An electroanalytical approach for evaluation of biochar adsorption characteristics and its application for Lead and Cadmium determination

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Talita Mayumi Suguihiro [a], Paulo Roberto de Oliveira [a], Edivaltrys Inayve Pissinati de Rezende [b], Antonio Sálvio Mangrich [b,c], Luiz Humberto Marcolino Junior [a], Márcio F. Bergamini [a,*]

[a] Laboratório de Sensores Eletroquímicos (LabSensE), Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81531-980, Curitiba–PR, Brazil
[b] Laboratório de Química de Húmus e Fertilizantes, Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81531-980, Curitiba–PR, Brazil
[c] Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente (INCT E&A/CNPq), Brazil

HIGHLIGHTS

- New electrochemical procedure for evaluation of biochar's proprieties adsorption.
- Analytical application of biochar obtained under low temperature pyrolysis conditions.
- Development of voltammetric sensor for determination of Pb^{2+} and Cd^{2+} using biochar.
- Low limit of detection, excellent sensitivity and stability of the proposed electrode.
- Analysis of simulated industrial waste water without any pretreatment of the sample.

GRAPHICAL ABSTRACT
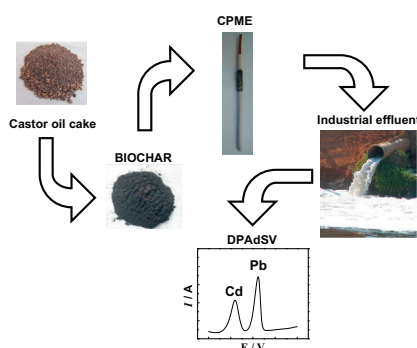
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ABSTRACT

This work describes for first time the use of electroanalytical techniques for evaluation of adsorptive pro-prieties of biochar using it as electrode modifier and its application for preconcentration and determina-tion of Lead(II) and Cadmium(II) under differential pulse adsorptive voltammetric conditions (DPAdSV). Samples of biochars were obtained from castor oil cake using a predefined set of experimental conditions varying the heating rate (*V*), final temperature (*T*) and warm-up period (*P*) and subsequently used for car-bon paste modified electrode (CPME) preparation. The proposed method was applied for Lead(II) and Cadmium(II) determination in spiked simulated industrial effluents and the limit of detection obtained for both metals were adequated for determination of these evaluated ions taking into account the limits established by Brazilian legislation. For all samples analyzed, recoveries ranged from 95% to 104% were obtained and no significative interferences were observed for common cations in water samples.

1. Introduction

Biochar is a form of charcoal produced through the pyrolysis process of biomass under low or no oxygen conditions. Various types of biomass such as agricultural crop residues, forestry residues, wood waste and animal manures have been proposed as feedstock for biochar production (Duku et al., 2011). It has a heterogeneous structure and can present a range of chemical structures and variable elemental composition based on the pyrolysis conditions and the biomass parent material (Spokas, 2010). The agricultural use of biochar is largely reported because it improves the soil pH control, nutrient retention and water hold-ing capacity of soils, reduces the total fertilizer requirements and

environmental deterioration associated with fertilizers (Lehmann and Joseph, 2009).

In recent years biochar has been applied for the remediation of contaminated soils and waters by several species (organic and/or inorganic) (Dong et al., 2011; Sun et al., 2011; Beesley and Marmiroli, 2011; Uchimiya et al., 2010). Biochar has great affinity for heavy metals and their sorption capacity is comparable with other biosorbents. Recently, Dong et al. reported the application of biochar obtained from sugar beet tailing for the removal of Cr(VI) from aqueous solutions. A sorption capacity for Cr(VI) of 123 mg/g was found which is comparable to other low-cost sorbents. Biochar prepared by pyrolysis of hardwood and corn straw for application as adsorbents for the removal of Cu(II) and Zn(II) from aqueous solution was reported by Chen et al. Adsorption efficiency of the metal ions increased with increasing biochar concentration, suggesting that plant-residue or agricultural waste derived biochar can act as effective surface sorbent. Sun et al. verified that biochar produced at different heat treatment temperatures shown significative difference in sorption behavior of two herbicides (norflurazon and fluridone) to biochars obtained from wood and grass feedstocks. Amorphous structural arrangement for biochar obtained at 400 °C exhibited the highest sorption parameter for the two herbicides. Uchimiya et al. reported the preparation of biochar from broiler litter manure samples and verified that it could immobilize organic contaminants. Authors proposed that both surface adsorption and partitioning mechanisms could happen in the heavy metal immobilization. In general, information about the biochar are mainly focused in its preparation and application as a soil conditioner or/and in the pollutants removal, however, its use in electroanalytical for sensor construction is not reported.

Electrochemical stripping analysis is a family of procedures involving a preconcentration of the analyte onto the working electrode, prior to its direct or indirect determination by means of an electroanalytical technique (Fogg and Wang, 1999). Chemically modified electrodes are widely investigated in stripping voltammetry due to their attractive preconcentration capability of species as a result of a selective interaction between modifier and the analyte. The preconcentration of given specie on an electrode surface may occur by different processes such as: ion exchange, complexation, bioaccumulation, salt formation, covalent binding, or hydrophobic interaction (Fogg and Wang, 1999; Bard and Faulkner, 1980). In this way, several materials have been evaluated in order to obtain an improvement in detection and quantification limits besides to provide adequate repeatability and reproducibility. On the other hand, voltammetric assays using chemically modified electrodes could be used as a powerful analytical tool for evaluation of sorption modifier capacity. In addition, voltammetric techniques are a good alternative to spectroscopic and chromatographic procedures, due its simple and low-cost instrumentation.

The existence of metals in the environment is a result of the natural as well as anthropic process. However, after the Industrial Revolution, the present-day levels of heavy metals in the environment are almost exclusively from anthropogenic sources. Chemical pollution with heavy metals has been one of the serious problems for the sustainable environment and some of them (for instance, lead, cadmium, chromium and mercury) have been pointed out as environmental endocrine disruptors due its strong estrogenic activity (Erfurth et al., 2001). Moreover, lead probably has the longest history of environmental contamination and arises from multiple sources (Matusiewicz and Krawczyk, 2006). The maximum levels for effluent discharge in water bodies of cadmium and lead are 0.2 and 0.5 mg L^{-1}, respectively; these values were established by CONAMA (National Council for the Environment in Brazil) (CONAMA, 2008). Thus, determination of these metal ions can provide important information on the environmental side.

In this article, a simple and effective modified carbon paste electrode prepared using biochar obtained from castor bean showed capacity for preconcentration of Pb(II) and Cd(II) ions at electrode surface which promoted a significative increase in the voltammetric signal in comparison with the unmodified electrode. This behavior is due to high functionalized surface shown by the biochar. The sensor was applied to the simultaneous determination of Pb(II) and Cd(II) by using differential pulse adsorptive stripping voltammetry (DPAdSV) in spiked water samples.

2. Methods

2.1. Apparatus

DPAdSV measurements were performed in a µAUTOLAB Type III (EcoChemie) connected to a microcomputer controlled by software (GPES 4.9) for data acquisition and experimental control. All the voltammetric measurements were carried out in a 30 mL thermostated glass cell at 25 °C, with a three-electrode configuration: modified carbon paste electrode as the working electrode, Ag/AgCl KCl saturated as the reference electrode and platinum wire auxiliary electrode. During the measurements, the solution in the cell was not stirred.

2.2. Reagents and solutions

All the solutions were prepared with water purified in a Millipore Milli-Q system. All the chemicals were of analytical grade and were used without further purification. A stock solution containing 1000 mg L^{-1} of ions (Merck) was used. By dilution with water, solutions containing different concentrations of Lead(II) and/or Cadmium(II) ions were prepared.

2.3. Preparation of biochars and characterization

The castor oil cake, gridding in ball mills to a particle size of 80 meshes, was placed in porcelain boats in the inner glass tube furnace EDG FT-40 microprocessor-controlled. The factors assessed by a 2^3 factorial design were: heating rate (V), final temperature (T) and warm-up period (P), at the levels of 5 and 10 °C min^{-1}, 300 and 350 °C and 30 and 60 min, respectively (Table 1).

The elementar composition (C, H and N) was determined using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. Information about functional groups present at surface of the biochar was provided by a FTIR Bomem MB100 spectrometer recording the spectrum scope from 4000 to 350 cm^{-1} with a resolution of 4 cm^{-1}.

Table 1
Set of experimental conditions adopted for biochar samples preparation considering the experimental procedure and the factorial design 2^3.

Biochar samples	Experimental conditions		
	V (°C min^{-1})	T (°C)	P (min)
P1	10	350	60
P2	5	350	60
P3	10	300	60
P4	5	300	60
P5	10	350	30
P6	5	350	30
P7	10	300	30
P8	5	300	30

V: heating rate, T: final temperature and P: warm-up period.

2.4. Carbon paste electrode construction

The carbon paste (1.0 g) was prepared by carefully mixing the dispersed graphite powder (45–75% (w/w)) (Aldrich), with biochar sample at a varying ratio (0–30% (w/w)) and subsequently added to 0.250 g of mineral oil (25% (w/w)). The components were mixed manually in a mortar and pestle for at least 10 min to obtain an appropriate homogenization. Modified carbon pastes were prepared using the several synthesized biochar samples and it was packed into an electrode body consisting of a plastic cylindrical tube (o.d. 5 mm, i.d. 3 mm) equipped with a copper rod serving as an external electric contact. Appropriate packing was achieved by pressing the electrode surface against a filter paper.

2.5. Voltammetric procedure

The analytical procedure comprised four steps (Bergamini et al., 2006): (1) Lead(II) or/and Cadmium(II) were directly preconcentrated at open circuit potential in the pretreatment sample under controlled agitation; (2) then, the electrode was removed from the preconcentration cell, briefly rinsed with deionized water, and placed in the electrochemical cell containing 10 mL of 0.1 mol L^{-1} acetate buffer solution (pH 5.0) as supporting electrolyte; and immediate cathodic reduction of the absorbate at controlled potential was performed; (3) Differential pulse adsorptive stripping voltammograms (DPAdSV) were registered and (4) finally, after the steps just described, the electrode surface was cleaned by putting it in 0.1 mol L^{-1} H$_2$SO$_4$ solution.

2.6. Sample preparation

A well-known amount of evaluated ions were spiked to an aliquot of 100.0 mL of simulated effluent in order to reach a final concentration of 0.5 mg L^{-1} and 0.2 mg L^{-1} in Lead(II) or Cadmium(II), respectively. The samples were prepared with species and concentration according established by CONAMA: Chloride (1.0 mg L^{-1}), Nitrate (20.0 mg L^{-1}), Sulfate (1.0 mg L^{-1}), Manganese(II) (1.0 mg L^{-1}), Copper (1.0 mg L^{-1}), Nickel (2.0 mg L^{-1}), Zinc (5.0 mg L^{-1}) and Mercury (0.01 mg L^{-1}). The pH was adjusted at 7.0 and preconcentration step was realized directly by immersion of the CPME in the solution. The ions content in these samples were quantified by four successive additions of a standard Cadmium or Lead solution.

3. Results and discussion

3.1. Voltammetric performance of the carbon paste modified electrode for preconcentration of Lead(II) and Cadmium(II) ions

Fig. 1 presents differential pulse voltammograms obtained with modified and unmodified carbon paste electrodes in 0.10 mol L^{-1} acetate buffer solution (pH 5.0) for different experimental conditions. For carbon paste electrode, any voltammetric peak was observed after preconcentration and cathodic reduction steps indicating that the unmodified electrode is unable to preconcentrate Cd(II) and/or Pb(II) (curve A). However, when the same procedure was carried out by using a carbon paste modified with 25% of P4 biochar sample (curve B), oxidation peaks at −0.76 V (Cadmium) and −0.55 V (Lead) could be observed with a higher intensity of the anodic current. Thus, it is possible to suggest that after an accumulation step, the next step involves the reduction of the ions preconcentrated in the biochar at a controlled potential of −1.0 V versus Ag/AgCl. No current peaks were observed for the modified carbon paste electrode before the accumulation step in solutions containing Lead(II) and Cadmium(II) ions (curve C). These
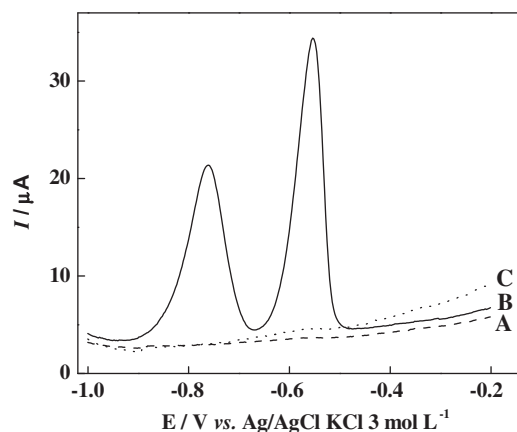

Fig. 1. Differential pulse stripping voltammetric responses obtained in acetate buffer pH 5.0 for the following: (A) CPE unmodified after preconcentration step; (B) CPME modified with 25% (w/w) biochar P4 after preconcentration step; (C) CPME modified with 25% (w/w) biochar P4 before preconcentration step. The preconcentration step was realized for 600 s in a aqueous solution adjusted at pH 5.0 content of 1.0 × 10^{-5} mol L^{-1} of Pb(II) and 5.0 × 10^{-5} mol L^{-1} of Cd(II).

results suggest that biochar obtained from castor bean is not electroactive in the potential range studied. So, incorporation of the biochar at the carbon paste electrode offers a beneficial alternative for the accumulation of ions.

The increase in anodic current at the modified electrode demonstrates that biochar in combination with DPAdSV measurements can promote a better response in comparison with the unmodified carbon paste electrode attributed to the high functionalized surface of biochar. These results suggest that the anodic surface processes could be systematically exploited by DPAdSV with some advantages in sensitivity and selectivity.

3.2. Voltammetric behavior of the carbon paste electrode modified with biochar samples prepared in different experimental conditions

In order to optimize the voltammetric procedure, modified carbon paste electrodes were prepared using different biochar samples. A total of eight samples (P1–P8) were prepared and characterized using infrared spectroscopy and elemental analysis. The preconcentration step was realized in aqueous solution (pH 5.0) containing 5.0 × 10^{-6} mol L^{-1} of Pb(II) and 2.0 × 10^{-5} mol L^{-1} of Cd(II) by immersion of the work electrode (CPME prepared using
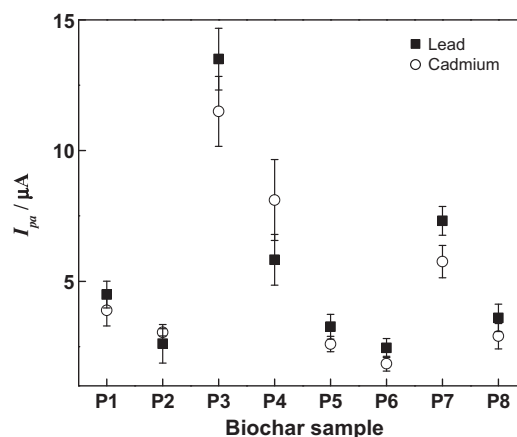

Fig. 2. Anodic peaks currents obtained for Pb(II) and Cd(II) ions using different biochar samples. Error bars are standard deviations corresponding to three replicates obtained for different electrode surfaces.
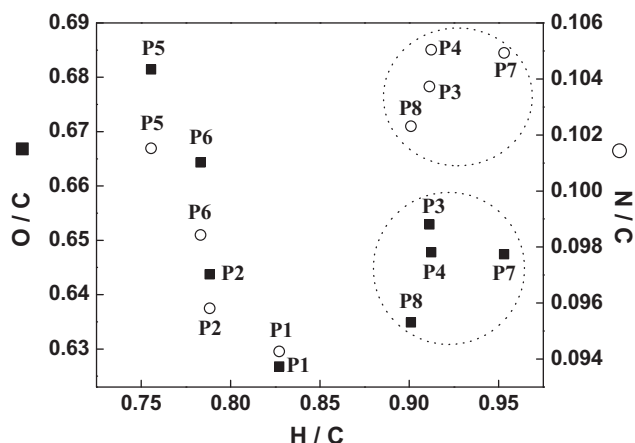
Fig. 3. Ratio of the elemental composition of C, O and N obtained for the samples used biochars.

25% w/w of modifier) by 600 s. The anodic current peak values obtained for Lead and Cadmium ions using a CPME with different biochar samples are shown in Fig. 2.

The results of the elemental compositions (Fig. 3) of biochar samples revealed that with the increase in the pyrolytic temperature, the C content increased in contrast with decreasing in the H content (samples P1, P2, P5 and P6). The estimative of H/C molar ratio suggests that H atoms are associated with plant organic matter. Higher H/C molar ratios obtained when the sample was submitted to the lower temperature (300 °C) suggest that biochar samples could contain a certain amount of aliphatic original plant organic residues such as cellulose. When pyrolytic temperature is at 350 °C, the H/C molar ratio decreases significantly suggesting that the original organic fraction was reduced and the structures are more aromatic (Mašek et al., 2013).

The molar oxygen/carbon ratio (O/C) of biochar has been used as an estimative of the surface hydrophilicity since it is indicative of polar-group content (Spokas, 2010; Zhang et al., 2011). In addition, a decreasing in the O/C and/or N/C ratios can indicate the increasing in the hydrophobicity and the reduction of polar groups.

In order to clarify the obtained voltammetric behavior, a correlation between sorption capacity of the modified electrode and characteristics of biochars was realized (Meyer et al., 2011). A positive correlation between voltammetric response and N/C ratio was observed suggesting that polar groups content at biochars surface can facilitate the sorption of Lead and Cadmium ions. Polar groups on the biochar surface can work as water binding centers and facilitate the formation of water clusters, which may increase the biochars accessibility to ions due to its hydrophilicity. In addition, the results showed that samples with elevated content of nitrogen atoms can exert a more significant effect on preconcentration of analytes. The results suggesting that both sorption and complexation process are the mechanisms by which those metals are retained at electrode surface.

The FTIR spectra of the samples were very similar, all featuring mainly a broad band at 3680–3300 cm^{-1}, associated with the O–H stretching from alcohol, carboxylic acids and water. The boarding characteristics of those absorptions are consequence of hydrogen bonding presence in different degrees. Energy absorption in 1625 cm^{-1} attributed to the structural vibrations of C=C aromatics, asymmetric stretching of C=O (COO–) and bending of O–H groups. Shoulder at 1720 cm^{-1} (P4, P7 and P8 samples) is assigned to C=O stretching of ketone, ester and carboxylic acid (Chen et al., 2008; Keiluweit et al., 2010). Biochar FTIR spectra data displayed a significant number of sorption peaks indicating the complex

nature of samples. Broad sorption peak at 3317 cm^{-1} was verified indicating the existence of hydroxyl group. Other sorption peaks reveal the presence of several functional groups: the sorption peak around 2927 cm^{-1} was assigned to CH stretching, 1620 cm^{-1} represented a carboxyl group and ionized non-coordinated and ionized coordinated COO– group (Chen et al., 2008; Keiluweit et al., 2010). The peak at 1420 cm^{-1} corresponded to aromatic C–C ring stretching. The peaks attributed to C–O stretch of carboxylate ions, hydroxyl bending vibration, CO stretching vibration of the alcoholic groups and aromatic compounds were observed at 1375, 1317, 1049 and 780 cm^{-1} respectively. So, the functional groups present on biochar samples may be responsible by Lead and Cadmium ions sorption. Thus, a P3 biochar sample was adopted as the best modifier to prepare carbon paste electrodes for Pb(II) and Cd(II) ions determination and it was used for further studies.

3.3. Influence of the experimental parameters on the voltammetric response

In order to optimize the anodic stripping voltammetry as analytical tool for Cadmium(II) and Lead(II) determination, the effect of some experimental parameters (electrode composition, pH variation, accumulation time (t_{acc}), clean solution and time of immersion) and instrumental parameters on the peak current by using carbon paste electrode modified with biochar was investigated.

The amount of biochar in the carbon paste had a significative influence on the voltammetric responses. The peak currents increased with increasing amount of biochar up to 25% (w/w) and decreased significantly when more than 25% (biochar, w/w) was used in the electrode preparation due to the decrease in the conductive area at the electrode surface. Based on these results, a carbon-paste composition of 25% (w/w) biochar, 50% (w/w) graphite and 25% (w/w) mineral oil was used in subsequent studies. Similar behavior was also observed in a previous work (Bergamini et al., 2006).

In order to prevent a memory effect, after preconcentration and voltammetric measurement steps the CPME was submitted to a clean step using a sulfuric acid solution 0.1 mol L^{-1} (Fig. 4). The electrode was immersed in acid solution and maintained for times varying from 0 s (without clean step) to 300 s. Voltammetric response decreases exponentially with the increase of the immersed time (Fig. 4 – detail). For times higher than 200 s no significative signal was verified for both ions evaluated. So, a desorption step (immersion by 240 s in 0.1 mol L^{-1} H$_2$SO$_4$ solution) was adopted because it promotes a better repeatability between voltammetric measurements.
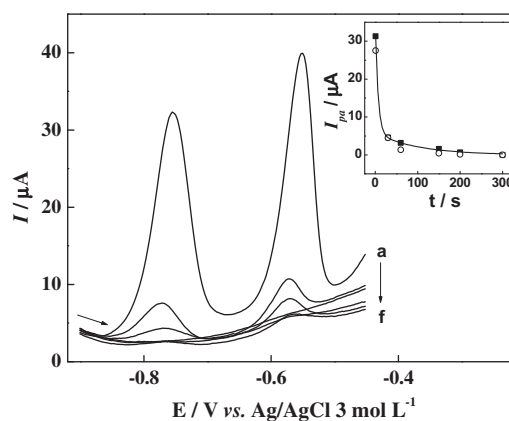

Fig. 4. DPAdSV obtained for CPEM (25% (w/w) biochar P3) after preconcentration in aqueous solution with 2.0×10^{-5} mol L^{-1} of Cd(II) and 3.3×10^{-6} mol L^{-1} Pb(II) for different cleaning time in 0.1 mol L^{-1} H$_2$SO$_4$ solution: 0 s (without cleaning step) (a), 30 s (b), 60 s (c), 150 s (d), 200 s (e) and 300 s (f). The effect of cleaning time on the current peak value was shown in detail.

The pH effect on the preconcentration solution is an important variable and it can affect the biochar's performance in the interaction with the studied ions (Fig. 5). So, in order to optimize the pH of the solution in the preconcentration step, this parameter was studied in the range of 2.0–9.0 (Fig. 5A). It was found that for acidic solutions of pH <3, no ions (Cd(II) and/or Pb(II)) are retained on the electrode surface; for pH values higher than 3.0 the intensities of current peaks increased significantly reaching a maximum value between pH 7.0 and 8.0 for both ions. These results could be attributed to weakly acid sites which are protonated in acid conditions and it becomes unavailable for ions preconcentration (Chen et al., 2011). Similar behavior could be expected for basic groups containing nitrogen atoms. Results obtained for pH above 8.0 promoted a significative decrease in anodic peak current for Pb(II) and Cd(II) ions investigated and almost absence of waves was observed at pH higher than 9.0. These results can be attributed to the hydrolysis reaction for both ions. Then, for further experiments, the pH 7.0 value in the preconcentration solution was chosen.

The pH effect on the voltammetric response was evaluated in the range of 3.0–7.0 (Fig. 5B). It was observed that pH <4.0 the peak current decreases markedly due the deposition of the ions affected by hydrogen overpotential, leading to decreasing of the corresponding signal (Bergamini et al., 2006). The maximum peak currents were obtained at pH = 5.0 for both ions and this value was chosen as adequate for further studies.

The influence of the accumulation time on the peak current was studied by using concentration levels of 1.0×10^{-6} mol L^{-1} and 1.0×10^{-5} mol L^{-1} of Cd(II) or Pb(II) in aqueous solution (pH 7.0), then submitted to a previous accumulation from 0 s to 1800 s. For 1.0×10^{-5} mol L^{-1} of both ions, the anodic peak current linearly increases up to 900 s and reaches a plateau at a longer accumulation time. Using a 1.0×10^{-6} mol L^{-1} of both ions, a linear increase of the anodic peak current is obtained up to 1200 s. This behavior indicates that there is an evident saturation of the available sites on the biochar surface, which depends on of ion concentration. Similar to other stripping methods, there is a correlation between accumulation time and analyte concentration. So, in order to obtain an adequated limit of detection for determination of low concentrations of Cd(II) and Pb(II) ions, an accumulation time of 1200 s was used for further studies.

In order to optimize the proposed voltammetric method, several instrumental parameters such as reduction potential (applied before scanning step), scan rate, potential pulse amplitude and pulse duration time were investigated. For choice of adequate values, was considered the magnitude of the anodic peak current

(sensibility) and width of peak (W$_{1/2}$, selectivity) as reference for both ions evaluated. So, the best voltammetric response was obtained using −1.0 V (vs. Ag/AgCl), 10 mV s^{-1}, 75 mV and 10 ms for reduction potential, scan rate, potential pulse amplitude and pulse duration time, respectively.

3.4. Analytical performance

Using the best experimental conditions for analysis of the studied ions, an analytical curve for Cadmium(II) and Lead(II) ions was constructed in aqueous solution with the set of optimum conditions summarized in Table 2.

Differential pulse stripping voltammograms were carried out after accumulation of the ions at open circuit potential in a solution containing 5.0×10^{-9}–1.0×10^{-5} mol L^{-1} of both ions evaluated. Differential pulse voltammograms for different Cd(II) and Pb(II) concentrations are presented in Fig. 6.

The anodic peak currents obtained for the carbon paste electrode modified with biochar was linearly proportional to the concentration in a range of 2.5×10^{-7}–5.0×10^{-5} mol L^{-1} and 5.0×10^{-8}–1.0×10^{-5} mol L^{-1} for Cd(II) and Pb(II), respectively. Limits of detection (three times the signal blank/slope (Miller and Miller, 1993)) of 6.9×10^{-8} mol L^{-1} and 9.8×10^{-9} mol L^{-1} were found for Cd(II) and Pb(II), respectively. For high concentrations of Cd(II) or Pb(II), a deviation from linearity was observed indicating a saturation of the available sites on the electrode surface (Souza et al., 2011; Bard and Faulkner, 1980; Bergamini et al., 2006). In addition, a relative standard deviation less than 4.6% (n = 5) was obtained for the same surface after preconcentration in solution containing 5.0×10^{-6}–1.0×10^{-6} mol L^{-1} for Cd(II) and Pb(II), respectively. Using different electrode surfaces a relative standard deviation less than 8.2% was found. This variation is attributed to aleatoric variations present in the carbon paste preparation procedure. In this way, the results demonstrate that the proposed sensor shows good repeatability and reproducibility.

3.5. Interfering studies and application of the proposed method

The effect of potential interferents of several ionic species in the voltammetric response for Pb(II) and Cd(II) at fixed concentration was carried out. The concentration of the analytes and the interfering ions were chosen based on limit established by CONAMA for maximum levels for discharge of the effluent in water bodies. The species evaluated, its concentration used and the percent signal recovery are shown in Table 3.

It was observed that the presence of several concomitant anions such as Cl$^-$, NO$_3^-$ and SO$_4^{2-}$ at limit concentration showed only little effect on the voltammetric response for both evaluated ions, causing a variation smaller than 8.0% in the voltammetric peak currents. These results suggest that there are no effective interaction between these anions with analytes and/or modifier agent (biochar). A slight negative variation in the anodic peak current was
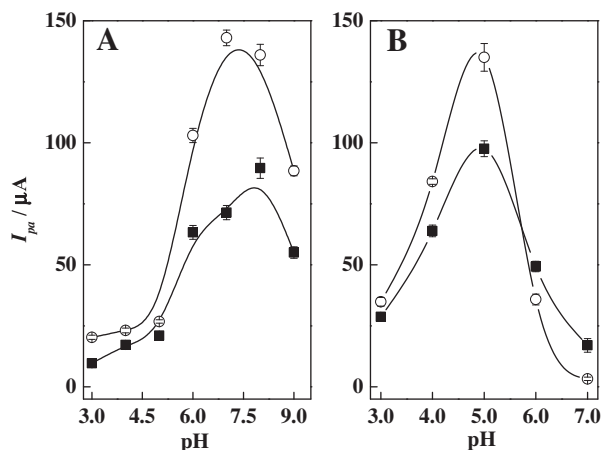

Fig. 5. Effect of pH of the preconcentration solution (A) and of solution used for voltammetric measurements (B) on the anodic peaks currents of Pb(II) and Cd(II) using a CMPE with 25% w/w of biochar P3. Error bars are standard deviations corresponding to three replicates obtained for different electrode surfaces.

Table 2
Optimized parameters for Cd(II) and Pb(II) determination using the carbon paste electrode modified with biochar (sample P3) by DPAdSV.

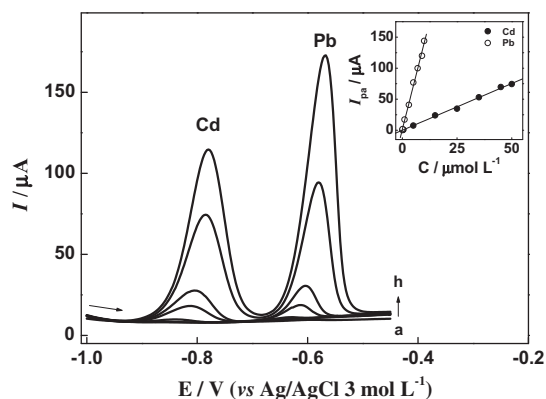| Parameter	Evaluated range	Optimized value
Modifier content	0–30% (w/w)	25% (w/w)
pH of preconcentration step	3.0–9.0	7.0
pH of measurement step	3.0–7.0	5.0
Preconcentration time	0–1800 s	1200 s
Solution of cleaning (time of immersion)	0–300 s	240 s
Scan rate	5–50 mV s^{-1}	20 mV s^{-1}
Potential pulse amplitude	5–150 mV	75 mV
Time of pulse duration	5–100 ms	10 ms

Fig. 6. DPAdSV of Cd(II) and Pb(II) with different concentrations at CPEM modified with 25% biochar P3 in phosphate buffer solutions (pH 5.0) after preconcentration by 1200 s in solution (pH 7.0) containing concentrations varying between 2.5×10^{-7} mol L^{-1} (a) and 5×10^{-5} mol L^{-1} (h) for Cd(II) ions and 5.0×10^{-8} mol L^{-1} (a) and 1.0×10^{-5} mol L^{-1} (h) for Pb(II) ions. The respective analytical curves are shown in detail.

Table 3
Interference studies of some ions in the Cd(II) and Pb(II) recovery under the optimized DPAdSV conditions.

Concomitant ions	C/ppm	C/mol L^{-1}	Signal recovery (%)	
			Cd(II)	Pb(II)
Tin(II)	4.0	3.4×10^{-5}	48.7	13.0
Chloride	1.0	2.8×10^{-5}	90.9	96.2
Nitrate	20.0	2.4×10^{-4}	94.5	99.2
Sulfate	1.0	7.0×10^{-6}	91.7	92.0
Iron(III)	15.0	2.7×10^{-4}	12.5	26.9
Manganese(II)	1.0	1.8×10^{-5}	83.8	98.3
Copper	1.0	1.6×10^{-5}	6.5	24.1
Nickel	2.0	3.4×10^{-5}	15.7	97.1
Zinc	5.0	7.6×10^{-5}	49.6	78.4
Mercury(II)	0.01	5.0×10^{-8}	93.7	99.3
Chromium(III)	0.5	9.6×10^{-6}	97.9	93.4
Chromium(VI)	0.5	9.6×10^{-6}	130.3	103.2

Cadmium and Lead concentrations fixed at 1.8×10^{-6} and 2.4×10^{-6} mol L^{-1}, respectively.

observed in the presence of manganese II and chromium III ions. These results shown that these ions do not exhibit an effective competition with the analytes by active sites of the modifier. The absence of the interference in presence of Mercury ions can be explained due its low concentration when compared to Pb(II) and Cd(II) ions. A significant decrease in the anodic peak currents was observed in the presence of Sn(II), Fe(III), Cu(II), Zn(II) and Ni(II) ions demonstrating that the modifier (biochar) is able to form complex with other metallic species besides the Cadmium(II) and Lead(II) ions. Nevertheless, interference effect observed is constant and it could be minimized by using of standard addition procedure.

In order to verify the efficiency of this approach, the voltammetric determination of Pb(II) and Cd(II) ions was realized in a simulated effluent spiked with analytes at concentration limit established of Brazilian legislation. Recoveries from 93.8% to 106.3% were obtained for both ions evaluated. This result reveals that Cd(II) and Pb(II) can be reliably determined by the proposed method even in the presence of interfering ions when the standard addition method is used.

4. Conclusions

Electroanalytical techniques could provide several information about properties adsorption of biochars for electroactive probe.

In addition, the use of carbon paste electrode modified with biochar can be a promising tool for construction of analytical sensors. Sensor developed was able to detect evaluated ions in real samples such as wastewater, by using a simple, rapid and economic way than other electroanalytical methods. By other hand, the manuscript offers a voltammetric method combined with the use of a composite electrode of simple preparation as an alternative probe for evaluate biochar's hability in preconcentration of the electroactive ions such as Lead and Cadmium.

References

Bard, A.J., Faulkner, L.R., 1980. Electrochemical Methods: Fundamentals and Applications, second ed. John Wiley & Sons, New York.

Beesley, L., Marmiroli, M., 2011. Biochar production potential in Ghana – a review. Environ. Pollut. 159, 474–480.

Bergamini, M.F., Vital, S.I., Santos, A.L., Stradiotto, N.R., 2006. Lead ions determination in ethanol fuel by differential pulse anodic stripping voltammetry using a carbon paste electrode modified with ion-exchange resin Amberlite IR120. Eclet. Quim. 31, 45–52.

Chen, B.L., Zhou, D.Q., Zhu, L.Z., 2008. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. Environ. Sci. Technol. 42, 5137–5143.

Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M.B., Hay, A.G., 2011. Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. Bioresour. Technol. 102, 8877–8884.

CONAMA, Conselho Nacional de Meio Ambiente, Resolução CONAMA No. 396, 04.2008.

Dong, X., Ma, L.Q., Li, Y., 2011. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. J. Hazard. Mater. 190, 909–915.

Duku, M.H., Gu, S., Hagan, E.B., 2011. Biochar production potential in Ghana – a review. Renew. Sust. Energy Rev. 15, 3539–3551.

Erfurth, E.M., Gerhardsson, L., Nilsson, A., Rylander, L., Schutz, A., Skerfving, S., Borjesson, J., 2001. Effects of lead on the endocrine system in lead smelter workers. Arch. Environ. Health 56, 449–455.

Fogg, A.G., Wang, J., 1999. Terminology and convention for electrochemical stripping analysis. Pure Appl. Chem. 71 (5), 891–897.

Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M., 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). Environ. Sci. Technol. 44, 1247–1253.

Lehmann, J., Joseph, S., 2009. Biochar for Environmental Management – Science and Technology. Earthscan, London.

Mašek, O., Brownsort, P., Cross, A.S., 2013. Influence of biochar production conditions on the yield and environmental stability of biochar. Fuel 103, 151–155.

Matusiewicz, H., Krawczyk, M., 2006. Determination of cadmium and lead in reference materials by volatile species generation with in situ trapping flame atomic absorption spectrometry. Microchem. J. 83, 17–23.

Meyer, S., Glaser, B., Quicker, P., 2011. Technical, economical, and climate-related aspects of biochar production technologies: a literature review. Environ. Sci. Technol. 45, 9473–9483.

Miller, J.C., Miller, J.N., 1993. Statistics for analytical chemistry, third ed. Ellis Horwood, New York.

Souza, L., Calegari, F., Zarbin, A., Marcolino-Junior, L., Bergamini, M.F., 2011. Voltammetric determination of the antioxidant capacity in wine samples using a carbon nanotubes modified electrode. J. Agric. Food Chem. 59, 7620–7625.

Spokas, K.A., 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. Carbon Manage. 1–2, 289–303.

Sun, K., Keiluweit, M., Kleber, M., Pan, Z., Xing, B., 2011. Sorption of fluorinated herbicides to plant biomass-derived biochars as a function of molecular structure. Bioresour. Technol. 102, 9897–9903.

Uchimiya, M., Lima, I.M., Klasson, K.T., Chang, S., Wartelle, L.H., Rodgers, J.E., 2010. Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. J. Agric. Food Chem. 58, 5538–5544.

Zhang, G., Zhang, Q., Sun, K., Liu, X., Zheng, W., Zhao, Y., 2011. Sorption of simazine to corn straw biochars prepared at different pyrolytic temperatures. Environ. Pollut. 159, 2594–2601.