Determination of Pb in *Brickellia Veronicifolia* for Anodic Stripping Voltammetry

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This study consists of the determination of lead concentration contained in soil and plant material (*Brickellia veronicifolia*) by means of Differential Pulse Anodic Stripping Voltammetry, using vitreous carbon as working electrode, SCE as reference and platinum as auxiliary. Samples were collected from sites near a tailings dam belonging to San Martín-Sombrerete-México; taking 12 sampling points and analyzing the lead content in soil and plant (root, stem, leaf), for determining the accumulation of this toxic element, in order to define its possible use as phytoextractant. The detection and quantification limits were 0.8 and 1.9 ppb respectively; it was found that the highest lead concentration was 1,115 ppm, which corresponds to 2.87 times the value established in NOM-147-SEMARNAT/SSA1-2004 for contaminated sites, while the plant accumulated 730 ppm with accumulation averages of 20-35% in root, 11-30% in stem and 37-58% in leaf, inferring that is an indicator plant of lead contamination in soil.

Introduction

The potentially toxic elements (PTE) are present in the soil as natural components thereof or as a consequence of human activity (1). The residues from the mine industry have contributed in great part to the dispersion of these components unleashing in this way an environmental problem, the composition of these residues include materials from excavation and separation supernatants of the mineral, these last are ones most to worry due to that contain high amounts of metals and metalloids generally denominated PTE (2).

The lead is considered a PTE, this element has been distinguished as a prevalent toxic heavy metal because of its non-biodegradability and accumulation in organism, this is one of the most toxic heavy metals because it exhibits neurotoxicity and results in serious brain disorder and affects the nervous system, which contributes to a major environmental health problem even in low concentrations. The lead contamination mainly occurs during extraction and processing the mining industry (3, 4, 5).

In this scenario the immobilization and extraction of lead using plants, it has as purpose to reduce the concentrations this elements in the soil without modifying its structure and functions (6). There are Metallophytes species that not only grow in contaminated soil whit these elements but also permits its catchment, accumulation, and its posterior translocation (7, 8).

There is a difference between phytoextraction and phytostabilization, the first one refers to the use of plants for extracting PTE in the soil and transporting them to their aerial part (stem and leaf), removing them from the soil, the last one refers to the use of plants that limit the bioavailability of these elements in the soil, reducing their mobility (8, 9). The process is carried out 'in situ' avoiding costs in transport, thus reducing the final costs of remediation. (10).

Brickellia veronicifolia is a native plant species that grows around the deposits of mining waste (containment dikes) so it is of interest to evaluate if this species accumulates PTE, such as lead (Pb), in a contaminated site, and how it distributes this metal in its morphology for a possible use in soil remediation

The conservation of native species of soils contaminated with metals (Metallophytes and pseudometallophytes) should be a priority for its possible use in environmental phytotechnologies of revegetation, phytostabilization and phytoextraction (11). A study carried out with a native species is presented.

Therefore, the determination and extraction of Pb ions are of long time interest for researchers, various analytical techniques such as UV–vis spectroscopy, flow injection analysis, atomic absorption spectroscopy, have been employed for the determination of heavy metal ions. Even though, these methods are highly sensitive for the determination of low concentrations of metal ions, the expensive instruments which should be specially maintained, tedious sample preparations, lengthy operational procedures and unsuitability for on-line monitoring have made these methods less attractive (12).

Voltammetry covers a group of electroanalytical methods in which the information on the analyte is derived from the measurement of the current intensity as a function of the applied potential, under conditions that favor the polarization of an indicator or work electrode. In general, the limits of detection with differential pulse voltammetry are of two orders of magnitude lower than those of classical voltammetry and lower cost (12).

Redissolution methods encompass a variety of electrochemical processes that have a characteristic and common initial stage. In all these procedures the analyte is first deposited on a working electrode, usually from a stirred solution, during this second stage of the analysis, the analyte deposited in the working electrode is removed from it by redissolving it. In anodic redissolution methods, the working electrode behaves as a cathode during the deposition stage and as an anode during the redissolution stage, in which the analyte is re-oxidized back to its original state (12).

As a result of the preconcentration stage, the redissolution methods have the lowest detection limits of all the voltammetric procedures. For example, anodic redissolution with pulse voltammetry can reach detection limits in the order of nanomoles for species that are important in the environment, as a Pb^{+2}, Ca^{+2}, Tl^{+} (12).

Methodology Experimental

Samples Treatment

A guided sampling was carried out, collecting 12 simple samples at no more than 10 cm of proficiently. Table I shows the coordinates of the sampling points that have been made in two tailings dams.

Table I. Coordinates geographic of the sampling points.

Soil	Sample	Coordinates UTM 13 Q	
		X	Y
Uncontaminated soil	Blank	791940	2520032
	1	628118	2619982
	2	628125	2620008
	3	628138	2620038
Tailing dam 1	4	628142	2620038
	5	628205	2620029
	6	628202	2620026
	7	628254	2620042
	8	628253	2620038
Tailing dam 2	9	628395	2618675
	10	628347	2618713
	11	628404	2618750

Electrochemistry Characterization

All the experiments were made in a three electrodes conventional electrochemical cell fabricated with glass and capacity of 10 mL, for the calculation of detection limit (LD) and limit of quantification (LC), it was carried out by the standard addition method. The solutions were prepared using 5 mL of amalgamating solution, $(Hg(NO_3)_2 \cdot H_2O$ 100 ppm (J.T. Baker), KNO_3 0.2M (Aldrich), gauge with HNO_3 10 % v/v (J.T. Baker)) and 5mL of digested sample. Each sample was placed in a process of purge with N_2 for 10 minutes (15), For the analysis of Pb^{+2} concentration of the samples of both *Brickellia veronicifolia* and soil, the same procedure was followed, 5mL of amalgamating solution and 5mL of the sample instead of deionized water.

A standard of 1000 ppm ± 4 Pb in 2% by weight HNO_3 (Sigma Aldrich) was used. It was prepared a standard curve for low concentration (0.1, 0.25, 0.5, 0.8 and 1 ppm from the Pb standard), gauging with deionized water.

The glassy carbon electrode surface was, firstly, adequately polished (alumina 0.3 µm) and cleaned, washing it with deionized water and putting it into an ultrasonic bath

for 15 minutes (15), using glassy carbon as working electrode, saturated calomel electrode (SCE) as reference and platinum as the auxiliary electrode.

The measurements were made in Differential Pulse Anodic Stripping Voltammetry. Potentiostat / Galvanostat (PAR, 283) using the method of standard addition for the quantification of Pb^{+2} in the vegetal material and soil samples. The conditions of operation applied were: first, the formation of a mercury film (Hg) and the deposition of the problem ions on the superficial of the working electrode applying a potential of -1.2 V during 5 minutes and maintaining the agitation to 900 rpm, then the agitation was stopped during 45 s for homogenizing the Hg amalgam.

Finally, the sweep was carried out from -1.2 to 0.1 V at a velocity of 20 mV/s, applying a pulse of 5 mV amplitude every 250 ms, with a height of 50 mV and a width of 50 ms obtaining voltamperograms in which the Pb^{+2} appears at -750 mV vs SCE.

The concentration in the samples was determined using the voltammograms without the baseline obtained, identifying the maximum height value in it, determining the concentration in the cell, and finally the dilution made in the cell, considering a ratio of 1: 2 (sample: cell volume), and the dilution made in the digestion, proportion 1: 125 (sample: total digested), thus obtaining the real concentration for each sample.

Statistical analysis

The calculation of the bioaccumulation factor (BAF) was made by dividing the bioaccumulated total *Brickellia veronicifolia* concentration of Pb and the concentration of Pb presents in the rhizosphere soil (adjacent), as is shown in the equation 1.

$$BAF= [([Pb]root) + ([Pb]stem) + ([Pb]leaf)] / ([Pb]soil) \qquad [1]$$

The Pearson correlation coefficient analysis was used between the response variables corresponding to the determination of the Pb content in the soil and the bioaccumulated Pb in vegetal material, using the software Minitab 17.1.5.

Results and Discussion

Figure 1 shows the voltammograms for the standard curve of low concentration of Pb. The peak of the voltamperogram is displayed at -760 mV. The blank was measured in quintuplicate for validate the analytical method.
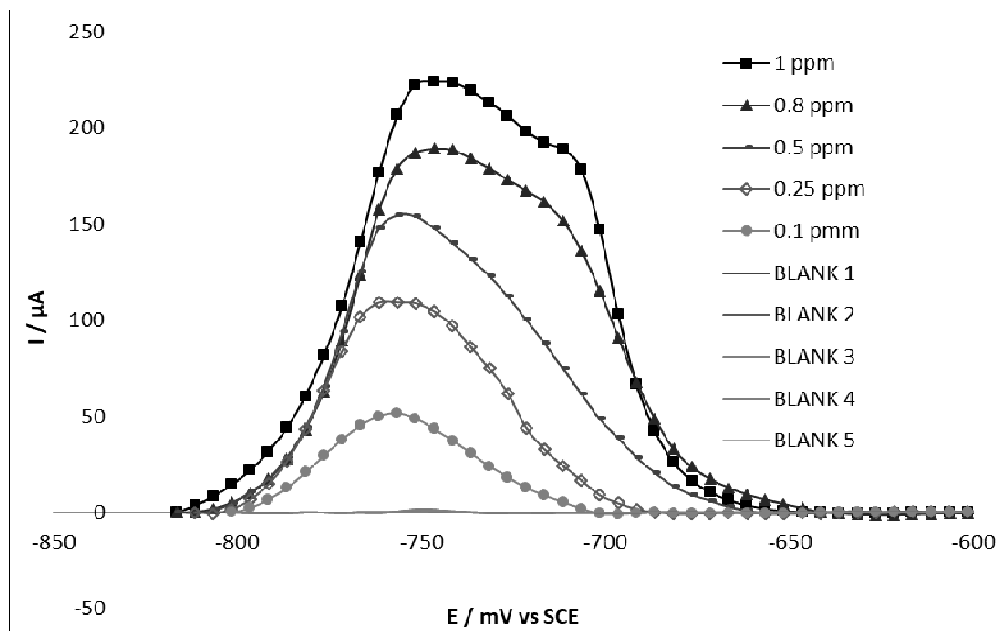
Figure 1. Differential Pulse Anodic Stripping Voltammetry, standard curve of low concentration of Pb corrected by the elimination of baseline.

Figure 2 shows the standard addition graph obtained from the maximum current peaks of the standard curve of low concentration of Pb and the average of the blanks. It can be seen that the correlation coefficient is 0.979, which indicates a linear relationship between the current and the concentration of the analyte.
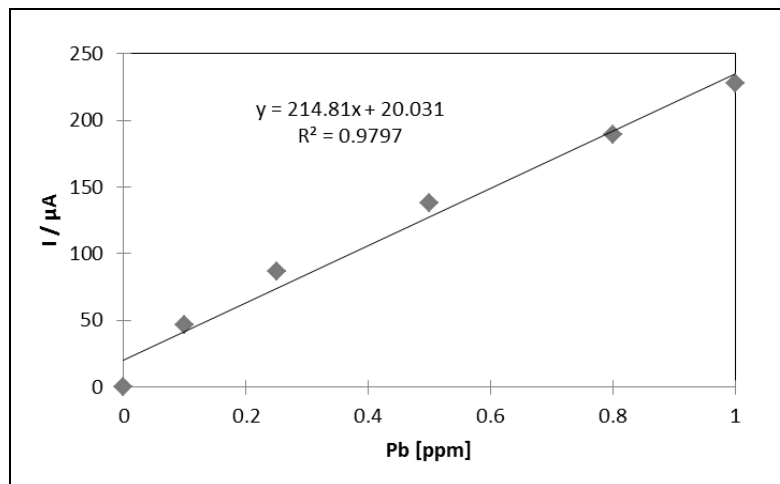

Figure 2. Linear regression of the standard curve of low concentration of Pb.

The detection and quantification limits correspond to 0.8 and 1.9 ppb, respectively. The Pb measurements in the samples yielded the data shown in Table II, with acceptable repeatability.

Soil samples 9, 10 and 11 exceed the limit of remediation of contaminated sites marked by the regulations for agricultural use soils with respect to Pb (400 ppm). These

soil sampling points exceed the limit 1.78, 1.81 and 2.87 times, respectively; so the soil of this site would have to be remediated according to the applicable regulations [15].

Based on reports of typical concentration ranges of Pb in uncontaminated soils and plants grown in uncontaminated sites, corresponding to 10-30 ppm and 0.1-0.5 ppm, respectively (17). In this sense, the results obtained from both blanks (soil and vegetal material) are consistent with these reports.

Likewise, bioaccumulation factors (BAF) have been reported for classifying the behavior of plants in contaminated sites, it is considered as an exclusionary plant with a BAF<0.1, as an indicator plant with a BAF of between 0.1 and 1 and as a accumulator plant with a BAF> 1 [17]. Based on this, *Brickellia veronicifolia* is considered to be an indicator plant of Pb contamination with a BAF = 0.51 ± 0.09, and according to previous reports, *Brickellia veronicifolia* can be thought of as a suitable plant for the phytoextraction of PTE in contaminated sites (19).

The Pearson correlation coefficient between the variables was calculated, resulting in a value of 0.994, which indicates a direct proportionality between the concentration of Pb in soil and the accumulation of this PTE in *Brickellia veronicifolia*.

TABLE II. Concentration of Pb in soil and vegetal material samples collected.

Sample	Concentration [ppm]				
	Soil	Root	Stem	Leaf	Vegetal material
Blank	11.25	0.50	0.25	0.50	0.50
1	74.74	7.50	12.47	19.95	39.92
2	87.28	12.48	12.50	20.00	44.98
3	100.00	17.44	7.49	30.00	54.93
4	149.24	22.41	19.94	24.88	67.23
5	149.62	27.43	19.93	32.39	79.75
6	149.93	19.95	14.94	44.82	79.71
7	249.50	20.00	22.50	44.88	87.38
8	274.03	27.40	32.50	49.82	109.72
9	715.00	120.00	52.50	243.50	421.00
10	725.00	162.50	54.81	244.37	461.68
11	1150.00	265.50	77.35	387.50	730.35
Accumulation intervals (%)		20 - 35	11 - 30	37 - 58	

Conclusions

The analytical method of Differential Pulse Anodic Stripping Voltammetry let determinate the concentration of lead in soil and vegetal material (*Brickellia veronicifolia*) in a contaminated site.

The limits of detection and quantification of the technique Differential Pulse Anodic Stripping Voltammetry to operation conditions were calculated, which correspond to 0.8 and 1.9 ppb respectively

It was carried out that the site is contaminated with lead due to that three of eleven soil samples exceeded the remediation limits established in the NOM-147-SEMARNAT-/ SSA1-2004 applicable in Mexico for contaminated sites, inferring that others potentially toxic elements could be presents in this soil, representing an environmental risk. This site must be remediated in short-term.

It was found bioaccumulation factor of 0.51 ± 0.09 of lead in *Brickellia veronicifolia,* corresponding to an indicator plant of sites contaminated, existing a direct proportionality between the concentration of lead in soil and the capacity of accumulation of this element by *Brickellia veronicifolia*.

Acknowledgments

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