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Innovative electrochemical process for a total removal and/or separation of soluble heavy metals

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Abstract

This study aims to extend an innovative electrochemical process for a total elimination and/or separation of different soluble heavy metals. This objective is very important because today the water pollution, due to intense anthropogenic activities by toxic chemical substances and heavy metals in particular, becomes a serious problem for environment and human health. In this context, we have developed recently an efficient electrochemical process for removing soluble Pb(II) as adherent oxide(s) films on conductive substrate, leading to reach directly acceptable concentration levels for the environment and drinking water, and even in a complex medium. In the present study, this electrochemical process of depollution was extended to remove separately other heavy metals, and to recover them in the form of adherent films according to the same principle. The adequate parameters were researched and tested for each heavy metals present alone before to be applied on a synthetic aqueous solution containing a mixture of the studied heavy metals such as Pb(II), Cu(II), Ni(II), and Cd(II). In complement, some tests were performed with success on effluents, coming from wastewater plant (WWTP) containing different heavy metals, confirming the real interests of this innovative electrochemical treatment. These all results are very promising for future applications either for wastewater depollution either for very easy separation of different heavy metals, which generally requires complex and energy consuming chemical steps.

KEY WORDS: Water pollution; Thin films; Metal oxides; Electrochemical treatment; Electrodeposition

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1 Introduction

Due to the particular intrinsic properties of heavy metals and associated compounds (e.g. oxides, hydroxides and oxyhydroxides), these materials are widely used in industries and new technologies such as metal processing, metal plating, electronics, textiles, paper, pesticides, etc. In this context, wastewater produced containing heavy metals and their direct or indirect discharge into the environment are relatively recent, and begin serious problems due to these vast anthropogenic sources and amount of heavy metals (mining and associated industries) [1-4]. In addition, there are also extrinsic environmental factors controlling pollution such as climate, precipitation, air temperature, hydrogeological conditions, etc. [5, 6].

Once the heavy metals are released into the environment either by anthropogenic activities from their source either by natural processes, they can pollute the air and water, with possible great consequences on the production of drinking water, which is an essential resource for life. The most common heavy metals found in wastewater coming from industrial effluents and/or terrestrial ecosystems are cadmium (Cd), copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni) Vanadium (V), Platinum

(Pt) and Titanium (Ti) [7, 8]. In complement, the concentrations are also an important parameter for characterizing their impact on environment, terrestrial and aquatic organisms, and human health [9]. This is particularly true for the most toxic heavy metals such as Pb, Cd, Cr, Ni and Ti. That is why their concentrations in produced wastewater before discharges into the environment are controlled and must be in coherence with the defined guideline for the acceptable concentration limits set by the World Health Organization (WHO) for drinking water and the environment standards [10].

Different methods are frequently applied for removing heavy metals from wastewater including adsorption, ion exchange, membrane filtration, chemical precipitation, inverse osmose, electrochemical treatments, etc. [11]. However, some of these largely used methods can be (i) energy intensive and/or expensive, (ii) lead to incomplete removal of metals, (iii) present low efficiencies for very high or low metals concentrations, (iv) require high consumption of reagents, more or less toxic or expensive or scarce, (v) produce toxic sludge or other wasted products that need complement treatments, (vi) require regeneration steps more or less complex or energy-intensive, (vii) need complex implementation and maintenance, etc. To ensure a less negative impact of these issues, constant improvements are necessary to respect the acceptable concentrations [12-16].

In this context, we have recently developed an innovative electrochemical process for a high efficient lead removal from wastewater in very easy conditions [16, 17]. The main idea is to remove lead in the form of adherent electrodeposited lead oxide(s) thin films onto conductive support at room temperature without addition of toxic reagents and / or complexing agents, and only based on the effect of an adequate applied potential at a given pH, with classical electrochemical materials. Even if the

electrodeposition of pure oxides thin films, and lead in particular, is already largely reported in the literature for synthesis and/or various applications, because lead oxides are particularly interest compounds, no study focusses on the depollution of aqueous solutions by this way. Moreover, our electrochemical process is particularly efficient since it allows the decontamination of aqueous solutions (e.g. model or effluents), loaded with Pb(II) until elimination of 99.99% with reached concentration level acceptable for the environment and drinking water standards [16, 17]. Therefore, no reagent was used, no waste was produced, and the development at large scales with low maintenance at low costs, since the electrical energy inputs are low, appears possible.

Considering the real advantages and interests of this innovating electrochemical process for eliminating lead, compared to other classical methods, the aim of the present article was to extend our studies to other toxic heavy metals such as Cu(II), Ni(II) and Cd(II), which are largely present in wastewater, industrial effluents and terrestrial ecosystems [7, 8].

First, the adequate electrochemical conditions were researched for each heavy metal present alone in pure water. Then, systematic analyses of the solutions coupled to the characterizations of the recovered thin films by XRD and SEM were performed. In a second part, this treatment was applied on a model solution containing a mixture of these all heavy metals (e.g. Pb(II), Cu(II), Ni(II), and Cd(II)), present at equivalent concentrations for studying the possibility of their total removal and/or separation. Finally, the same procedure was applied on effluents coming from wastewater treatment plants (WWTP) and containing these heavy metals for evaluating the efficiency and the real interests of this innovative electrochemical treatment. The possibility to have a total elimination and separation of heavy

metals in these complex solutions in simple and eco-compatible conditions is very promising for future applications in many fields.

2 Materials and methods

2.1 Chemicals

Standard solutions of Cu(II), Ni(II), Cd(II) and Pb(II) ($1002 \pm 4 \text{ mg. L}^{-1}$, 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 for preparing all model solutions. NaOH (1M) and nitric acid (1M) (ACS Reagent Sigma Aldrich) were used for adjusting the pH and for the treatment of real effluents. All synthetic solutions were prepared by using Milli-Q water.

2.2 Experimental methodology

All electrochemical measurements were performed by using a microautolab potentiostat piloted by its associated software GPES (*General Purpose for Electrochemical System*).

All electrochemical studies were performed into a conventional electrochemical setup with three electrodes: a commercial glass plate covered with tin dioxide $\text{SnO}_2\text{:F}$ (FTO Fluorine-doped Tin Oxide, Solems, noted SnO_2), with a delimited surface to 3 cm^2 by an adhesive mask, as a working electrode, a platinum wire wound spirally, for having a higher surface to the working electrode, as a counter electrode, and a mercurous sulphate electrode (MSE, $E = 0.6513 \text{ V/SHE}$) as a reference electrode. All values of potential reported in this study are referred to this reference electrode. All experiments were realized at room temperature, in the air at atmospheric pressure with a gentle agitation of the solution (250 rpm).

In first, cyclic voltammetry measurements ($v = 10 \text{ mV.s}^{-1}$; five successive scans) were performed for determining the potential ranges corresponding to the oxidation and/or

reduction reactions of the soluble metal studied alone according to the pH value. Then, the electrochemical treatment for the elimination of heavy metals was carried out by chronoamperometry for different durations by imposing the adequate potential determined by cyclic voltammetry according to the pH value.

The experiments with model solutions were performed on 50 ml of milli-Q water at different pH adjusted by adding NaOH (1M) if necessary (no buffer), and containing 6.5 μmol of heavy metal, alone or in mixture, as soluble form (e.g. M(II), such as Cu(II), or Ni(II) or Cd(II)). In all cases, no precipitate was present, initially in the bulk solution and at the end of the treatment. The solutions being always clear, no filtration step was required and the analyses for determining the concentration of each heavy metal were directly performed without any preparation. Each condition was repeated several times for confirming the good repeatability and reproducibility of the treatment in terms of elimination and/or separation of heavy metal studied alone or in mixture. In complement of these experiments performed on model solutions, some tests were realized in similar experimental conditions on effluents coming from wastewater plants (WWTP).

The concentrations of heavy metals present in the aqueous solutions as soluble cation (noted M(II)), were determined by using the appropriate Spectroquant® test for each heavy metal: Cu(II) (1.14767.0001; 0.10 mg. L⁻¹ to 6.00 mg. L⁻¹), Ni(II) (1.14785.0001; 0.10 mg. L⁻¹ to 5.00 mg. L⁻¹), Cd(II) (1.01745.0001; 0.01 mg. L⁻¹ to 0.50 mg. L⁻¹) and Pb(II) (1.09717.0001; 0.10 mg. L⁻¹ to 5.00 mg. L⁻¹). Absorbance measurements were performed at the adequate wavelength by a spectrophotometer (Varian Cary® 50 UV-visible Agilent): 600 nm for Cu(II), 450 nm for Ni(II), 520 nm for Pb(II) and Cd(II).

The amount of each removed metal cations ($n_{M(II) \text{ removed}}$) was calculated by the difference between the initial amount and the equilibrium one using **Eq. 1**, and the percentage of M(II) removed from the solution after the electrochemical treatment using **Eq.2**:

$$n_{M(II) \text{ removed}} = n_{M(II) \text{ initial}} - n_{M(II) \text{ at } t} \quad \text{Eq.1}$$

$$M(II) \text{ removed } (\%) = \frac{n_{M(II) \text{ initial}} - n_{M(II) \text{ at } t}}{n_{M(II) \text{ initial}}} * 100 \quad \text{Eq.2}$$

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

The values reported for each condition in the figures correspond to the mean value of several experiments with the associated incertitude.

After each electrochemical treatment, in the case of recovered adherent deposits onto the working electrode (e.g. SnO_2), X-Ray Diffraction (XRD) was performed with classical measurements ($\theta/2\theta$) by a BRUKER $\theta - \theta$ diffractometer equipped with a copper anode ($\lambda_{\text{Cu}}=1.540600 \text{ \AA}$) and a LYNXEYE detector. In addition, the thin films were observed by a MEB-FEG MERLIN Zeiss Scanning Electron Microscopy (SEM). All characterizations were carried out directly without any preparation step since the thin films were well adherent and sufficient conductive. The characterization by XRD and the observations by SEM of the deposits are reproducible for each eliminated metal for similar experimental conditions (pH and applied potential) and whatever species present in solution.

3 Results and discussion

Recently, we have developed an innovative electrochemical process for removing soluble Pb(II) present in wastewater as adherent thin films deposited onto a conductive substrate, at room temperature without addition of toxic reagents and/or complexing agents

[16, 17]. The general principle is based only under the effect of an applied potential and at a given pH for inducing the change of the lead oxidation state. 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). It was found that Pb(II) can be quantitatively eliminated as a mixture of oxides (e.g. mainly of β -PbO₂ with few amount of Pb₃O₄) under an imposed potential of 0.7 V at pH adjusted to 4.2, or as pure β -PbO₂ in acidic solution (pH \approx 2) under imposed potentials equal to 1.0 V or 1.2 V [16, 17]. This process is so effective that it achieves a depollution percentage up to 99.99% with concentrations reached that meet environmental norms and even those of drinking water [16, 17]. In view of the real potentialities of this elimination process, it seemed very interesting to extend studies to other heavy metals.

Cu(II) and Ni(II) present different oxidation states and their eliminations in the form of adherent films deposited onto a conductive substrate seem theoretically possible according to the same principle and methodology already developed for lead. However, this is not the case for Cd(II), which possess only one soluble oxidation state that is why its elimination by this process will not be possible. Nevertheless, it was important to validate this assumption, for scientific rigor, and to study in the same time its possible effect on the elimination of the other heavy metals in the case of mixtures since they are often present together in wastewater. Each heavy metal having a specific chemistry in solution that is why it was necessary to study them separately before studying mixtures.

3.1 *Extension of the innovative electrochemical treatment on other heavy metal present alone in model solution*

3.1.1 *Case of Cu(II)*

Copper has three oxidation states (0, +I and +II), and can form different solid compounds, either in metallic form (Cu(0) (s)), either in oxidized form such as CuO and Cu₂O, according to pH and/or potential, as reported on the diagram of Pourbaix in the absence of complexing agent [18]. In accordance to the copper chemistry, it should be possible to eliminate it by this electrochemical process but the main difference compared to the case of lead is that copper, present initially in solution as soluble Cu(II), must be reduced.

Although many research papers report the electrodeposition of copper oxides and the studies of key parameters on their nanostructures for different applications (e.g. solar energy conversion, catalysis) [19, 20], never in the aim to have a total elimination of soluble Cu(II) as adherent electrodeposited thin films for water depollution. For that, cyclic voltammetry measurements were performed for determining the best potential(s) in reduction. Measurements were carried out with the conventional electrochemical cell, equipped with the three electrodes cited above, and containing 50 mL of milli-Q water and 6.5 μmol of Cu(II) (corresponding to 8.2 $\text{mg} \cdot \text{L}^{-1}$) at different pH (free pH \approx 2, 4.2 and 7) by the addition of NaOH (1M) (no buffer). Only in the case of pH = 7, two different cathodic signals were observed with significant intensities: a small first peak between - 0.35 V and - 0.5 V, and a large second peak between -0.55 V and -1 V, **Table 1**. These signals could correspond to the reduction reactions of Cu(II) into Cu(I) and/or Cu(0) according to the thermodynamic data and the diagram of Pourbaix [18].

For testing the possibility to eliminate soluble copper, two electrochemical treatments were carried out by chronoamperometry on similar Cu(II) solutions (6.5

μmol into 50 mL of milli Q water at pH 7) under a potential imposed respectively at -0.45 V and -0.85 V. In both cases, an adherent deposit was formed onto the SnO_2 substrate with a visual aspect of these two thin films clearly different according to the value of potential, pinkish brown for -0.45 V and yellowish for $E = -0.85$ V, suggesting possible differences in nature and/or crystallinity of these electrodeposited materials.

In addition, the solutions were analysed by using the Spectroquant® test for Cu(II) after different durations and for these two values of potential. It appears that the elimination of copper is largely quicker at -0.45 V than at -0.85 V, **Figure 1**, since 91 % of the initial amount of copper was already eliminated after only 24 h compared to experiments performed at -0.85 V that required 72 h to obtain equivalent results. The total elimination of Cu(II) was reached after 48 h at -0.45 V and 96 h under a potential of -0.85 V, according to the detection limit of the Spectroquant® test ($0.10 \text{ mg} \cdot \text{L}^{-1}$), which is largely inferior to the limit value fixed for drinking water (e.g. $2 \text{ mg} \cdot \text{L}^{-1}$) [10].

These results appear coherent with the difference of current intensities observed during the electrodeposition, which could be due to the nature of the electrodeposited oxide(s) copper, with electrical properties more or less pronounced, their crystallinity, and/or the covering rate of the substrate causing possible parasitic electrochemical reactions, **Insertion Figure 1**. However, in these two conditions, the intensities of currents stay always very low, and the elimination was total with concentrations reached directly acceptable for drinking water standards [10].

3.1.2 Case of Ni(II)

The chemistry of nickel is complex since nickel have many degrees of oxidation (0, + II, + III and + IV), with the possibility of forming different solid compounds, as reported by the Pourbaix diagram of nickel in the absence of complexing agent [18].

According to this diagram, the thermodynamic expected compounds in function of pH and potential are nickel in metallic form (Ni (0)) or in oxidized form such as Ni(OH)₂, Ni₂O₃ and NiO₂.

In accordance to the chemistry of nickel, it appears possible to envisage its elimination from aqueous solutions according to the same principle (e.g. oxidation state change). However, it was necessary to define the adequate potential ranges and pH since different types of oxides can be formed by oxidation reactions (e.g. Ni₂O₃ and NiO₂) in addition to NiO(OH), which can be also electrodeposited as thin films [21]. While many research papers in the literature report the electrodeposition of nickel oxides and the studies of parameters on the nanostructure for different applications [22, 23], never in the aim to have a total elimination of soluble Ni(II) for depollution context.

For that, cyclic voltammetry measurements were carried out on Ni(II) model solutions with different pH (2.5, 4.2 and 7) as cited above. In the case of pH 4.2, an anodic peak was observed in the potential range comprised between 0.5 V and 0.8 V in contrary to the other values of pH (no significant peak), **Table 1**. For confirming this result, an electrochemical treatment was carried out at room temperature by chronoamperometry on a Ni(II) solution (6.5 μmol in 50 mL prepared with milli-Q water corresponding to 7.6 mg. L⁻¹) at pH 4.2 by adding NaOH (1M), under an imposed potential of 0,7 V, with gentle stirring. After 24 h, an adherent deposit was recovered onto the SnO₂ substrate with a removal of 26 % of the initial amount of Ni(II) according to the analyses performed by the specific Spectroquant® kit. A total elimination of Ni(II), according to the detection limit of the Spectroquant® test (0.10 mg. L⁻¹), was obtained after 72 h, associated to the obtention of a deposit, which has a colour between yellow and orange. The intensity of the current is low (inferior to 10⁻⁵ A), **Figure 2**,

suggesting a relatively good electrical conductivity of the electrodeposited thin film, and no parasite electrochemical reactions.

In our previous study, we have reported that lead can be eliminated under these same experimental conditions (e.g. pH and potential), and even in the presence of Ni(II), which stayed quantitatively in solution [17]. Therefore, it appeared important to test inversely the possibility to eliminate Ni(II) in the presence of Pb(II) and for that complementary measurements were performed. Based on these results, an equivalent treatment was made on a solution containing Pb(II) and Ni(II), at the same initial concentration (6.5 μmol each in 50 ml in milli-Q water at fixed pH = 4.2) but for a longer time (e.g. 7 days). After this duration, it appears that Pb(II) was totally eliminated, but Ni(II) remained quantitatively in solution, while previously nickel present alone in solution can be eliminated.

It appears therefore that the presence of lead in solution and its elimination as thin film seems to hinder the elimination of nickel, due to possible chemical interferences in solution. However, this could be due also to the evolution of the working electrode, which was modified during the electrochemical treatment by the presence of the adherent lead oxide thin film electrodeposited. To verify this latter assumption, the working electrode was changed during the treatment of such mixture. For that, the working electrode of SnO₂ covered with the deposit of lead oxides, was thus exchanged by a novel working electrode of SnO₂. In these conditions, Ni(II) was totally eliminated in the form of an adherent film after 72 h, exactly like previously observed in the absence of lead. Consequently, it appears that the removal of Ni(II) seems more difficult to carry out than lead or copper, and that it requires a specific surface such as SnO₂ to be able to be electrodeposited as an adherent thin film. This could be due to the necessity to have a specific crystalline structure for initiating the germination process.

3.1.3 Case of Cd(II)

As already mentioned, cadmium has only two degrees of oxidation, 0 and (+ II), with only one as soluble specie (+ II). According to the Pourbaix diagram in absence of complexing agent [18], cadmium forms a solid compound either in metallic form (Cd(0)) either in the oxide or hydroxide form. Therefore, it appears impossible to remove Cd(II) in solution according to the same methodology based on oxidation state changes. Only the formation of cadmium oxide or hydroxide is possible, however, under these conditions, it is only a precipitation reaction based on a local pH change as already reported for the electrodeposition of various materials such as AgO [24] Y₂O₃ [25] Cu₂O [26], PbO₂ [27], and ZnO in particular [28, 29].

Even if we expected theoretically the non-removal of Cd(II) according to this depollution process, it was important for scientific rigor to study its behaviour alone. Particularly, it was important to validate the absence of precipitation onto the working electrode, which could modify the efficiency of the treatment for the other heavy metals in the case of a mixture (nature change and/or conductivity of the working electrode).

According to the same experimental procedure, cyclic voltammetry measurements were carried out into the conventional electrochemical cell with the three electrodes described before. Different Cd(II) solutions, with various pH as cited above (2, 4.2 and 7), were studied, and in all cases, no peaks were reported. Moreover, the values of the oxidation and reduction potentials of water were not modified, in comparison to the other cyclic voltammetry measurements for similar pH, confirming the absence of the modification of the working electrode due to possible precipitation reaction. In addition, the SnO₂ working electrode was not visually modified. Clearly,

Cd(II) cannot be eliminated from the solution in this way, whatever the pH and / or potential conditions.

3.2 Characterization of the recovered films by XRD and SEM

3.2.1 Case of Cu(II)

For confirming the nature of the solids, the adherent deposits obtained after a total elimination of Cu(II) at pH = 7 under imposed potentials fixed to - 0.45 V or - 0.85 V respectively, were characterized by XRD and SEM.

Figure 3 reports the X-ray diffractograms of these deposits. According to the observed peaks, and based on JCPDS 00-005-0667 card, it appears that Cu(II) was electrodeposited in the form of Cu₂O (cuprite, cubic structure) in the two experimental conditions. The colour of the natural cuprite can be varied between yellow, red or brown, which is in good agreement with the visual aspect of the obtained thin films reported previously (e.g. pinkish brown for - 0.45 V and yellowish for E = -0.85 V). Moreover, the characteristic peaks of Cu₂O are particularly intense for the treatment performed under a potential of - 0.45 V compared to - 0.85 V, meaning that the sample under these conditions must be more crystallized since the total amount was equivalent (total elimination). This result is also in good coherence with the difference of colour observed for each thin film.

The formation of Cu₂O is particularly in good agreement with the diagram of Pourbaix as thermodynamic compound expected in this range of pH and value of applied potential (e.g. pH = 7 and E = -0.45 V), [18]. In contrary, the treatment performed at - 0.85 V is slightly lower to the limit of the Cu₂O formation zone, according to the diagram of Pourbaix, which can justify the difference of the efficiency of treatment observed in this case. Indeed, the electrical energy input required must be more important for initiating the germination process. Moreover, this value of potential

is close to the reduction potential of water, which can be also a parasitic electrochemical reaction. This can justify why the intensity of current was largely higher in this case.

Figure 3 reports also the associated SEM images of these two thin films. These observations show that the soluble copper was eliminated in the two cases as cubic crystals but with different sizes according to the experimental conditions. Therefore, the removal Cu(II) mechanism by this electrochemical treatment, made by reduction reaction, is a nucleation process according to the model of Volmer-Weber [30, 31], as already reported for the elimination of lead [16, 17]. Indeed, whatever the conditions, the growth of the electrodeposited thin films was performed with the formation of 3D islands and not as a uniform thin film. This observation is relatively classical for electrodeposition process that begins generally from surface or nucleation site defects.

The cubes have very large sizes for the deposit formed at -0.45 V, which vary between 2 and 3 μm , compared to those obtained at -0.85 V (well below the micrometer). However, in both cases the cubes are well homogeneously distributed onto the surface of the SnO₂ working electrode. These observations are in good coherence with the more or less intense peaks obtained by XRD measurements and the difference of intensities of current observed during their elimination by electrodeposition.

Based on literature studies, Cu₂O is a p-type semiconductor with a reported resistivity varying from a few $\Omega\cdot\text{cm}$ to 1014 $\Omega\cdot\text{cm}$ depending on the synthesis conditions [31]. Cu₂O preparation techniques include thermal oxidation, chemical oxidation, anodization, vacuum evaporation and electrochemical methods [20, 31, 32]. Thus, it is possible to suppose that the resistivity of the materials electrodeposited could change according to the value of potential, which can explain also these differences in term of the values of intensities, sizes of crystals, and covering rate

during the total elimination of Cu(II). Cu₂O has potential applications in solar energy conversion and catalysis [32]. This compound is also often used as an absorbent layer or hole transport layer in solar cells, [33-35]. Synthesizing Cu₂O deposits with very different crystal sizes according to the experimental conditions can be an asset for possible applications of these materials [19, 20] obtained moreover within the framework of the total depollution of solutions loaded with copper.

3.2.2 Case of Ni(II)

The deposit recovered after the total Ni(II) removal with a yellow/ orange colour was characterized by XRD. The observed peaks correspond to the characteristic peaks of SnO₂ substrate but they can also well matched to γ -NiO(OH) according to the JCPDS 00-006-0075 card, **Figure 4**. According to the diagram of Pourbaix, at these potential and pH values, nickel can be expected rather in the form of NiO₂, but the formation of Ni₂O₃ cannot be excluded. Moreover, the electrodeposition of other compounds such as NiO(OH), could be also possible [21]. Therefore, we cannot conclude formally on the structural form of the Ni electrodeposited solid by XRD measurements, however, it is classical that Ni compounds are difficult to be identified by XRD [36]. For that, specific other measurements and/or change of the substrate nature would be required.

In complement, the thin film was observed by SEM but the morphology was not really defined with two different types of crystals, **Figure 4**. Other complementary techniques such as infrared spectroscopy or XPS would be interesting to identify precisely the nature of the compound electrodeposited, but this is out of the scope of this work.

3.3 Determination of the Faraday efficiency and the yield of experimental energy consumption (R) for the elimination of each heavy metal present alone in solution.

After the electrochemical treatment, each heavy metal, e.g. Cu(II) and Ni(II), present alone in model solution was totally eliminated based on the analyses of solution. As a result, the faradic efficiency of recovered soluble metal in solution in the form of metal oxide is 100%.

However, it was interesting to compare the experimental electrical charge, calculated according to **Eq. 3**, in relation to the theoretical electrical charge, calculated according to the Faraday's law, **Eq. 4**, to estimate the yield of the experimental energy consumption for having a total elimination of each heavy metal, **Eq. 5**:

$$Q_{\text{experimental}} = I \cdot t \quad \text{Eq. 3}$$

Where I (A) the average current recorded during the elimination by electrodeposition of each heavy metal, and t (s) the time needed for the total elimination.

$$Q_{\text{theory}} = n \cdot F \cdot z \quad \text{Eq. 4}$$

Where n (mol) the molar number of the heavy metal eliminated from the started solution ($6.5 \cdot 10^{-6}$ mol), z the electrons transferred for the oxidation (Ni(II) case) or the reduction (Cu(II) case) to produce the solid (NiO(OH) and Cu₂O respectively), F Faradaic Constant (96485 C mol^{-1}).

$$\text{Yield of experimental energy consumption (R)} = \frac{Q_{\text{exp}}}{Q_{\text{theo}}} * 100 \quad \text{Eq. 5}$$

All values required for these calculations are regrouped in **Table 2**. As reported previously, Cu(II) can be eliminated at pH = 7 under an applied potential of -0.45 V or -0.85 V, and the yields of energy consumption for each case are 136 % and 3312 % respectively.

This means that the experimental energy consumption is more than the theoretically expected by a factor of 1.3 and 33 respectively.

These results confirm clearly that the elimination of Cu(II) is largely more efficient and easy for an applied potential equal to -0.45 V, in good agreement with the diagram of Pourbaix. The difference of energy consumption is relatively low, given that the duration and the reactor were not optimized yet. In contrary, the elimination of Cu(II) in the case of an applied potential fixed to - 0.85 V is clearly unfavourable. As already reported above, this is probably due to the presence of parasitic reactions and/or the requirement of more energy for initiating the nucleation process. By consequently, the most effective removal of Cu(II) for depollution purposes must be performed in priority under an applied potential of -0.45V.

Likewise, Ni(II) was removed under an applied potential of 0.7V at pH = 4.2. The yield of experimental energy consumption is 100 % and close to the theoretical value expected one, without parasite reaction.

3.4 Application of the electrochemical treatment on a synthetic solution containing a mixture of heavy metals: Determination of the separation efficiency and energy costs.

The purpose was (i) to confirm first the real efficiency of this treatment to remove and to separate totally the different heavy metals present in a mixture for determining eventual interference problems, and in the second part (ii) to estimate the energy costs for the implementation of the elimination of each heavy metal by this electrochemical process [16].

The consumption of the electrical energy consumed for the elimination of each heavy metal by this electrochemical treatment was estimated using the following equation:

$$E_{\text{consumed}} = (I.V.t) / 1000 \quad \text{Eq. 6}$$

With E , the electrical 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).

3.4.1 Determination of the separation efficiency

After the determination of the adequate conditions for removal each metal cation, an electrochemical treatment was carried out by chronoamperometry on 50 ml of a solution under stirring containing 6.5 μmol of each soluble metal, Pb(II), Cu(II), Ni(II), and Cd(II), corresponding to 27 mg. L⁻¹, 8.2 mg. L⁻¹, 7.6 mg. L⁻¹ and 14.6 mg. L⁻¹ respectively. For that, the following protocol was performed at room temperature, and only by changing the pH and the imposed potential for each step as illustrated on **Figure 5**. After each step, a systematic analysis of the solution was performed to determine the concentration of the heavy metal studied, in complement to the observation by SEM of the recovered thin film and its characterization by XRD. In all cases, the presence of other heavy metals in solution has any effect on the nature, crystalline structure and/or the morphology of the recovered metal, confirming the absence of chemical interference problems.

➤ Step 1: Elimination of Pb(II)

According to our previous study, we have demonstrated that Pb(II) can be eliminated at pH = 4.2 but also in acidic medium (pH \approx 2) under an imposed potential of 1.2 V for 24 h [16, 17]. To avoid possible competition with Ni(II) at pH=4.2, as reported and discussed above (paragraph 3.1.2), we have chosen to eliminate lead the first in acidic conditions. After 24h, the solution analysis confirms that Pb(II) was totally eliminated from the solution as a brown adherent thin film. The crystalline structure of the deposit is pure β -PbO₂, as observed in the case of its elimination alone in solution with the same morphology of branches (dendrites) as reported in our previous study. This result prove that soluble lead can be totally removed

alone or in the presence of these other heavy metals with the same efficacy and without any effect on the nature and/or morphology of the deposit [16]. Then, the separation of lead in the presence of these other heavy metals appears easy at room temperature, and this point is very interesting for future applications (depollution, separation).

➤ **Step 2: Elimination of Ni(II)**

A novel SnO₂ working electrode was put in the cell, and the pH of the solution was adjusted to 4.2 by adding NaOH. Under the imposition of a potential of 0.7 V, Ni(II) was quantitatively eliminated after 72 h as an adherent deposit with a yellow/orange colour onto the SnO₂ working electrode. In addition, the SEM observation shows that the deposit did not have a well-defined morphology, as observed previously, and in good agreement with the XRD characterization, which reports exactly a similar diffractogram obtained during its elimination alone in solution without characteristic peaks except those of the substrate, **Figure 4**. This result signifies then that the elimination of soluble nickel is total and easy at room temperature, even in the presence of Cu(II) and Cd(II).

➤ **Step 3: Elimination of Cu(II)**

Then, a novel SnO₂ working electrode was put in the cell and the pH of the solution was adjusted to 7 by the addition of NaOH (1M). Under a potential of -0.45 V for 48 h, Cu(II) was quantitatively eliminated from the solution as a pinkish brown adherent thin film onto the SnO₂ electrode. The characterizations by XRD and SEM show that the crystal structure is purely Cu₂O with a cubic morphology as observed above in the case of its elimination alone in solution. This result signifies then that the elimination of soluble copper is total and easy at room temperature, even in the presence of Cd(II).

At the end, the concentration of Cd(II) was analysed and it stays quantitatively in solution. These all result are important for future applications in order to separate Cd(II) to other heavy metals.

However, for obtaining a total depollution of the solution, it was possible to eliminate Cd(II) in a last step by only sorption reaction onto the eco-friendly sorbent based on electrodeposited manganese oxides thin films (birnessite), that we have recently developed and optimized particularly for the elimination of cadmium [12].

3.4.2 Determination of the energy costs

For each case, the energy cost was estimated using **Eq. 6** with the maximal current intensity (I_{\max}) and not the average value over the entire period of the treatment meaning that the energy costs are largely overestimated. The parameters used for the energy consumption calculations were regrouped in **Table 3**.

According to these calculations, the estimations of energy consumptions for the depollution of this sample, after the different electrochemical steps are equal to $2.8 \cdot 10^{-6}$ kWh for Pb(II), corresponding to 2.1 kWh for one kg of lead, $2.6 \cdot 10^{-7}$ kWh for Ni(II), corresponding to 0.7 kWh for one kg of nickel, and $3.2 \cdot 10^{-7}$ kWh for Cu(II), corresponding to 0.8 kWh for one kg of copper. These overestimated values vary between 0.7 and 2.1 kWh/Kg of metal, which are largely inferior compared to the values reported in the literature for the recuperation of these metals [37]. Indeed, for example, the removal of Ni(II) and Cu(II) was reported in the literature by electrochemical processes (reduction reaction) by using Stainless-steel sheets with surface area of 0.011 m^2 and titanium coated with ruthenium oxide used as cathode and anode respectively. The electrolyte was circulated at a constant flow rate and the pH was kept constant at 1. Applied current densities were 10 and 90 A/m^2 . More than 99% of metal reduction was achieved, with the energy consumptions estimated to 42.30 kWh/kg of metal [38].

Therefore, we were able to eliminate and separate quantitatively heavy metals, which were initially present in solution at a non-negligible concentration by an easy electrochemical treatment based solely on change of pH and potential, with reduced electrical energy requirements. In addition, it is important to highlight that all treatments always took place in the same conventional reactor at ambient temperature and in the air (no degassing), without addition of reagents and without production of wastes. These results are very promising for future applications.

3.5 Application of the electrochemical treatment on real effluents coming from wastewater treatment plants (WWTP)

Until now, studies were performed with synthetic solutions to search the optimal conditions needed for the elimination and separation of these heavy metals. In this part, this electrochemical treatment was applied on two effluents coming from wastewater treatment plant (e.g. at the entrance and exit) for testing its real capacities in complex media (experimental conditions and efficiency).

Before applying the electrochemical treatment on such samples, chemical steps were carried out in the conventional way. Firstly, the pH of the sample was measured (7.3 for the entrance sample and 7.9 for the exit sample respectively), and then an acidification by the addition of nitric acid was carried out to reach $\text{pH} \approx 2$, in the aim to dissociate all complexes formed between heavy metals and organic micro pollutants [39]. The filtration of the samples 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 concentrations of heavy metals, present in these two samples, were determined by UV-visible measurements using the Spectroquant® tests. Lead, Nickel and cadmium were highlighted and the values of the concentrations found for each sample (input and output) are regrouped in **Table 4**, in comparison to the limits defined for drinking water and environment standards [10].

The electrochemical treatment of these two samples was carried out following the same methodology as cited above for the mixture. In the first step, Pb(II) was eliminated by imposing a potential equal to $E = 1.2$ V since the $\text{pH} = 2$. For the two samples, a very thin yellowish film was electrodeposited onto the SnO_2 working electrodes, and lead was not detected in the solution after the electrochemical treatment. The recovered deposit was too thin to be controlled by XRD and SEM due to the very small quantity of Pb(II) present initially in the solution (0.64 mg.L^{-1}). Then, in a second step, the pH was adjusted to 4.2, and a potential equal to 0.7 V was applied during 72 h, for eliminating Ni(II) present in the two samples. At the end, a very thin film was electrodeposited onto the SnO_2 electrodes, and nickel was not detected in the two samples after the electrochemical treatment. As previously, these very thin deposits did not have sufficient amount to be controlled by SEM and XRD. At the end, only Cd(II) stayed in solution, but complementary experiments confirmed its total elimination by sorption reaction with our eco-friendly sorbent based on electrodeposited manganese oxides thin films [12].

These results therefore confirm that this easy electrochemical treatment is effective even on real samples to remove and to separate heavy metals such as Pb(II) and Ni(II) dissolved in complex media in the form of adherent films onto a conductive substrate, and even in the presence of Cd(II). These all result are important for future applications in order to separate Cd(II) to other heavy metals. Indeed, in the literature the processes developed for their separation are often complicated to implement and / or energy consuming, [40-42]. On the other hand, this result allowed us to confirm the principle of this innovative electrochemical process already developed.

4 Conclusion

A very simple and innovative electrochemical process was developed in our previous study leading to a total removal of soluble lead present in aqueous solutions as adherent oxide(s) films by changing the oxidation states. In this study, and in order to extend this treatment on a wide range of toxic heavy metals, this electrochemical process of depollution was tested with success to remove Ni(II) and Cu(II), present alone or in mixture with other heavy metals in solutions, and to recover them in the form of adherent films according to the same principle. This study confirms also that this treatment cannot be applied to recover Cd(II) due to its own chemistry (only one soluble oxidation state). Indeed, it is required that the metal present different oxidation states to be eliminated by this electrochemical process, however its presence do not affect the efficacy of the elimination and the separation of the other heavy metals, which is a very important point for potential applications.

Firstly, the adequate conditions were determined on model solutions containing only one heavy metal before application with success on a synthetic mixture and real effluents. This process shows a high efficiency for removing these heavy metals in the form of adherent films on the substrate. It appears also efficient for a total separation of the metals present in solution, which is very interesting for many applications.

All results are extremely encouraging because this efficient simple process can be done at room temperature with low energy consumption, without the addition of reagents and / or complexing agents, and consequently without the production of wastes. Moreover, it appears possible to be applied with success on wastewater.

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Tables:

Table 1: Potential range values of electrochemical signals observed following cyclic voltammetry analyses for a solution containing M(II) (6.5 μmol) in 50 mL of milli-Q water with different adjusted pH by adding NaOH (no buffer).

<i>Potential range signals (V)</i>			
pH	2	4.2	7
Heavy metals			
Cu(II)	Non-observed	Non-observed	- 0.35 V to - 1 V
Ni(II)	Non-observed	0.5 V to 0.8 V	Non-
Cd(II)	-	-	-

Table 2: Parameters used for the calculation of the yield of experimental energy consumption (R)

	E (V)	I (A)	t (s)	Q_{exp} (C)	Q_{theo} (C)	R (%)
$2Cu^{2+} + H_2O + 2e^- \rightarrow$ $Cu_2O + 2H^+$	-	-1.0	172800	1.71	1.25	136
$2Cu^{2+} + H_2O + 2e^- \rightarrow$ $Cu_2O + 2H^+$	0.45	10^{-5}				
$2Cu^{2+} + H_2O + 2e^- \rightarrow$ $Cu_2O + 2H^+$	-	-1.2	345600	41.40	1.25	3312
$Ni^{2+} + 2H_2O \rightarrow$ $NiO(OH) + 3H^+ + 1e^-$	0.70	$2.4 \cdot 10^{-6}$	259200	0.62	0.62	100

Table 3: Parameters used for the energy consumption calculations.

	I_{max} (A)	E (V)	t (h)
<i>Lead</i>	$9.7 \cdot 10^{-5}$	1.2	24
<i>Nickel</i>	$5.1 \cdot 10^{-6}$	0.7	72
<i>Copper</i>	$-1.5 \cdot 10^{-5}$	- 0.45	48

Table 4: Concentrations of heavy metals measured ($mg.L^{-1}$) in samples at the input and output of the WWTP, with the Environmental Quality Standards (EQS) for water of internal surfaces (in $mg.L^{-1}$) and the quality standards of drinking water according to the World Health Organization (WHO) (in $mg.L^{-1}$).

	<i>Input</i>	<i>Output</i>	<i>EQS</i>	<i>WHO</i>
<i>Lead</i>	0.64	0.64	0.0072	0.01
<i>Cadmium</i>	0.017	-	0.005	0.003
<i>Nickel</i>	0.65	0.65	0.02	0.07
<i>Copper</i>	-	-	-	2

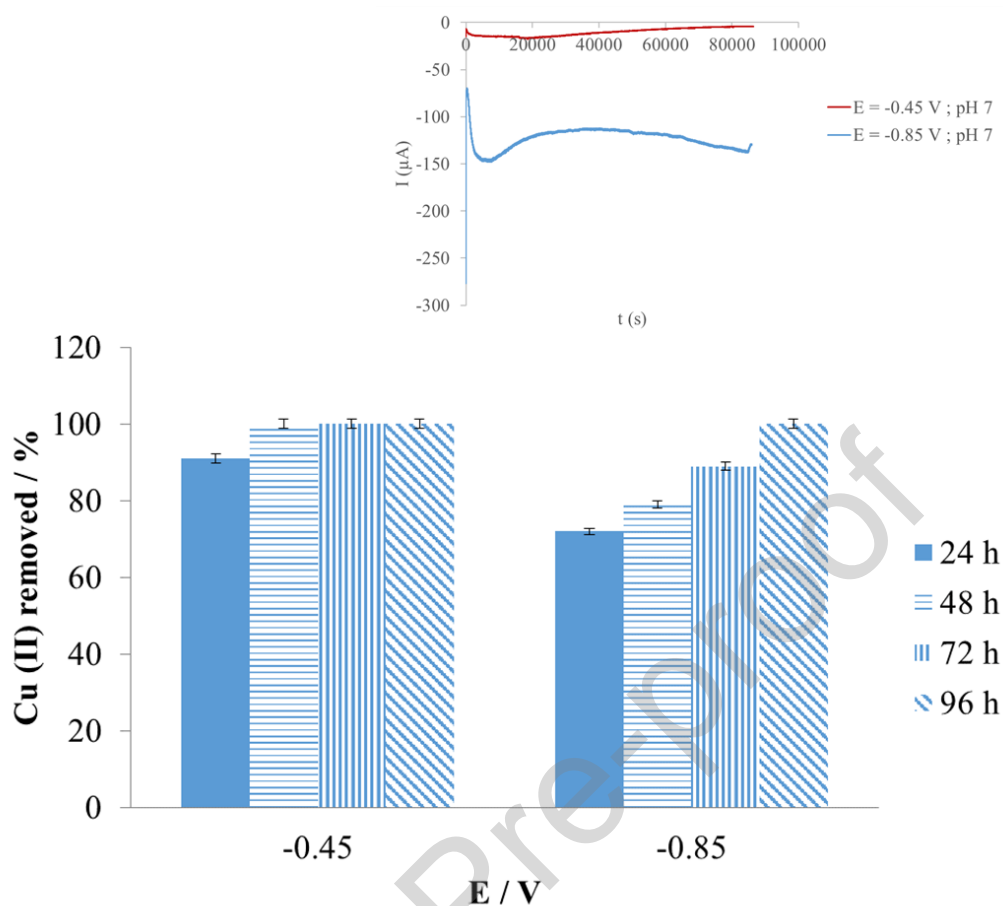


Figure 1: Percentages of Cu(II) eliminated after electrochemical treatments carried out on a model solution of Cu(II) alone, and treated under different potentials and durations. **Insertion:** Variation of current during chronoamperometry for $E_{\text{imposed}} = -0.45$ V and $E_{\text{imposed}} = -0.85$ V during 24 h.

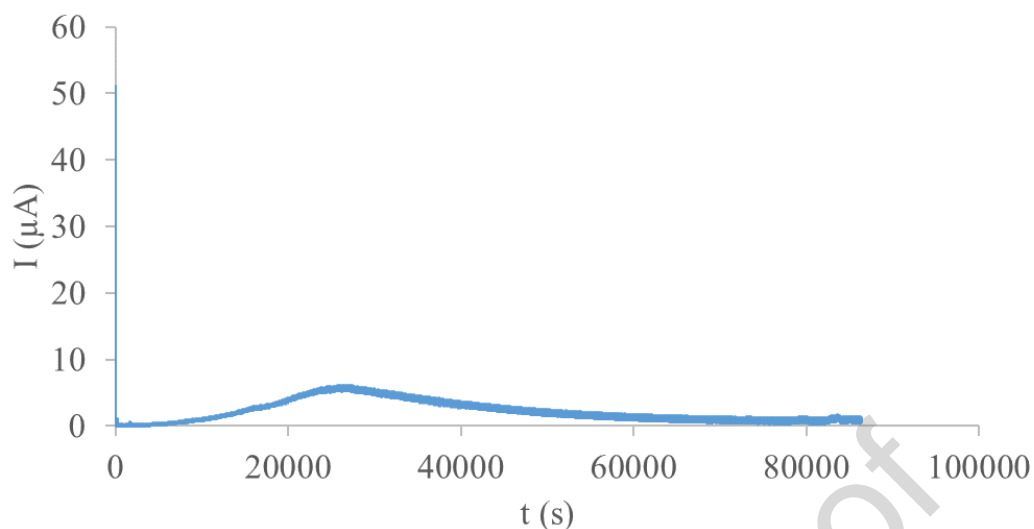


Figure 2: Variation of current during chronoamperometry performed on a model solution of Ni(II) alone with adjusted pH = 4.2 for $E_{\text{imposed}} = 0.7\text{V}$.

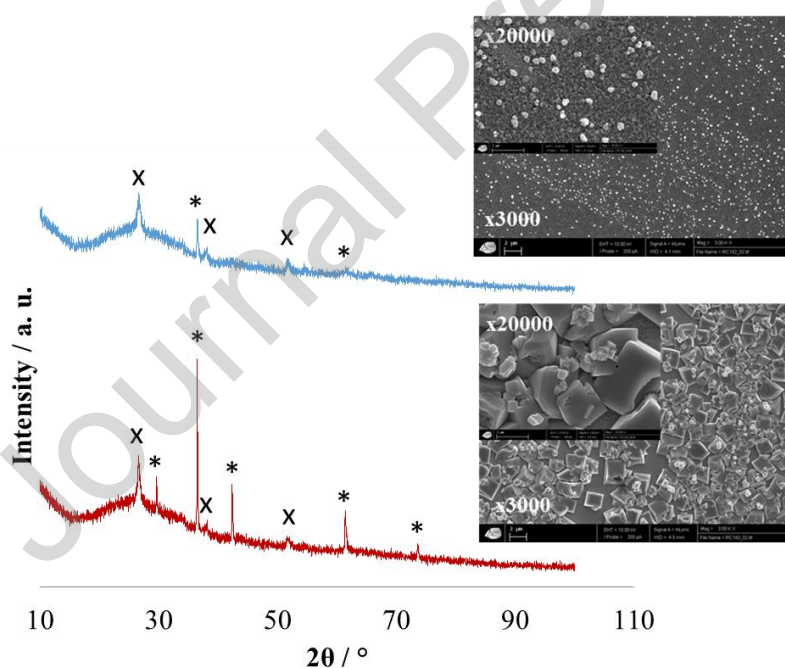


Figure 3: X-ray diffractograms of the adherent films obtained after the total elimination of Cu(II) at pH = 7 for imposed potentials of - 0.45 V (red curve) and - 0.85 V (blue curve) for durations of treatment fixed to 48 hours and 96 hours respectively, with the SEM observations associated for each one. (x) SnO₂ (*) Cu₂O.

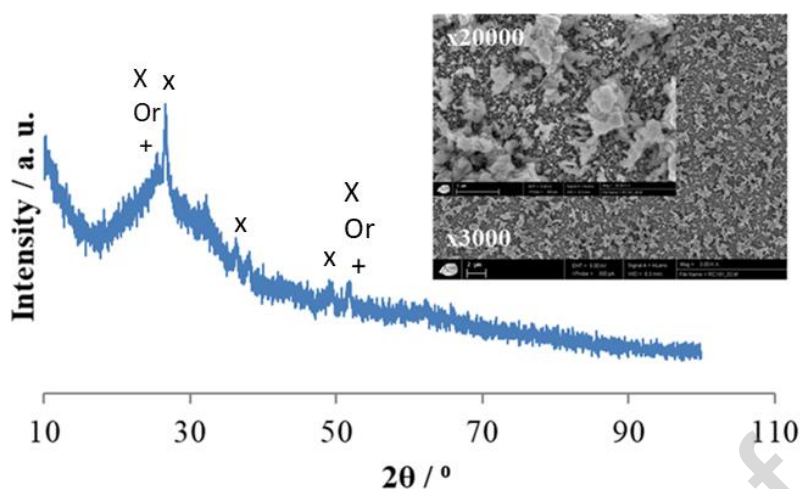


Figure 4: X-ray diffractogram of the adherent film obtained after the total elimination of Ni(II) alone in solution at pH 4.2 for imposed potential of 0.7 V during 72 hours ((+) γ -NiO(OH), (x) SnO₂) with the SEM observation associated.

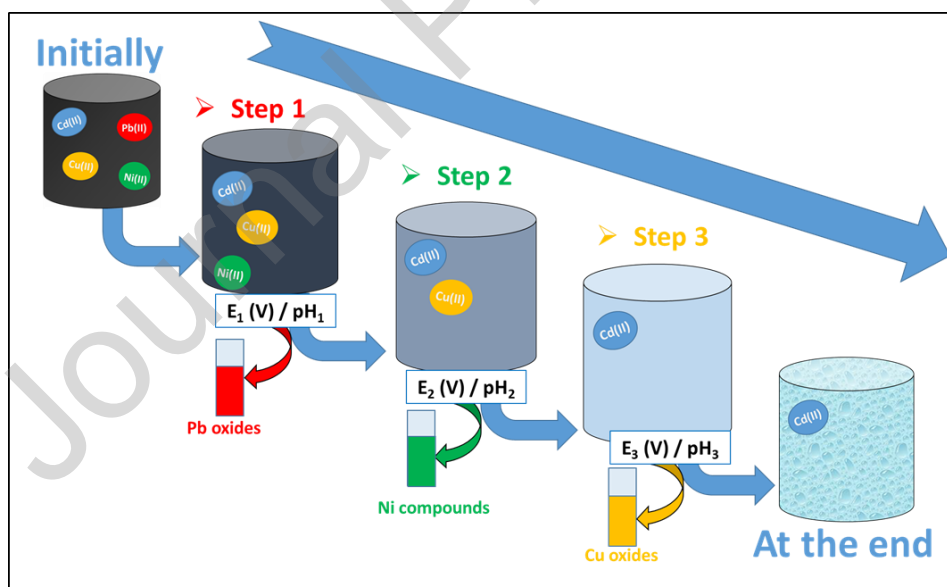


Figure 5: Schematic procedure of the recovery of each heavy metal separately in the case of a mixture containing Pb(II), Ni(II), Cu(II) and Cd(II) present in aqueous solution at equivalent concentrations.

Sample CRediT author statement

Rana Choumane: Experiments, Data exploitation, Writing-Original draft preparation.

Sophie Peulon: Supervision, Validation, Writing-Original draft preparation. Reviewing and Editing.

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

5 Highlights

- This innovative process can eliminate and separate quantitatively heavy metals
- It is a very simple electrochemical treatment based on change of pH and potential
- It is performed at ambient temperature and pressure without adding toxic reagent
- The energy input are reduced and lower than classical electrochemical methods
- This treatment seems very interesting for future applications on wastewater

Journal Pre-proof