treatment for different values of potentials (E) and/or pH.

Treatment conditions of the solution	Compounds electrodeposited	Preferential orientation of ß-PbO_2	Crystallite size of ß-PbO_2 (nm)
pH 2 ; $E_{imposed} = 1.0$ V	Pure ß-PbO_2	(200) (36.19^0)	40
pH 2 ; $E_{imposed} = 1.2$ V	Pure ß-PbO_2	-	40
pH 4,2 ; $E_{imposed} = 0.7$ V	Pb_3O_4 + ß-PbO_2	(200) (36.19^0)	20

Development of an efficient electrochemical process for removing and separating soluble Pb(II) in aqueous solutions in presence of other heavy metals:

Studies of key parameters.

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KEY WORDS: Depollution; Electrodeposition; Heavy metal; Thin film; Separation; Oxides

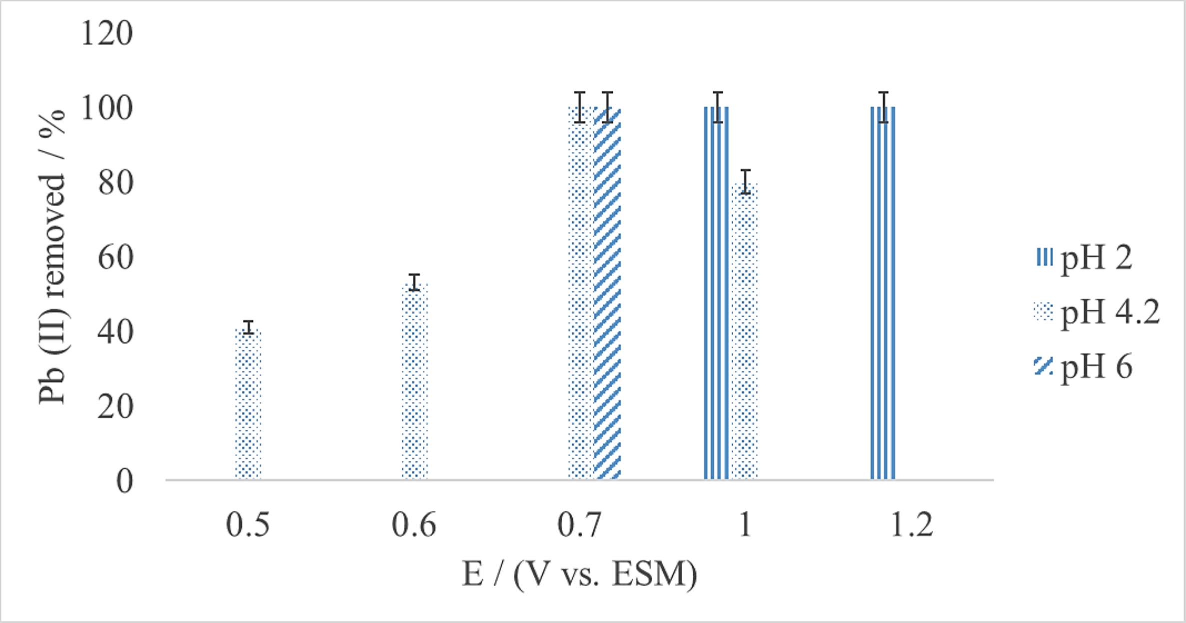


Figure 1: Percentages of Pb(II) removed according to the imposed potential for a solution of [Pb(II)] = 27 mg.L^{-1}, at room temperature, with stirring of the solution (250 rpm) for 24 hours. S (SnO_2) = 3 cm^2

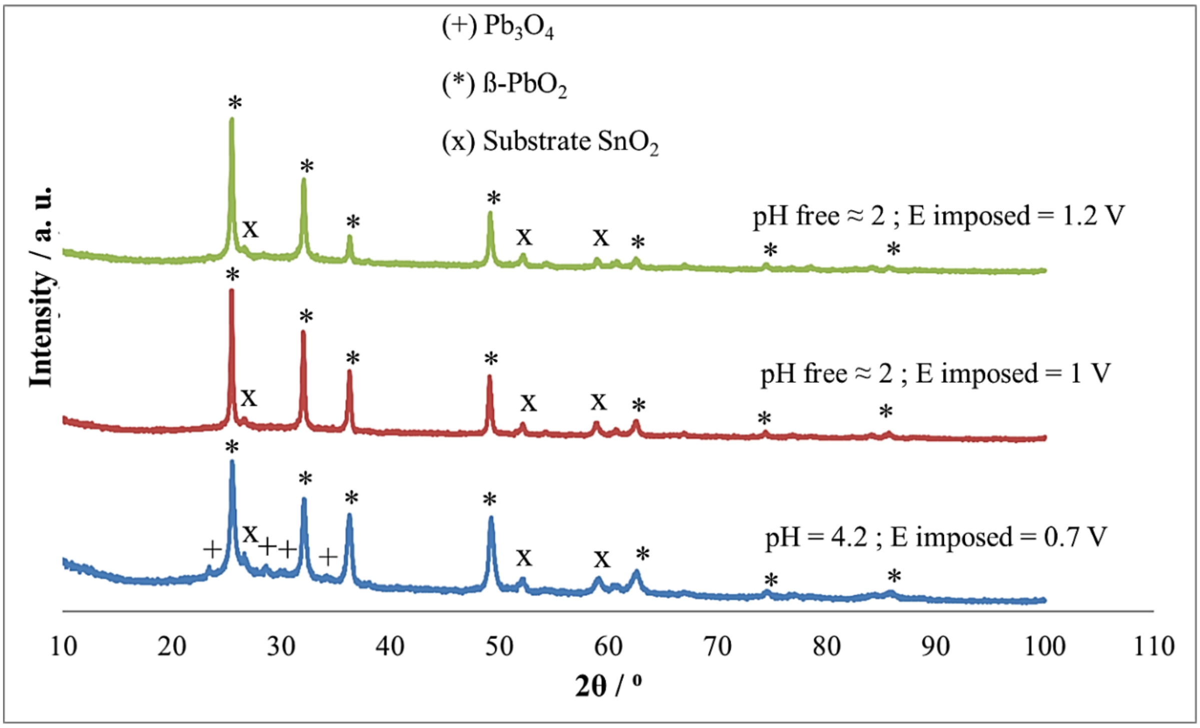
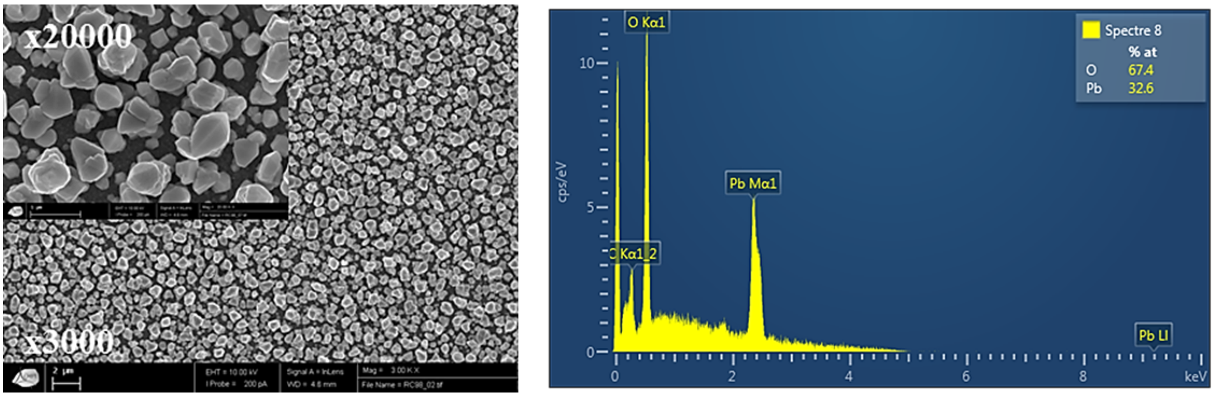


Figure 2: X-ray diffractograms of the adherent thin films obtained after the electrochemical treatment of a lead solution ([Pb(II)] = 27 mg.L^{-1}), for different values of imposed potentials and pH (pH free ≈2 and pH adjusted to 4.2 by adding of NaOH (1M)), at room temperature, with stirring of the solution (250 rpm) for 24 hours. S (SnO_2) = 3 cm^2

A



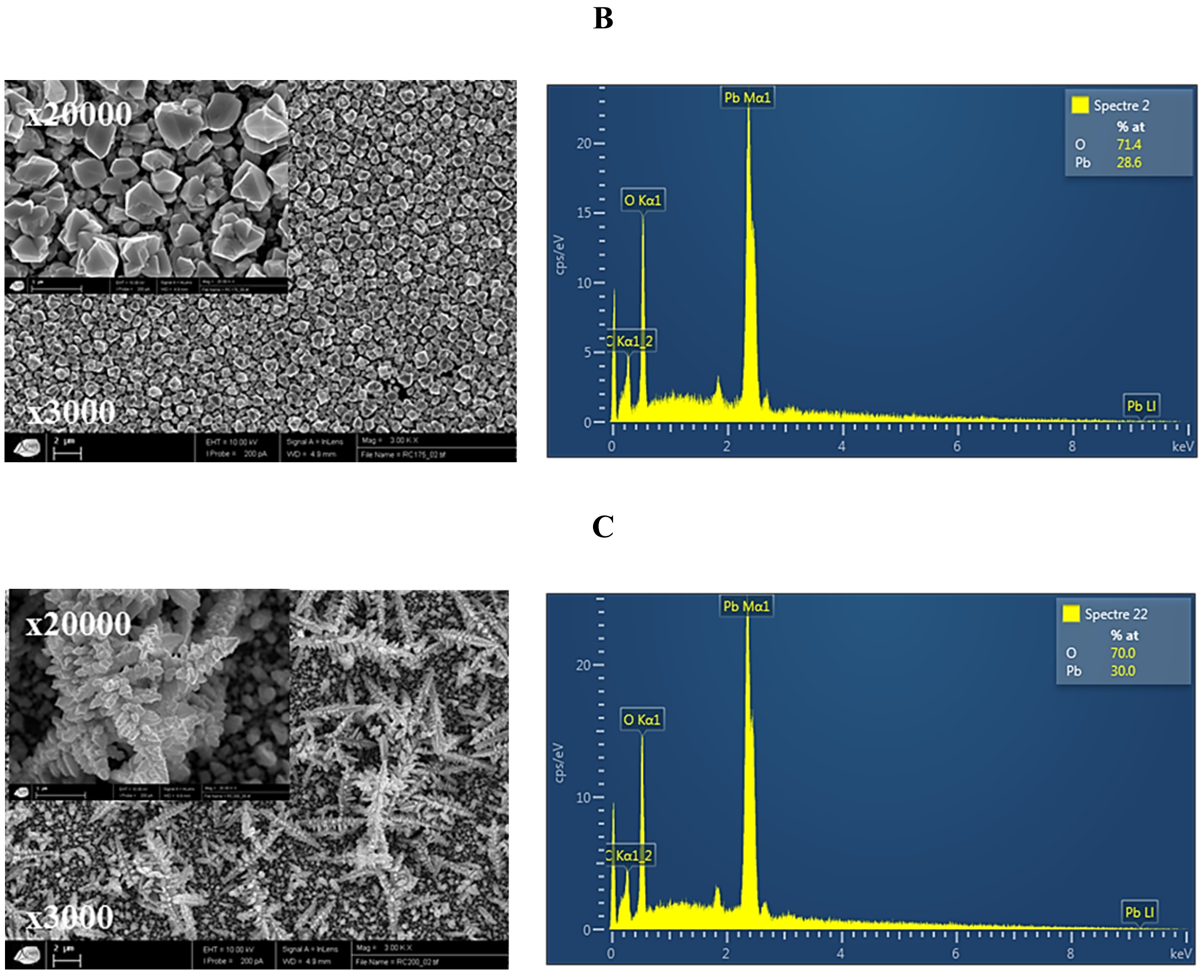


Figure 3: SEM observations and analyzes by EDS of the adherent thin films obtained after the electrochemical treatment of a lead solution ([Pb(II)] = 27 mg. L^{-1}), at room temperature, with stirring, for 24 hours, with different values of imposed potential and pH, S (SnO_2) = 3 cm^2. **(A)** pH = 4.2, E = 0.7 V; **(B)** free pH ≈ 2, E = 1 V; **(C)** free pH ≈ 2, E = 1.2 V. Scale (x3000: 0.3 cm = 2 µm) and (x 20000: 0.6 cm = 1 µm).

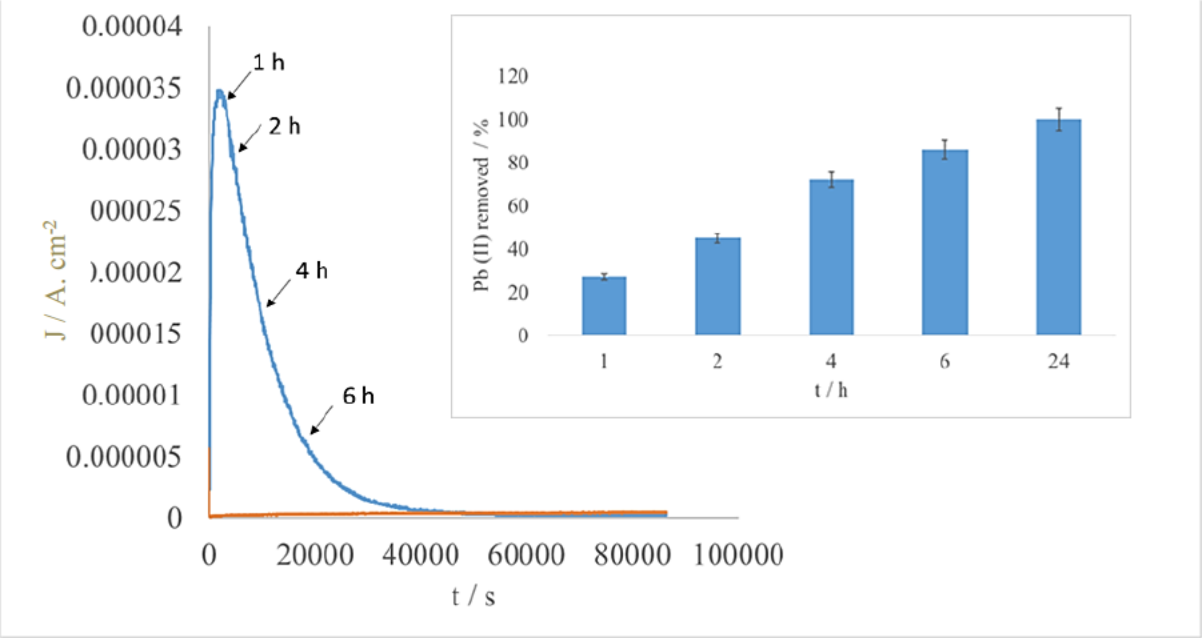


Figure 4: Current densities measured during electrochemical treatments for two solutions with [Pb(II)] = 27 mg. L^{-1} (blue curve) and without the presence of Pb(II) (red curve): E imposed = 0.7V; pH ≈ 4.2 by adding NaOH (1M); with stirring, at room temperature, for 24 h, S (SnO_2) = 3 cm^2. ***Insertion***: Percentages of Pb(II) removed as function of the treatment duration for solutions containing initially 27 mg. L^{-1}.

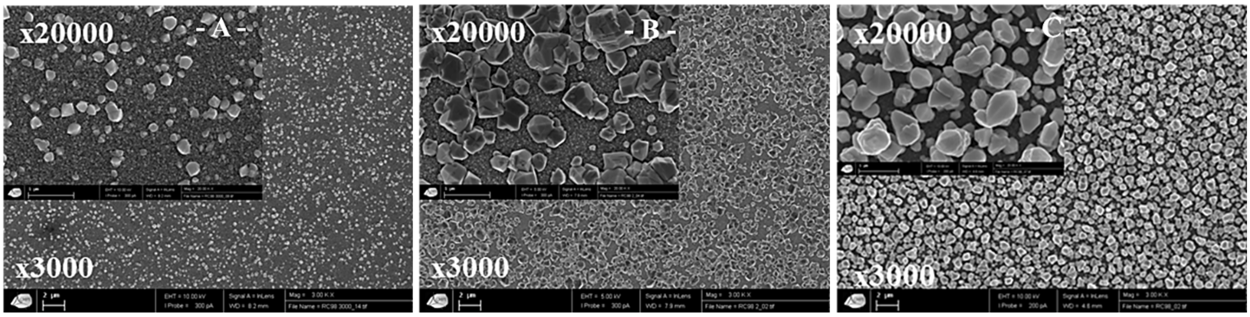


Figure 5: Observations by SEM of adherent thin films obtained after the electrochemical treatment at E imposed = 0.7V; [Pb(II)] = 27 mg. L^{-1}; pH = 4.2 by adding NaOH (1M); with stirring at 250 rpm, at room temperature, S (SnO_2) = 3 cm^2, after **(A)** 1 h; **(B)** 2 h, and **(C)** 24 h. Scale (x 3000: 0.3 cm = 2 µm) and (x 2000: 0.6 cm = 1 µm)

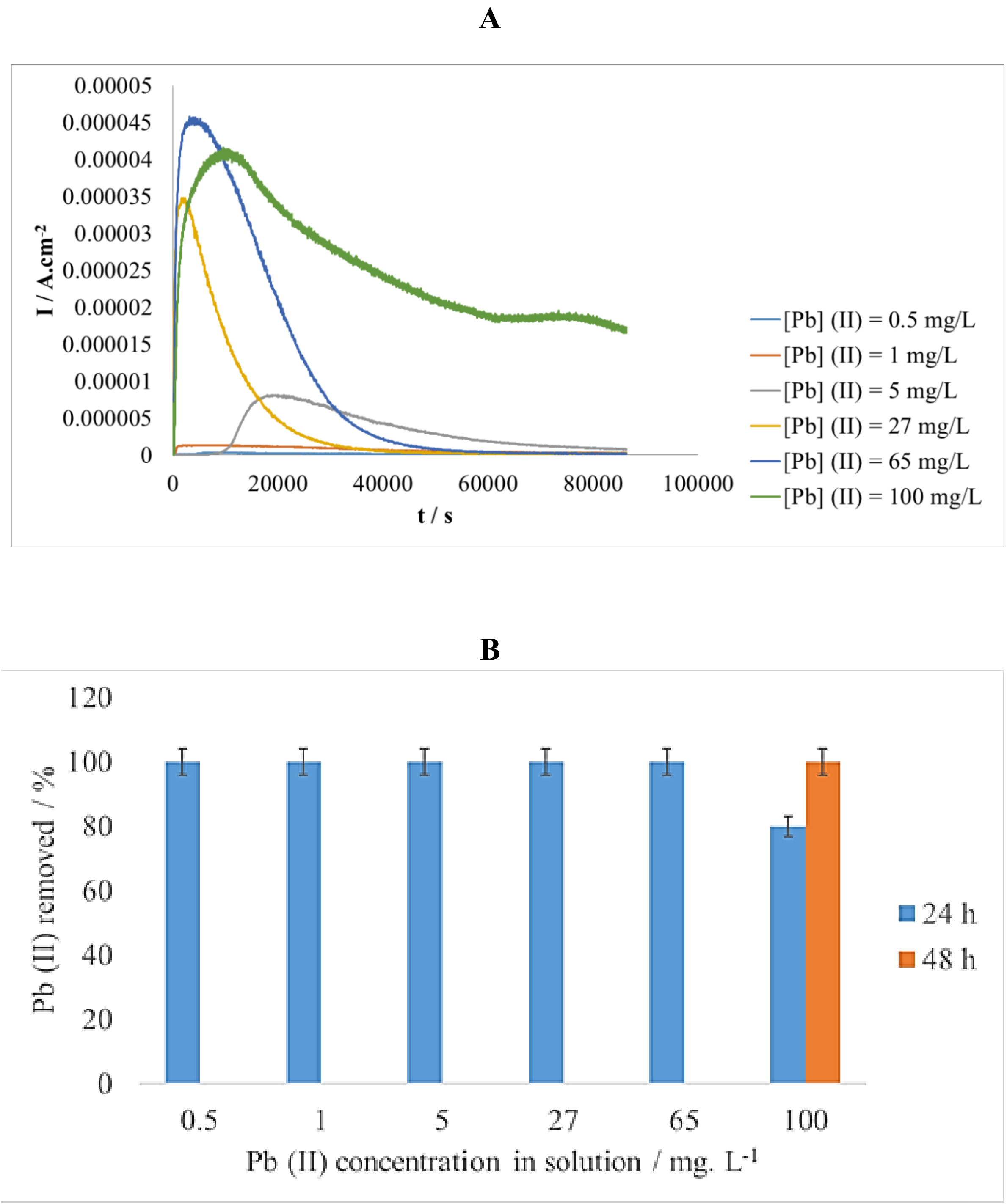


Figure 6: (A) Current densities measured during electrochemical treatments carried out at 0.7 V for solutions of different initial concentrations of Pb(II) at pH = 4.2 by adding NaOH (1M) if necessary, for 24 h, with stirring; S (SnO_2) = 3 cm²; at room temperature: **[Pb(II)] = 0.5 mg. L^{-1}** (pale blue); **1 mg. L^{-1}** (red); **5 mg. L^{-1}** (grey); **27 mg. L^{-1}** (yellow); **65 mg. L^{-1}** (dark blue); **100 mg. L^{-1}** (green). **(B)** Percentages of Pb(II) removed after the electrochemical treatment.

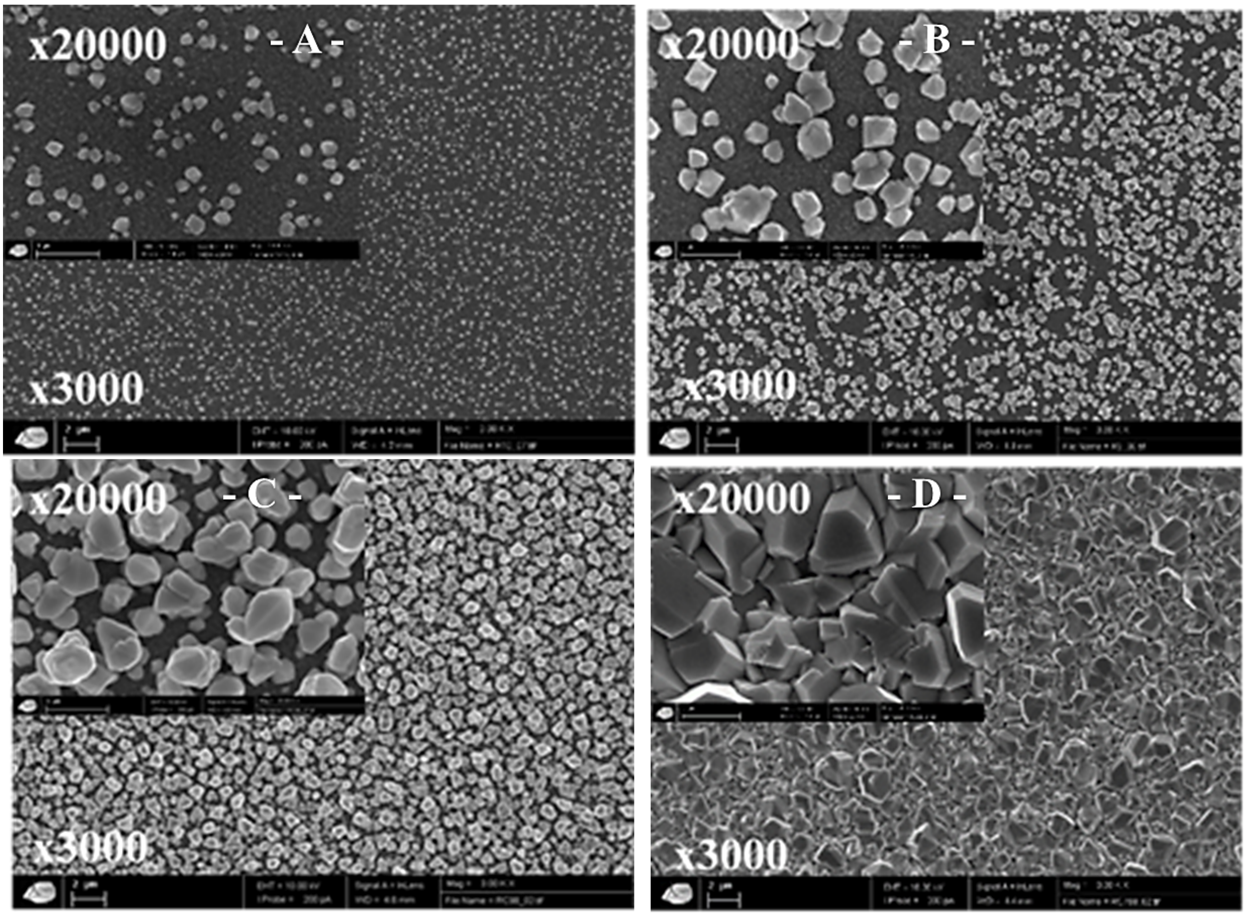
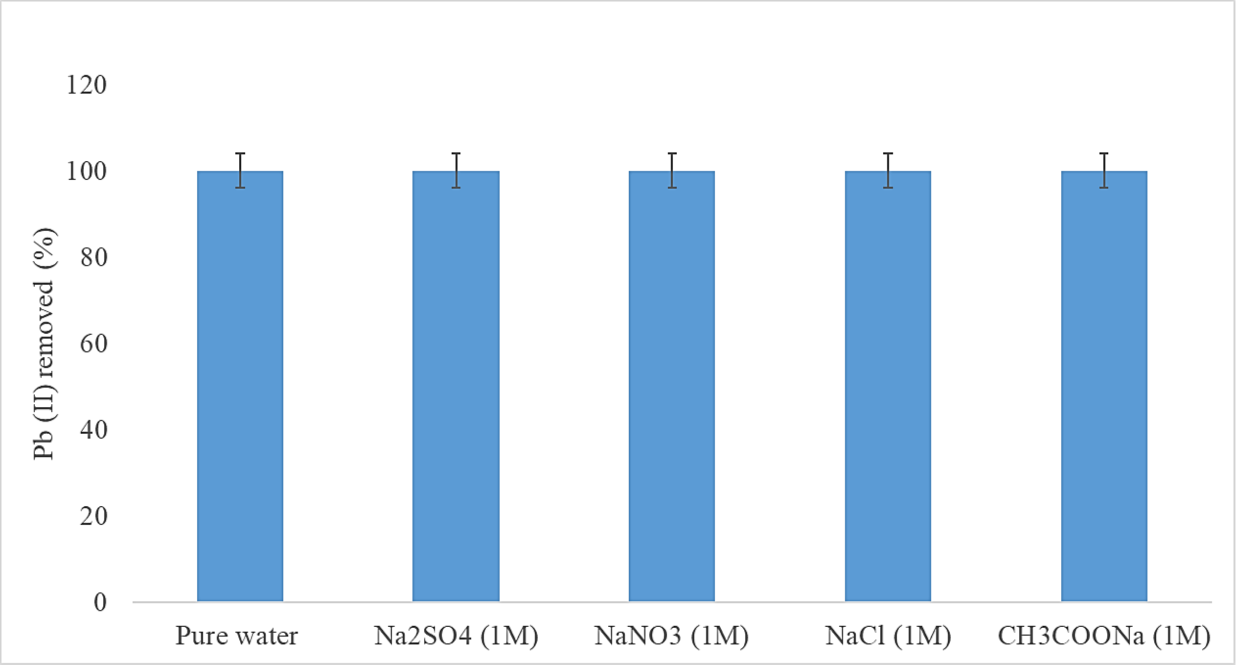


Figure 7: SEM observations of adherent thin films obtained after electrochemical treatment of solutions with different initial Pb(II) concentrations (E imposed = 0.7 V, pH ≈ 4.2 by adding NaOH (1M), with stirring; S (SnO$_2$) = 3 cm^2; at room temperature) during 24 h for (**A**) 1 mg.L^{-1} ; (**B**) 5 mg.L^{-1} and (**C**) 27 mg.L^{-1} , and 48 h for (**D**) 100 mg.L^{-1}. Scale (x 3000: 0.3 cm = 2 µm) and (x 2000: 0.6 cm = 1 µm)

-A-



-B-

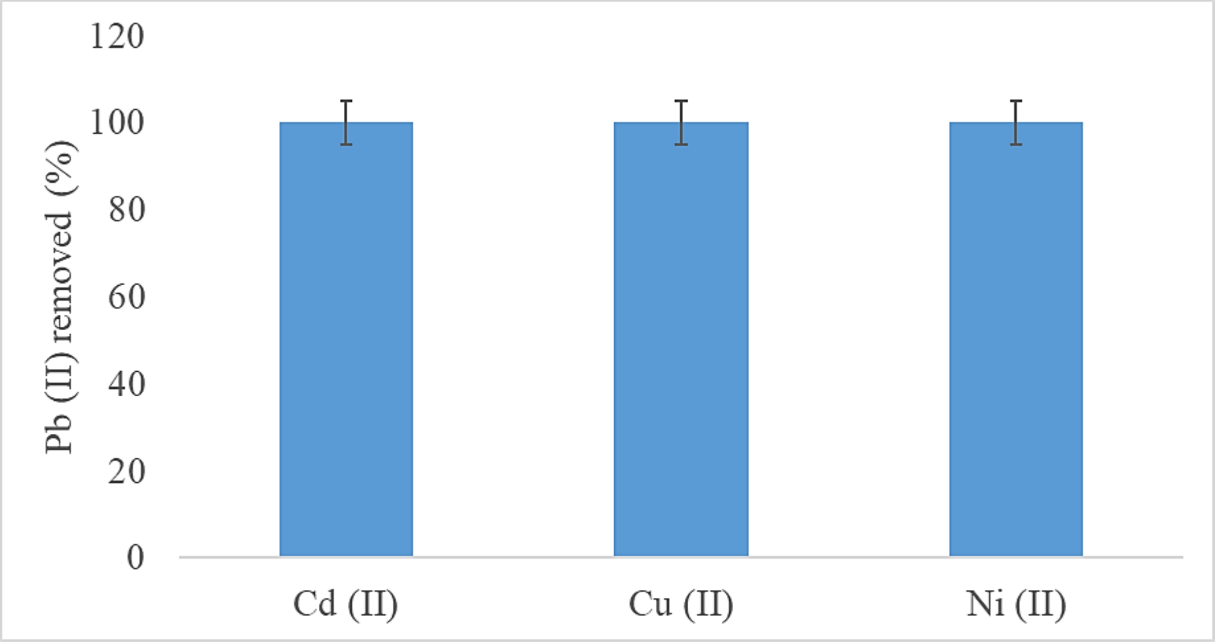
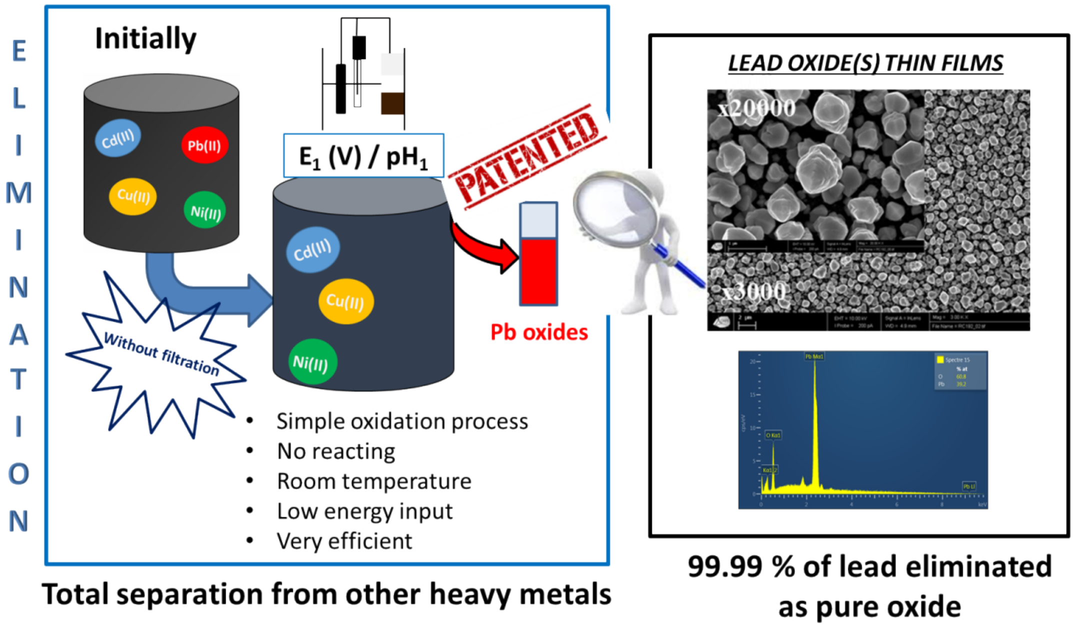


Figure 8: Percentages of Pb (II) removed as a function of the presence of chemical species **(A)** or other heavy metals **(B)** in a lead solution containing initially [Pb(II)] = 27 mg. L^{-1}, under an imposed potential of 0.7 V, S(SnO_2) = 3 cm^2, at room temperature, with stirring for 24 hours.



5 Research highlights

- Innovative treatment for removal Pb (II) from solutions as adherent oxide thin film
- Very simple and efficient treatment without adding reactants at room temperature
- Elimination of 99.99 % of Pb with concentrations directly acceptable for standards
- Total separation of soluble lead to other heavy metals in the optimal conditions
- Successful test on real sample highlighting possible applications