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Modified Carbon Paste Electrodes Used to Evaluate the Retention Properties of Cd^{2+}, Pb^{2+} and Cu^{2+} on Biosolids, Soils and Biocomposites

José Manuel Flores Álvarez[1,4,*], *Ignacio González Martínez*[2], *Héctor Guillen Bonilla*[3],
Lorenzo Gildo Ortíz[4], *Juan Reyes Gómez*[3]

[1]Facultad de Ingeniería Mecánica y Eléctrica, Universidad de Colima, Carr. Colima-Coquimatlán, km. 9, C. P. 28400, Coquimatlán, Colima, México.
[2]Universidad Autónoma Metropolitana - Iztapalapa, Departamento de Química, 55-534, C.P. 09340, México, D.F., México.
[3]Facultad de Ciencias, Universidad de Colima, Bernal Díaz del Castillo 340,Colima, Colima, México.
[4]Facultad de Ciencias Químicas, Universidad de Colima, Carr. Colima-Coquimatlán, km. 9, C. P. 28400, Coquimatlán, Colima, México.
[*]E-mail: josemanuel@ucol.mx

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The retention properties of Cd(II), Cu(II) and Pb(II) ions were assessed and compared using modified carbon paste electrodes (MCPEs). A biosolid, two different soils and two biocomposites were used as modifying material. Comparing the reactions from the different MCPEs when parameters such as pH, preconcentration time and adsorption/desorption capacity varied, the soils showed that there is a similar adsorption mechanism between them, but very different from that of the biosolid; while the biocomposites show adsorption mechanisms that are intermediate between the soils and the biosolid. The anodic stripping voltammetry (ASV) electrochemical technique proved to be a versatile tool for the metal ions speciation, since it made it possible to distinguish different Cu oxidation states when it is incorporated into the biosolid. In addition, it makes it possible to detect only the heavy metal ions which can be considered bioavailable in the different substrates that were analyzed. Similarly, when ASV coupled with SEM/EDS was used, it made it possible to differentiate the reaction products that result on the surface of the MCPEs.

Keywords: Biosolid, Soil, Heavy metal, Carbon paste electrode, SEM/EDS, electroanalysis

1. INTRODUCTION

Biosolids (treated and stabilized sewage sludge) are an organic solid produced by wastewater treatment processes that can be beneficially recycled applied to land to condition the soil or fertilize the crops or other vegetation grown in the soil [1]; that because the biosolid contains a large amount of organic matter and plant macro-nutrients, especially N and P, which avoid the environmental, agricultural and economic impacts associated with other disposal options such as dump it in landfills or incinerate it [2-4].

However, the biosolid land application is controversial due to possible presence of potentially toxic elements like the heavy metals, wich is one of the main disadvantages of biosolids for agricultural use, due to its accumulation in the soils resulting from the repeated application of the biosolids [5], leading to the accumulation of heavy metals in living tissue, thus resulting in a biomagnification through the food chain [6, 7] and/or affecting the groundwater quality, which increases environmental risk [8-10].

The heavy metals are associated with various components of the biosolids, soils or soils amended with biosolids, thus giving rise to chemical forms that determine the physical, chemical, and biochemical phenomena that bind, unbind, expose, or solubilize a heavy metal associated with soil or sediment [11-13]. Therefore, it is necessary to study the heavy metal bioavailability and the retention properties of the soils and sediments to understand the potential risk or the certainty of amending soils with biosolids.

Sequential extraction methods are used to determine the bioavailability and toxicity of heavy metals in sewage sludge and soil [14,15]; however, such techniques need expensive infrastructure and consume a lot of time and chemical reagents [16].

Electroanalysis techniques are a very useful, versatile and extensively used tool in trace metal ions speciation, since these techniques distinguish between bound and dissolved (unbound) ions and their oxidation state [17]. Carbon paste electrodes (CPEs) are one of the most popular types of carbon electrodes used in electroanalysis, mainly due to that they are inexpensive, easy to prepare and regenerate, they have a wide potential window, low ohmic resistance, low background current, and good selectivity and sensitivity towards target species [18-20]. Another advantages of using CPEs include the fact of that the operational mechanism of the CPEs depends on the properties of the modifier materials used [21]; because of that, the modifier and its interaction with the environment, can be studied by electrochemical techniques using modified carbon paste electrodes (MCPEs); followed later by SEM-EDS in order to complement the studies of the metals reactions that were carried out on the surface of the CPEs due to the presence of metallic films plated onto the carbon paste surface.

There have been many studies by means of MCPEs on the electrochemical determination of heavy metals using one component soil or sediment as modifier [22-24] and only a few studies have focused on the interaction between heavy metals and the soil and sediments components [20]. Notwithstanding, these studies are only an approximation of what happens in the soils and sediments in their native state, because these contain a larger amount of components that can affect such interaction [25]. Therefore, this study focused on the analysis of the interaction of heavy metal with two soils, a biosolid, and two soils amended with a biosolid in their native state using MCPEs and SEM-EDS analysis, with the aim of studying and comparing the influence of the pH, salinity, amount of organic matter and contact time of metals on the interaction and the retention capacity of the samples, when exposed to Cd^{2+}, Cu^{2+} and Pb^{2+} solutions, as well as chemical and electrochemical reaction that occur mainly on the surface of the MCPEs.

2. EXPERIMENTAL

2.1. Samples

Two different soils from Mexico were obtained. The loamy sandy soil (LSS) and the sandy loam soil (SLS) were collected from the following coordinates respectively: 19° 27’ 37.01” N, 103° 42’ 27.01” O and 19° 17’ 03.82” N, 103° 44’ 38.17” O. The biosolid sample was collected from the sand drying bed of the wastewater treatment plant located in Salagua, Manzanillo, in the state of Colima, in Mexico. The sampling, homogenization, and storage of the biosolid and soils were in compliance with Mexican regulations [26, 27]. The soils and the biosolid were air-dried and crushed. The sieved fraction (< 2 mm for soils and < 150μm for biosolid) of each sample was used in the analysis.

The biocomposites (amended soils) were obtained mixing 1.5 g of the biosolid with 2.5 g of soil, which is the same as applying 150 tons of biosolid per hectare of soil to dry matter. The proportion established here is the same as that used in the field.

2.2. Solutions and Reagents

Analytical reagents grade chemicals and deionized water (18.2 MΩ cm^{-1}) obtained from a Millipore Milli-Q system, were used for preparing all solutions. A Briton-Robinson (B-R) buffer stock solution (pH 5) was prepared by mixing equal volumes of 0.04 mol L^{-1} in phosphoric, acetic and boric acid. The B-R buffer with 0.1 mol L^{-1} KNO_3 was used as supporting electrolyte for voltammetric measurements. A 1 mol L^{-1} NaOH solution or concentrated HNO_3 was used in order to adjust the pH of the supporting electrolyte. Standard stock solutions of heavy metal ions were prepared from a sufficient quantity of $CuSO_4{\cdot}5H_2O$ for Cu, $3CdSO_4{\cdot}\ H_2O$ for Cd and $Pb(NO_3)_2$ for Pb dissolved in deionized water. All electrochemical experiments were performed under a nitrogen atmosphere.

2.3. Instrumentation

All the linear sweep anodic stripping voltammetric measurements were performed in a PGZ 301 Voltalab potentiostat (Voltalab Radiometer Analytical) driven by a Voltamaster 4 software, version 6.0.2.25130 using a conventional voltammetry cell equipped with three electrodes: a MCPEs with a 0.96 mm^2 geometric area, a graphite rod (Alfa Aesar, Johnson Matthey 99.9995%) with a 0.85 cm^2 geometric area and a saturated calomel electrode (SCE), corresponding to the working, counter and reference electrode, respectively. All the potentials are given versus the reference electrode.

A scanning electron microscope coupled with an energy-dispersive spectrometer (SEM/EDS, JEOL 6390LV/LGS) was used for the microscopy analysis.

2.4. Physicochemical characterization of the biosolid and the soils

The cation-exchange capacity (CEC) [27], percentage of OM [28] and soil texture [29] were determined according the corresponding literature.

2.5. Preparation of the modified carbon paste electrodes

The MCPE was made by hand mixing 0.2 g of natural graphite powder (Alfa-Aesar, particle size 2-15 μm, 99.9995% purity) and 0.02 g of the sample in an agate mortar. Then, 150 μL of paraffin oil (Golden Bell, $\rho = 0.85$ g cm^{-3}) were added to the mixture and mixed until obtain a uniform paste. Once the modified paste was ready, it was introduced into a 3 mm in diameter and 7 cm in length polyethylene tube that was used as the working electrode body. Platinum wire silver-soldered to a copper wire was used as electrical contact. The electrode body had a plunger to compact and to press the paste down when renewal of the electrode surface was needed. Smoothing of the electrodes surfaces were made by hand polishing on a sheet of paper. Once finished, the electrodes were immersed in deionized water for 24 hours to allow their final “self-homogenization” [30] and the electrochemical experiments were conducted afterwards.

The non-modified CPEs (blank-CPE) were prepared in the same way as the MCPE but without sample (modifier).

2.6. Electrochemical procedures

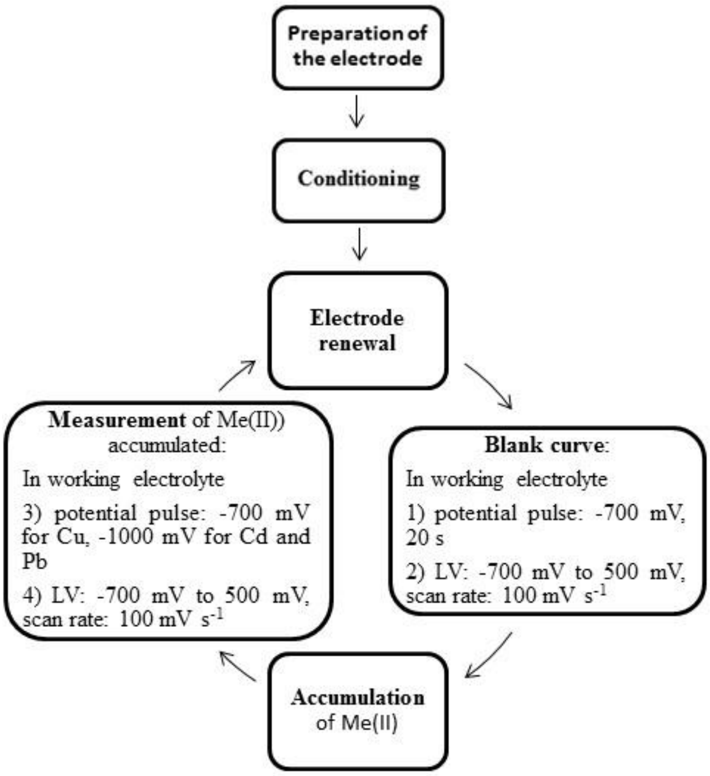

Figure 1. Schematic diagram of the methodology used for the measurement of heavy metals accumulated on the surface of the electrodes.

Figure 1 shows the procedure used for the accumulation and the electrochemical measurement of Me(II) (Cd(II), Cu(II) or Pb(II). In this work, cations labeled with roman numerals in parentheses are complexes ions interacting with ligands found in biosolid, soils or biocomposites and, on the other hand, solvated cations in solution are indicated by a superscript) in the electrodes.

A new prepared electrode was first immersed in Milli Q water for 24 h. After the conditioning step, the electrode renewal was performed followed by a surface activation in a separate de-aerated working electrolyte, applying a potential pulse of -0.7 V for 20 s followed by a linear voltammetry (LV) procedure of -0.7 V at 0.5 V at a scan rate of 100 mV s^{-1} (blank curve), to enhance the sensitivity of the electrodes [31]. Subsequently the electrode was washed and placed, for a predetermined accumulation time, into a stirred solution of Me^{2+} under open-circuit conditions in accordance with the $Me^{n+} + mL \rightarrow [Me^{n+}L_m]$ reaction (where L represents the chemical species contained in the sites of adsorption and exchange of the biosolid, or of the soils in the MCPEs). Once the Me^{2+} is adsorbed, the electrode was removed, rinsed with water placed again in the cell containing working electrolyte solution and connected to the potentiostat. Immediately an anodic stripping voltammetry (ASV) procedure was applied for the electrochemical detection of accumulated metal ions. The ASV includes a preconcentration/reduction step according to the following reaction $[Me^{n+}L_m] + ne^- \rightarrow ([Me^0L_m]) \rightarrow [Me^0] + [mL]$ with a potential pulse of -0.7 V for Cu and -1 V for Cd and Pb for 20 s , followed by a dissolution/oxidation step applying a LV procedure of -0.7 V at 0.5 V at a scan rate of 100 mV s^{-1} according to the following reaction: $Me^0 \rightarrow Me^{n+} + ne^-$. Once the voltammogram is obtained, the maximum current density obtained in each experiment, is sampled for further analysis and comparison between different electrochemical responses of the MCPEs. Once this process was completed, the electrode was withdrawn from the electrolyte, the surface was rinsed, renewed, and the cycle started all over again.

In order to study the stabilization and crystallization of the metals, the procedure used in figure 1 was stopped after the preconcentration/reduction step to analyze the surface of the electrodes in the SEM/EDS.

During the salinity analysis there was a modification: the solution used at the accumulation stage, was made of 0.64 ppm Me^{2+} and 0.01 mol L^{-1} KCl. The same procedure described in figure 1 was used.

For the analysis of the stability of the complexes, the procedure described in figure 1 was modified adding one more step: after the accumulation stage, the electrodes were placed in a solution of 0.01 mol L^{-1} KNO_3 for a predetermined period of time. Afterwards, the procedure was the same described in figure 1.

3. RESULTS AND DISCUSSION

The physicochemical characterization of the biosolid and the two soils studied here are show that the texture of the soils is 1) Loamy sandy soil (LSS) and 2) Sandy loam soil (SLS). The amount of organic matter (OM) and the cation exchange capacity (CEC) in the biosolid, the LSS and the SLS is: OM 49.08% / CEC 63.4 Cmol(+) kg^{-1},OM 14.79% / CEC 23.4 Cmol(+) kg^{-1} and OM 1.21% / CEC 5.5 Cmol(+) kg^{-1}, respectively.

3.1. Electrochemical Behavior of Me(II) on the MCPEs.

Figure 2 shows the typical anodic stripping voltammograms of the different systems analyzed obtained with the CPE modified with the biosolid (curves a, b, c and d) and with the non-modified CPE (curves a', b' and c').

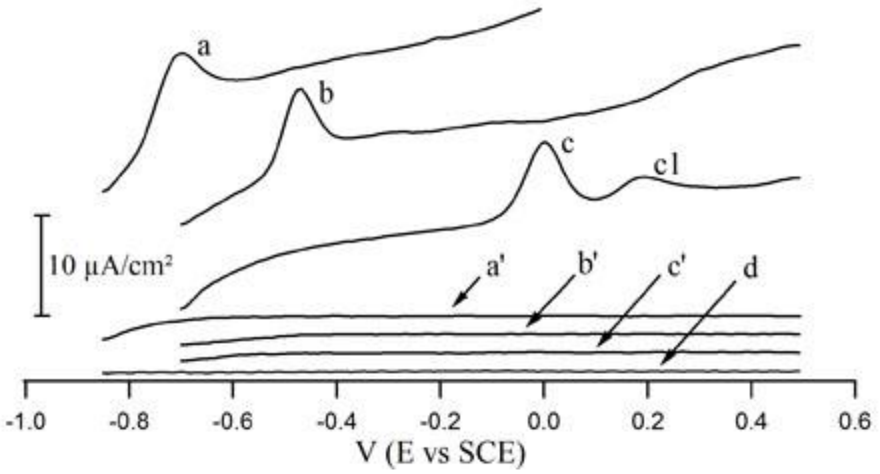

Figure 2. Linear anodic stripping voltammograms, for the metals previously deposited, obtained on the CPE modified with the biosolid (Biosolid-MCPE): (a) Cd(II), (b) Pb(II), (c) Cu(II) and (d) without metal. The ASVs obtained under the same conditions, but on the non-modified CPE, correspond to curves (a'), (b') and (c'), for Cd(II), Pb(II) and Cu(II), respectively. Conditions: Time during which the MCPE was exposed in the solution containing the metal: 2 min. Concentration of the metal ion in the solution: 0.64 ppm; reduction time 20 s, at a potential of -0.7 V for Cu and -1 V for Pb and Cd. Anodic stripping electrolyte: BR buffer + 0.1 mol L^{-1} KNO_3, pH 5 for Cu and Cd and pH 2 for Pb. Scan rate: 100 mV s^{-1}.

The blank curve (figure 2, curve d) does not show any oxidation peak, which means that the biosolid does not contain electroactive elements or compounds that could oxidize and interfere in the current-density responses of the metals used in this paper. With regard to the current-density responses of the non-modified CPEs (figure 2, curves a', b' and c'), even when these had been in contact with the Me^{2+}, and the preconcentration protocol had been carried out, no current peaks were detected either. This means that the non-modified CPEs used in this paper did not show that enough Me^{2+} ions were adsorbed by the graphite in the prescribed time, so as to detect it through ASV. However, when using the CPE modified with the biosolid (figure 2, curves a, b and c), the metals are adsorbed and detected by oxidation peaks, which means that the adsorption and preconcentration of the Me(II) occur mainly on the active sites incorporated into the CPE by the soil samples and the biosolid [32] and not on the graphite.

A current peak, which corresponds to the stripping of the metal, appears in every case (figure 2, curves a, b and c). The peak (a) located at -0.7 V approximately, corresponds to the oxidation of Cd(0)/Cd(II), and the oxidation peak (b) at -0.47 V is the result of to the oxidation of Pb(0)/Pb(II). The ASV of Cu shows two oxidation peaks: at 0.0 mV (peak c) which is the result of the oxidation of

Cu(0)/Cu(II) and at 0.2 V (peak c1), resulting from the oxidation of Cu(I)/Cu(II)[33]. Since Cu shows two oxidation states, this paper will focus on the study of peak c.

3.2. Influence of the accumulation time of the metal on the samples

The accumulation time of the metals on the different MCPEs was a study variable used to determine the adsorption of Me^{2+} as a function of time. Figure 3 shows the variation in the current density of the stripping peaks of the Me that was adsorbed on the surface of the MCPEs versus the immersion time of the MCPEs in a solution of a concentration in Me^{2+} of 0.64 ppm.

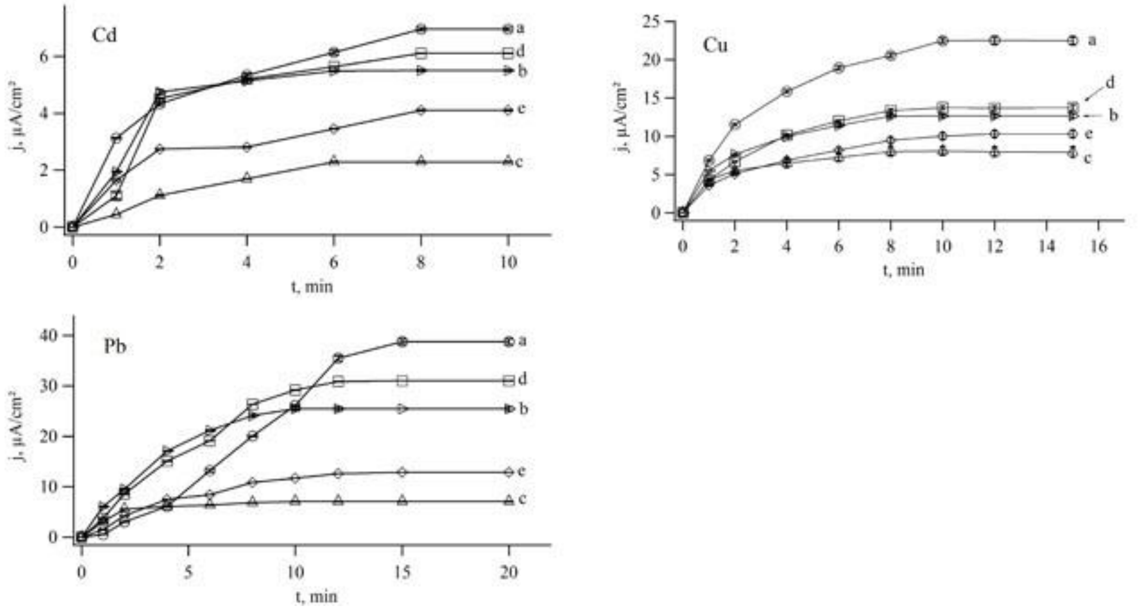

Figure 3. Amount of Me^{2+} adsorbed on the surface of the MCPE (associated with the current density of the oxidation peak, in the ASV) versus accumulation time in the solution of Me^{2+} of the MCPEs. Biosolid (a), LSS (b), SLS (c), LSS + Biosolid (d), and SLS + Biosolid (e). Conditions see figure 2.

In every case, the same behavior occurred, as the immersion time of the MCPEs in the solution containing Me^{2+} increases, the value of the anodic current density also increases until reaching a limit value. According to Ogorevc et al.[32], the limit value is the result of the equilibrium between the Me(II) ions that are adsorbed on the modifier and the Me^{2+} ions of the solution. In every case, the current density in the limit value varies according to the modifier of the CPE and follows this descending order (figure 3): biosolid (a) > LSS+biosolid (d) > LSS (b) > SLS+biosolid (e) > SLS (c); this order is consistent with the order corresponding to the content of OM and CEC (the LSS+biosolid and the *SLS*+biosolid contain 27.48% and 19.32% OM, respectively). This suggests that the greater the amount of OM contained in the samples is, the greater their CEC[34] and the greater the adsorption of Me(II) will be[35].

Although the adsorption kinetics of the samples is similar in every case, figure 3 also shows a great difference in the current densities obtained with the different MCPEs, which is directly connected with the concentration of metal adsorbed by the samples, following the descending order of concentration: Pb^{2+}>Cu^{2+}>Cd^{2+}, which means that there are different affinities of the samples for the metals. The preferential adsorption by the samples of one metal over another one is called selective adsorption [36].

McBride [37] associates the selective adsorption with the electronegativity of the metals, whereas Sposito [38] associates it with the ionic radius and the ionization potential; however, Abd-Elfattah and Wada [39] found sequences that are not associated with the ionic radius or the electronegativity of the metals, but with the hydrolysis properties of the metal cations. Therefore, the selective adsorption can depend on the valence of the metal as well as on the hydrated radius (hrd); i.e., on the ionic size of the heavy metals once hydrated [35, 40]. Smaller ions with the same valence, such as Cd^{2+} compared with Pb^{2+} have greater charge density and attract a larger amount of water molecules, resulting in a greater hrd. The metals with the greatest hrd exert smaller electrostatic attraction forces between the metal and the active sites of the sample; therefore, the ions with less hrd have greater affinity for most of the functional groups of the OM and are more likely to form inner-sphere stable complexes[41]. The hrd of Pb^{2+}, Cu^{2+} and Cd^{2+} are 0.187 nm, 0.21 nm and 0.23 nm, respectively[42], which follows the same descending order of the amount of the adsorbed ions shown in figure 3 (Pb^{2+}>Cu^{2+}>Cd^{2+}). The results obtained in this experiment can be attributed to the selective adsorption associated with the hydrated radii.

Another important aspect shown in figure 3 is the time taken by the different MCPEs to reach the limit current-density value or time of equilibrium. In all the cases analyzed in figure 3, the CPE-biosolid is the one that adsorbs the largest concentration of ions in comparison with the other MCPEs for the same metal species; however, it is also the one that needs more accumulation time to reach the current-density limit value or equilibrium time (15, 10 and 8 minutes for Pb^{2+}, Cu^{2+} and Cd^{2+}, respectively). Similarly, the MCPEs containing biocomposites (curves "d" and "e" for each metal) need approximately the same time needed by the biosolid to reach the limit value (15, 10 and 8 minutes for Pb^{2+}, Cu^{2+} and Cd^{2+}, respectively). The MCPEs containing soils (curves "b" and "c" for each metal) are the ones that reach the limit current-density value in less time (10, 8 and 6 minutes for Pb^{2+}, Cu^{2+} and Cd^{2+}, respectively).

The fact that it takes the CPEs modified with soils less time to reach the limit current-density value than those containing the biosolid and the biocomposites shows that the active sites of the soils have greater affinity for the metals than the active sites of the biosolid, since their adsorption kinetics is faster in the soils than in the biosolid. On the other hand, although the two soils (LSS and SLS) show different physicochemical properties, it takes them approximately the same time to reach the limit current-density value, which means that there are similar interaction processes between the two soils and the Me(II); as a result, the Me(II) may be bound to the soils through functional groups with similar binding properties[33].

The curves obtained through the CPEs modified with biocomposites, when compared with the CPEs modified with soils (Figure 3), show a common spot, where the current density is the same; in other words, where the curves overlap at a certain time. This behavior is especially seen between the curves of the LSS soil (curve b) and the LSS biocomposite (curve d) in the graphs for Pb^{2+}, Cd^{2+} and Cu^{2+} (for example, in the graph for Pb, on curves b and d, at 7 min. approximately). This behavior can be explained as follows:

As seen before, the soils contain a smaller amount of OM than the biosolid. Therefore, they adsorb a smaller amount of Me(II); however, the soils have active sites with greater affinity for Me(II) than the biosolid; this is why they adsorb heavy metals faster than the biosolid. Since the biocomposites contain active sites of both the soils and the biosolids, they adsorb heavy metals at a slower rate than the soils, but also a larger amount of such metals, since they contain a greater concentration of OM.

3.3. Influence of pH on the adsorption of Me (II) on the MCPEs.

The pH plays an important role in the adsorption and desorption of heavy metals, since it is one of the principal factors affecting mobility of the metals in sediment, as it directly controls the solubility of the metal hydroxides, as well as that of the carbonates and phosphates, and, in a similar way, it affects the hydrolysis of the metal, the formation of ionic pairs, the surface charge of the OM and clay[41]. Figure 4 shows the variation of the adsorption of Me(II) on the MCPEs as a function of the pH of the preconcentration solution. The variation in pH causes a considerable change in the current-density response due to the adsorption of the Me(II) ions on the surface of the MCPEs.

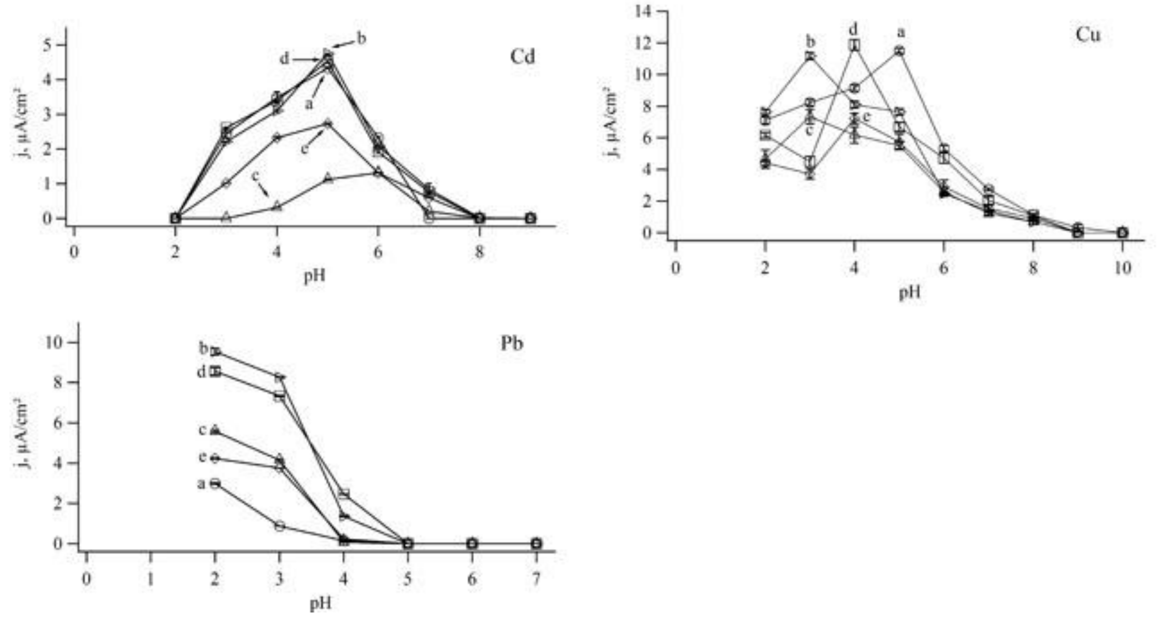

Figure 4. Effect of the pH change on the current-density response of the CPEs modified with (a) biosolid, (b) LSS, (c) SLS, (d) LSS + biosolid and (e) SLS + biosolid. Conditions see figure 2.

Adsorption tendencies of figure 4 show that in the case of Pb^{2+}, the current density decreases when the pH value increases; while in the cases of Cd^{2+} and Cu^{2+}, when the pH increases, the current density also increases until reaching a maximum current-density value and decreases afterwards. With regard to Cd^{2+}, the current-density maximum is reached at the same pH (pH 5, approximately) for all the materials contained in the CPE; however, in the case of Cu^{2+}, the current-density maximum is reached at different pH values, depending on the sample contained in the CPE; therefore, in this case, the adsorption depends on pH and on the type of electrode used; while in the case of Pb^{2+} and Cd^{2+}, when the current density maximum is achieved at the same pH respectively, with the exception of the CPE modified with the LSS soil when Cd^{2+} is used, it shows that the adsorption of Pb^{2+} and Cd^{2+} highly depends on the pH and not on the sample.

The adsorption tendency showed by Cu^{2+} and Cd^{2+} (Figure 4) can be split up in two parts: (1) as the pH increases, the current density increases as well until it reaches a maximum, and (2) from such maximum, the current density decreases. The adsorption tendency (1) is the result of the competition between the H^+ ions and the Me^{2+} ions for the active sites of the samples [43, 44]. When the pH increases, the concentration of the H^+ species decreases, thus increasing the adsorption of Me^{2+} on the samples and therefore increasing the current density until the current density maximum is reached. As the pH value continues to rise from the current maximum, the current density decreases due to the hydrolysis of the metal, until Me(II) precipitate totally as hydroxides or phosphates at a pH of 5, 8 and 9 for Pb^{2+}, Cd^{2+} and Cu^{2+} respectively [41, 45-47], which explains the adsorption tendency (2).

Moreover, in the case of Pb^{2+}, due to its low solubility when forming phosphates (Kps $Pb_3(PO_4)$ = $7.9\text{x}10^{-43}$)[48], lead begins to precipitate even at acid pH levels, which is why only tendency number (2) is followed (figure 4, Pb). According to Grabec and Ogorevc [17], the different current-density maximums reached by the MCPEs at different pH values, specially observed in figure 4 for Cu, is explained by the different affinities of the compounds in the soils and the biosolid, to the H^+ ions.

All these pH results are supported by the SEM/EDS analysis of the crystals formed on the surface of the MCPEs (Supplementary material, section 1). Such analysis reveals a greater concentration of crystals as the pH increases and the subsequent decrease as the pH continues to increase, as happens with the current density in figure 4. In addition, the EDS analyses confirmed that the MCPEs used in this project and the ASV electrochemical techniques only detect metal species adsorbed in the active sites of the biosolid or the soil, and that these could be bioavailable (environmentally dangerous), since the non-bioavailable species (precipitates) do not generate a current that could be detected using MCPEs and the ASV.

3.4. Influence of salinity on the adsorption of Me (II) on the MCPEs

In the soils, there are significant concentrations of ions in a natural form (endogenous ions) or by anthropogenic action, which include both inorganic (Cl^-, NO_3^-, SO_4^{2-}, etc.) and organic anions; from plants, microbial sources and fertilizers [49]. Ions, as well as the salinity of the soils and the biosolid, can significantly affect the adsorption and distribution of the metals in the soils [50, 51]; therefore, the adsorption of the Me(II) in the presence of other ions (K^+ and Cl^-) is studied next. Figure 5 shows the variation of the current-density value of the stripping peaks in function of the immersion time of the MCPEs in a solution containing 0.64 ppm in Me^{2+} and 0.01 mol L^{-1} KCl.

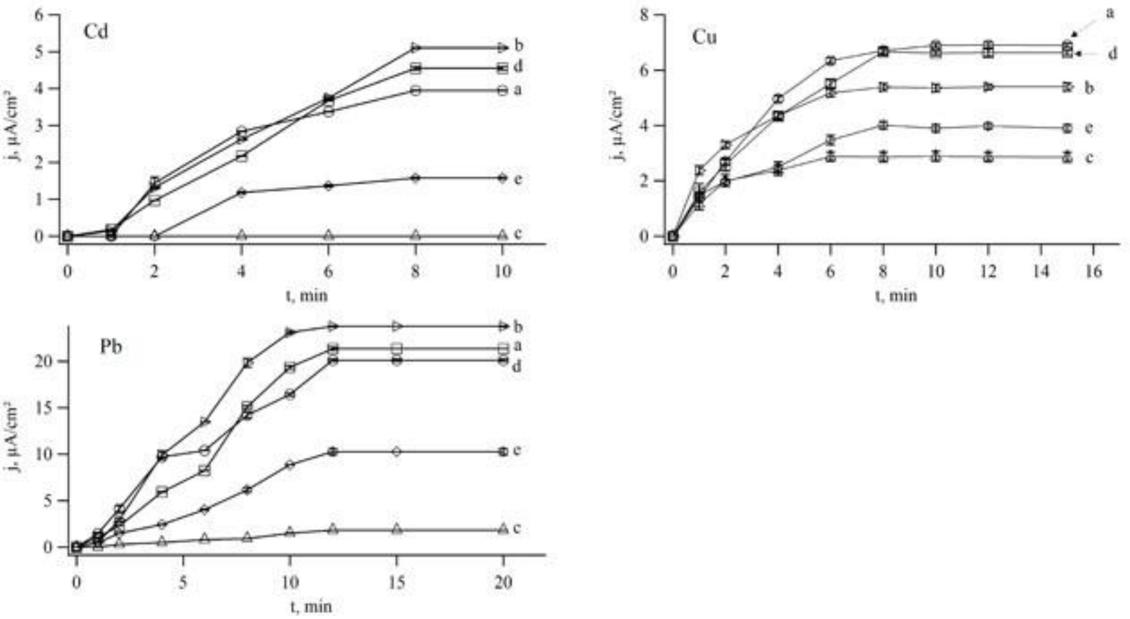

Figure 5. Effect of Cl^- and K^+ ions on the adsorption of Cd, Cu and Pb. Solution for the accumulation of Me(II) made up of 0.64 ppm of Me^{2+} and 0.01 mol L^{-1} KCl. (a) Biosolid, (b) LSS, (c) SLS, (d) LSS + biosolid and (e) SLS + biosolid. Conditions see figure 2.

In order to analyze the adsorption of metals in the presence of other ions, this system was compared with the results obtained from the adsorption of the metal without the presence of other ions (figure 3). For such comparison, the limit value of current density obtained in the absence of Cl^- y K^+ ions was considered a 100% adsorption; in other words, the product of the division of the limit value of the current density obtained from the metal ion adsorbed in the presence of the Cl^- and K^+ ions (figure 5) and the limit value of the current density obtained in the absence of the Cl^- and K^+ ions (figure 3), for the different MCPEs, is presented as a percentage and is shown in table 1. This product makes it possible to determine the percentage variation existing between these two systems (figures 3 and 5).

Table 1. Percentage of the ratio of the current density of the ASVs for equilibrium on the metal ion adsorption in the presence (figure 5) and in absence of of KCl (figure 3), for the different MCPEs.

Metal	Biosolid	*LSS*	*SLS*	*LSS*+Biosolid	*SLS*+Biosolid
Cd	56.73	92.62	0.00	74.50	38.35
Cu	30.63	42.65	35.48	48.25	37.35
Pb	51.90	93.29	25.86	68.87	79.89

In every case, (figure 5 and table 1), a decrease in current density was seen in comparison with the values in figure 3. In general, the current density decreases due to the presence of the K^+ and the

Cl^- ions, which compete against Me(II) for the active sites on the surface of the MCPEs [43, 52]. Among the three metals that were studied, Cu(II) was the one that reported lower adsorption when the K^+ and the Cl^- ions were on the surface of the MCPEs according to the values presented in table 1.

The adsorption of Cd on the CPE modified with SLS shows that the current density is 0. Subsequent analyses (Figure 6, next section) showed that Cd forms complexes of poor stability with the samples, and this, in addition to the small OM contained in this SLS, inhibits the adsorption of Cd on such soil (Supplementary material, section 2).

3.5. Stability analysis of the Me(II) complexes on the MCPEs

In order to analyze the stability of the complexes that are formed between the active sites and Me(II), there was a change in the methodology described in figure 1. In this case, the accumulation of Me^{2+} was completed in 2 minutes. Afterwards, the MCPE is removed from the solution and immersed in another one free of Me^{2+} and containing 0.01 mol L^{-1} KCl for a predetermined period of time. Later, we proceed normally as described in the methodology. The accumulation of Me^{2+} for 2 minutes without immersing it in the solution of 0.01 mol L^{-1} KCl afterwards is considered the measurement at zero.

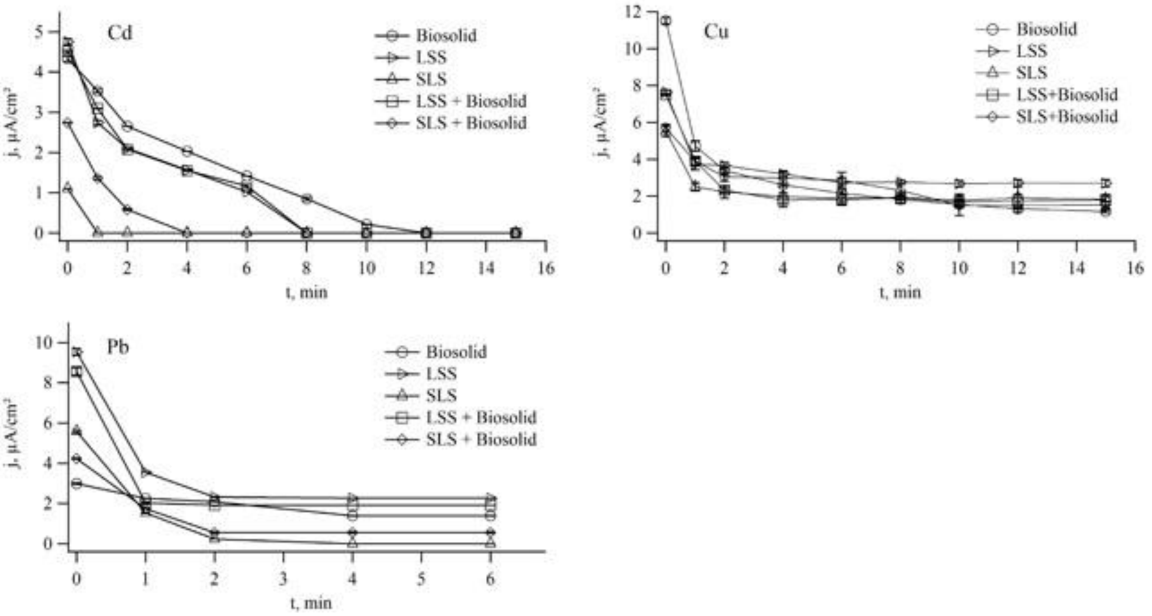

Figure 6. Desorption of the Me(II) on the surface of the MCPEs to the solution. Time of exposure to the solution of 0.64 ppm in Me^{2+}: 2 min. Concentration of the KCl solution: 0.01 mol L^{-1}. Conditions see figure 2.

Every case presented in figure 6 shows a decrease in the current density as the immersion time of the MCPEs in the KCl solution increases, which means that there is a desorption of the Me(II) ions towards the solution. This desorption is due to the cation exchange between the Me(II) adsorbed and the K^+ of the solution, as well as to the formation of the Me(II) chlorides [45, 53] and the formation of oxides promoted by the presence of Cl^- [54].

In addition, it is seen that Pb(II) and Cu(II) reach an equilibrium without the total desorption of the metal (with the exception of the SLS soil with Pb) while the desorption of Cd(II) is total in every case. This means that Pb(II) and Cu(II) form more stable complexes with the samples contained in the MCPEs, than Cd(II); the conclusion from this is that there can be specific adsorption mechanisms for Pb(II) and Cu(II), and non-specific for Cd(II); this also means that Pb and Cu may have been adsorbed on active sites of high activation energies, and they cannot therefore be displaced by means of cation exchange with K^+ or by the formation of complexes; while Cd(II) is probably bound to low-energy active sites and may be displaced by K^+ [55] or by the formation of Cd-Cl ionic pairs [53].

On the other hand, it is also shown (figure 6) that the desorption of the Me(II) is slower with the biosolid than in the rest of the samples. This behavior of the metals on the biosolid is explained by the concentration of sulfur found in this sediment. An X-ray fluorescence analysis of the samples used in this paper (results non shown) shows that the concentration of sulfur (S) in the soils is 0.55% and 0.11% for the LSS and SLS, respectively, and 10.46% for the biosolid.

It has been shown that metals tend to coordinate with oxygens [56, 57]; however, Karlsson et al. [58] proved that the metals when in contact with natural organic matter containing sulfur tend to coordinate with a mixture of oxygen and sulfur, thus forming more stable complexes than with oxygen, which would explain why the desorption is slower with the biosolid than with the soils, and as a consequence, the metals tends to form more stable complexes with the biosolid than with the soils [59].

4. CONCLUSIONS

The advantage of using carbon-paste electrodes modified is the use of a minimum amount of reagents and time in the preparation of the samples prior and during the analyses. The MCPE depend strongly on the material with which it was modified, therefore the conditions applied simulate well the environmental conditions that would result naturally. Moreover, the results of these analyzes made it possible to better understand the interactions occurring among the sediments with the contaminants to which they were exposed. It was evident that the anodic stripping voltammetry (ASV) electrochemical technique used in combination with the MCPEs is a very versatile tool for the metal ions speciation.

The OM is the one that more greatly contributes to the adsorption of the metals in the samples. The biosolid adsorbed a greater concentration of metals, however the adsorption kinetics was smaller in comparison with the soils and biocomposites. The hrd also contribute to the adsorption of the metals and the formation of inner-sphere stable complexes when the hrd are small (Pb and Cu) and outer-sphere complexes when the hrd are large (Cd).

The adsorption of Pb(II) and Cd(II) depends very heavily on the pH, while the adsorption of Cu(II) not only depends on the pH, but also on the type of sample on which it is adsorbed.

The use of the ASV technique coupled with the SEM/EDS analyses made it possible to corroborate the products of the reactions occurring on the surface of the MCPEs. Using the MCPEs and the ASV technique only the metal ions that are bioavailable are detected, as well as their oxidation state, which is important, since the bioavailability and the oxidation state of the metals are characteristics that make it possible to corroborate whether a metal is dangerous to the environment.

These results lead to the understanding of the interactions between metals and soils and sediments, which in turn leads to an improved management of biosolids to amend soils and, similarly, plays a very important role in the selection and creation of proper management as well as strategies aimed at remediating and cleaning soils and sediments contaminated with heavy metal.

SUPPLEMENTARY DATA:

Section 1

Figures 1, 2 and 3 show SEM microphotographs of the surfaces of the CPE modified with the biosolid after the ions of Cu(II), Cd(II) and Pb(II) are adsorbed in solutions with different pH, and these ions are subsequently reduced. Figure 1 shows copper crystals growing in dendritic form. The EDS analysis showed that at pH values of 2, 5 and 7 copper is found as Cu^0, while at a pH of 9 copper is found as a precipitate in the form of copper hydroxides. Figure 2 shows cadmium crystals in granular and dendritic form. An EDS analysis shows that at pH 2 and 5 the crystals are formed by metallic cadmium (Cd^0), while at a pH of 7 and 9 the cadmium is mainly found as a precipitate in the form of cadmium hydroxides. On the other hand, figure 3 shows lead crystals growing in granular and dendritic form. The EDS analysis shows that at pH 2 the lead is found in metallic form (Pb^0), while at a pH of 5, 7 and 9 the lead is found as a precipitate in the form of lead phosphates. The EDS analysis shows that the crystals are formed through two distinct mechanisms. Metallic crystals (Cd^0, Cu^0 and Pb^0) are formed by reduction of Me(II), especially at acidic pH, while the hydroxides and phosphates are formed by precipitation of Me(II) at neutral and alkaline pH.

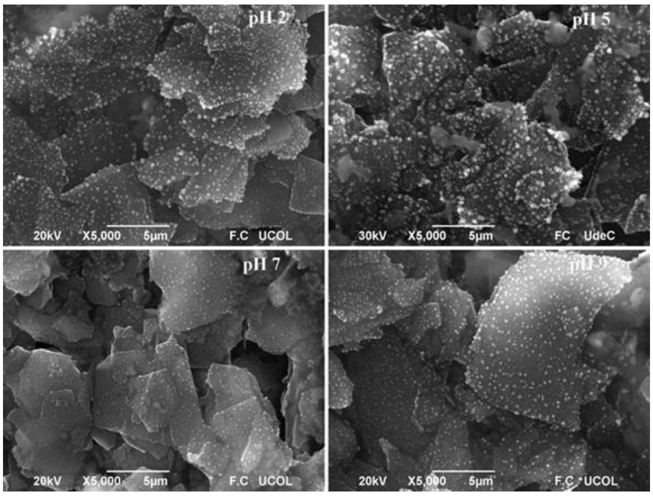

Figure 1. SEM images of the copper deposits on the surface of the CPE modified with the biosolid after being immersed in a solution of 0.1 mol L^{-1} Cu^{2+} for 10 minutes in order to promote the adsorption of Cu^{2+} on the surface of the electrode, so as to subsequently reduce Cu^{2+} in the BR buffer solution + 0.1 mol L^{-1} KNO_3 at different pH values, when applying a potential pulse of -0.7 V for 5 minutes

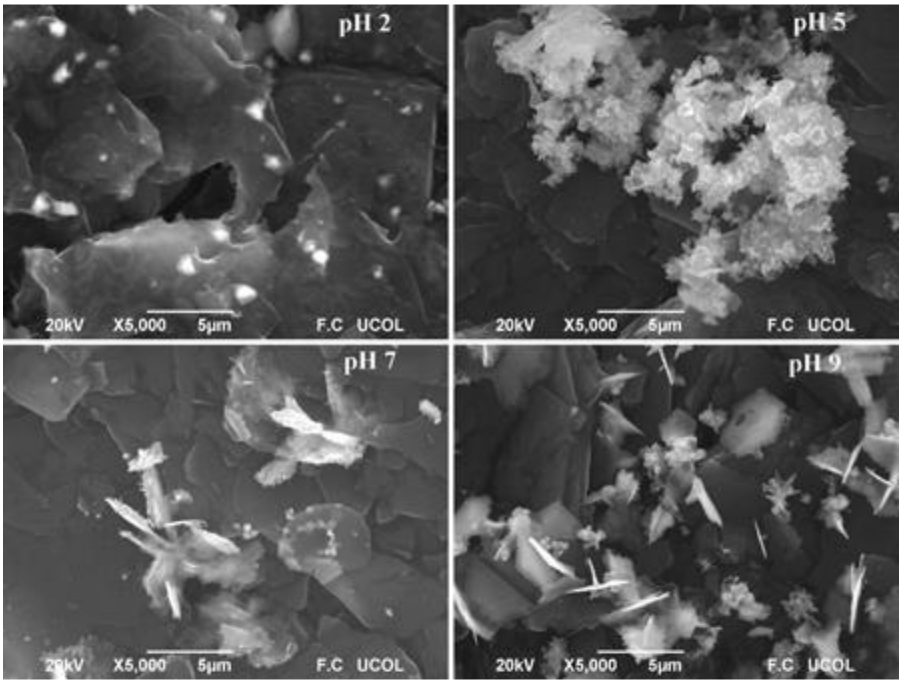

Figure 2. SEM images of the cadmium deposits on the surface of the CPE modified with the biosolid after being immersed in a solution of 0.1 mol L^{-1} in Cd^{2+} for 10 minutes in order to promote the adsorption of Cd^{2+} on the surface of the electrode, so as to subsequently reduce Cd^{2+} in the BR buffer solution + 0.1 mol L^{-1} KNO_3 at different pH values, when applying a potential pulse of -1 V for 5 minutes

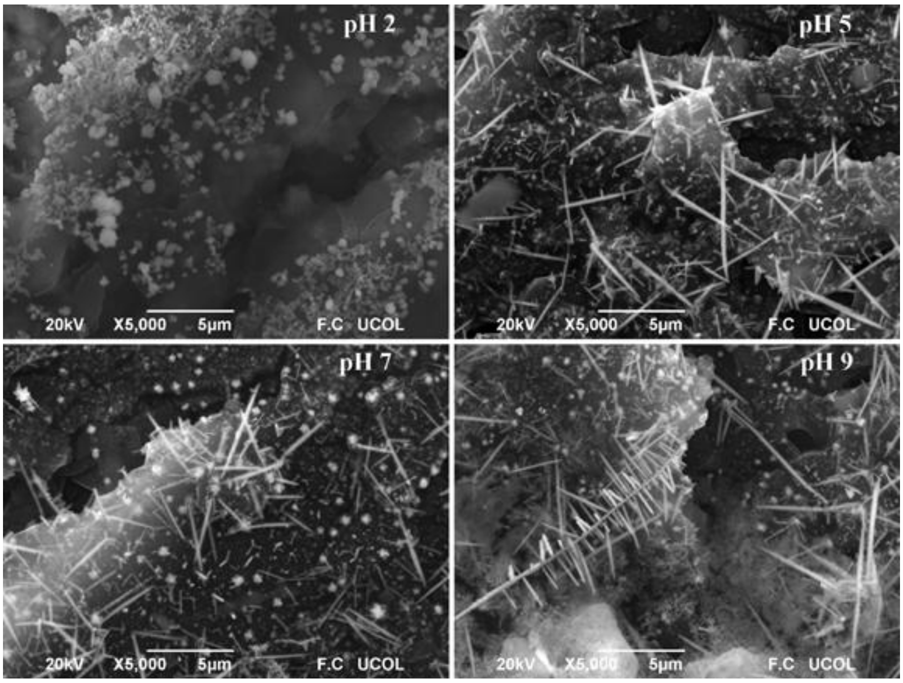

Figure 3. SEM images of the lead deposits on the surface of the CPE modified with the biosolid after being immersed in a solution of 0.1 mol L^{-1} in Pb^{2+} for 10 minutes in order to promote the adsorption of Pb^{2+} on the surface of the electrode, so as to subsequently reduce Pb^{2+} in the BR buffer solution + 0.1 mol L^{-1} KNO_3 at different pH values, when applying a potential pulse of -1 V for 5 minutes

On the other hand, when the formation and concentration of the crystals is analyzed, a behavior consistent with the variation of the current density in figure 3 (paper) is seen. When comparing the figure 3 (paper) with the growth of Cu and Cd crystals (figure 1 and 2, respectively), it can be seen that when the pH value increases, the amount of crystals increases as well, until reaching a maximum at approximately a pH of 5. At a pH of 7, a decrease in crystals in both cases (figure 1 and 2) can be seen. This variation in the concentration of crystal coincides with the increase and decrease in current density in the graphs of Cd and Cu in figure 3 (paper).

Moreover, when the pH value is increased to 9 (figure 1 and 2), an increase in the amount of crystals formed mainly by precipitation (crystals that have a structure different from that of the crystals formed at acid pH levels), however, the current density is zero at a pH of 9 (figure 3 (paper)). Lead shows a similar behavior: the current density decreases when the pH increases (figure 3 (paper), Pb). But figure 4 shows that the amount of crystal increases as the pH increases as well.

The increase in the amount of crystals and the change in their morphology, to alkaline pH (figure 1, 2 and 3), show that different precipitates are formed on the surface of the CPE with the metal ions present in the preconcentration solution during the preconcentration and they are not reduced by the potential pulse.

These analyses reveal that the metals in precipitate form do not decrease; therefore, they are neither detected when the ASV technique is applied. This explains the increased concentration of crystals at alkaline pH, but with low current densities. Accordingly, when the precipitates are formed, the amount of "free" ions available for reduction and detection decreases as the pH increases.

Section 2

Figure 4 shows the influence of the K^+ and Cl^- ions in the formation of the microcrystals on the surface of the MCPE. In general, when the adsorption takes place in the presence of K^+ and Cl^-, the amount of microcrystals decreases. When Cu and Cd are adsorbed with interference (Figure 4(a) and 4(c), respectively) with regard to the adsorption of Cu and Cd without interference (Figure 4(b) and 4(d), respectively), the decrease in the concentration of crystals is noticeable. When the solution is in the presence of the Cl^- ion, Cu(II) forms complexes like $[CuCl_4]^{2-}$, which is stable in a solution and, due to its negative charge, partially inhibits the adsorption of Cu on the MCPE, since the surface is negatively charged as well [45]. Similarly, Cd tends to form complexes with Cl^-, which are very soluble [53,60,61], which in turn explains the reduced concentration of crystals and the reduced current density observed in the graph seen in figure 5 (paper) with regard to figure 3 (paper).

On the other hand, when comparing the adsorption of lead without the presence of K^+ and Cl^- (figure 4(f)) with regard to the adsorption of lead in the presence of K^+ and Cl^- (figure 4(e)), an increase in the concentration and the size of the crystals is seen. An EDS analysis proved that the crystals in figure 4(e) are lead oxides, which means that those crystals are formed by precipitation, which has been shown when Pb is in the presence of Cl^- [54, 62], which in turn explains the reduced current density and the increased amount of crystals with regard to Figure 4(f).

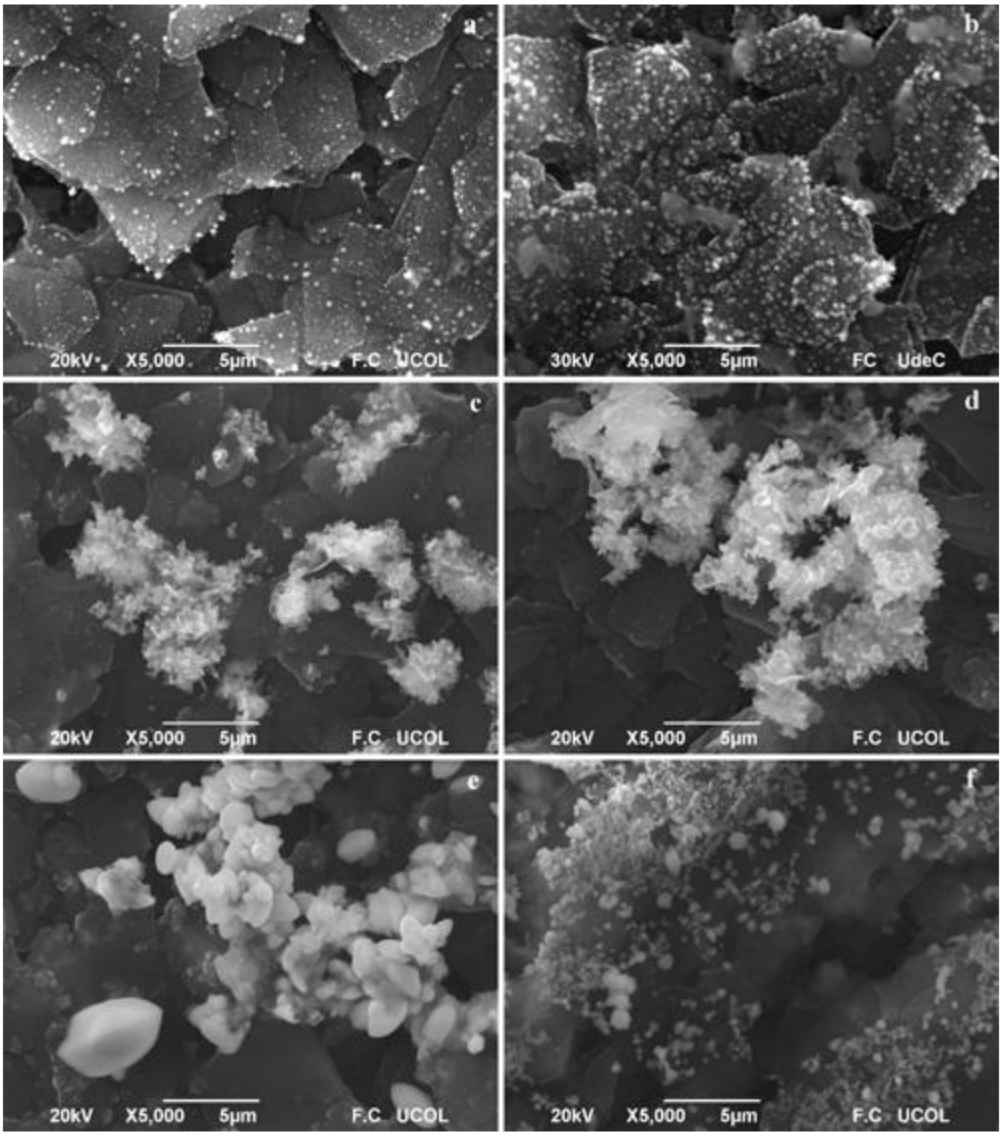

Figure 4. SEM images of the Me deposits formed on the surface of the CPE modified with the biosolid after being immersed in a solution in 0.1 mol L^{-1} Me(II) for 10 minutes and the subsequent reduction of Me^{2+} in the BR buffer electrolyte + 0.1 mol L^{-1} KNO_3 at pH 2 for Pb^{2+} and pH 5 for Cu^{2+} and Cd^{2+}, when applying a potential pulse of -0.7 V and -1.0 V *vs* SCE for 5 minutes. (a) Cu adsorbed in a solution of KCl, (b) Cu adsorbed without interference, (c) Cd adsorbed in a solution of KCl, (d) Cd adsorbed without interference, (e) Pb adsorbed in a solution of KCl and (f) Pb adsorbed without interference

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