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Biochar prepared from castor oil cake at different temperatures: A voltammetric study applied for Pb^{2+}, Cd^{2+} and Cu^{2+} ions preconcentration

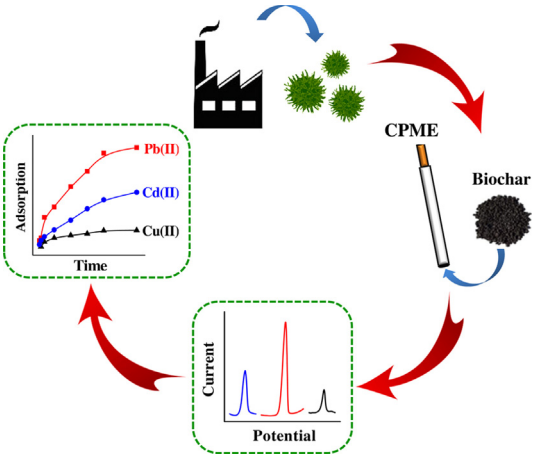
Cristiane Kalinke[a], Antonio Sálvio Mangrich[b,c], Luiz H. Marcolino-Junior[a], Márcio F. Bergamini[a,*]

[a] Laboratório de Sensores Eletroquímicos (LabSensE), Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81.531-980 Curitiba, PR, Brazil
[b] Laboratório de Química de Húmus e Fertilizantes, Departamento de Química, Universidade Federal do Paraná (UFPR), CEP 81.531-980 Curitiba, PR, Brazil
[c] Instituto Nacional de Ciência e Tecnologia de Energia e Ambiente (INCT E&A/CNPq), Brazil

HIGHLIGHTS

- Effect of temperature of pyrolysis in the adsorption properties of biochar.
- Electroanalytical application of biochar obtained from castor cake oil under different temperature pyrolysis.
- Simple and feasible voltammetric procedure for evaluation of adsorption of Pb(II), Cd(II) and Cu(II) ions by biochar.
- Carbon paste electrodes for evaluation of biochar ability in the preconcentration of electroactive cations.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar is a carbonaceous material similar produced by pyrolysis of biomass under oxygen-limited conditions. Pyrolysis temperature is an important parameter that can alters biochar characteristics (e.g. surface area, pore size distribution and surface functional groups) and affects it efficacy for adsorption of several probes. In this work, biochar samples have been prepared from castor oil cake using different temperatures of pyrolysis (200–600 °C). For the first time, a voltammetric procedure based on carbon paste modified electrode (CPME) was used to investigate the effect of temperature of pyrolysis on the adsorptive characteristics of biochar for Pb(II), Cd(II) and Cu(II) ions. Besides the electrochemical techniques, several characterizations have been performed to evaluate the physicochemical properties of biochar in function of the increase of the pyrolysis temperature. Results suggest that biochar pyrolized at 400 °C

* Corresponding author.
E-mail addresses: bergamini@ufpr.br, marciobergamini@gmail.com (M.F. Bergamini).

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(BC400) showed a better potential for ions adsorption. The CPME modified with BC400 showed better relative current signal with adsorption affinity: Pb(II) > Cd(II) > Cu(II). Kinetic studies revealed that the pseudo-second order model describes more accurately the adsorption process suggesting that the surface reactions control the adsorption rate. Values found for amount adsorbed were 15.94 ± 0.09; 4.29 ± 0.13 and 2.38 ± 0.39 $\mu g\, g^{-1}$ for Pb(II), Cd(II) and Cu(II) ions, respectively.

1. Introduction

Biochar can be defined as a carbonaceous material similar to charcoal produced by pyrolysis of biomass under oxygen-limited conditions [1,2]. It is a porous grained material, with high carbon content and largely resistant to decomposition [3]. The peripheral structure (surface) of biochar exhibits a high amount of chemical groups, which can be used as a sorbent for different compounds, such as metallic ions and organic molecules [4–6]. Moreover, it has an inert internal structure, which can act in carbon sequestration as well as organic soil conditioner [7,8]. In this sense, several works have been reported the use of biochar, obtained from several feedstock and prepared using different pyrolysis conditions, for soil amendment improving agricultural production by nutrient retention, sorbing of organic/inorganic pollutants besides that it is a recalcitrant carbon stock [9–11].

In general, experimental conditions used for biochar production are low temperatures (<700 °C) [1], slow pyrolysis with heating rates of 1–100 °C min^{-1} and long residence times (minutes–hours) [12]. Pyrolysis conditions and features of the feedstock can alter the physical and chemical properties of the final product (biochar) such as concentrations of elemental constituents, density, pore size distribution and surface characteristics, among others [13–15].

Different feedstock, mainly of ligno-cellulosic materials, such as peanut hull [13], pine wood [16], wheat straw [17], corn stover [18] and several others [9] have been used for biochar preparation. Although, biomass composition presents different thermal behavior, the temperature used in the pyrolysis process can be considered the most important condition and it can influence on the final product characteristics [1,19].

Biochar is used for soil amendment or remediation of contaminated soils and waters by organic and/or inorganic species [20–27], for bio-oils hydrocracking and hydrodeoxygenation upgrading processes [28,29], for improving air quality [30,31] and for developing catalysts [32,33]. The highly functionalized surface of biochar promotes an elevate sorption capacity when compared to other adsorbent materials such as activated carbon [5]. Besides of agricultural applications, features of biochar surface can be explored in the development of electrochemical devices. Suguihiro et al. [34] were pioneers in the use of biochar for development of electrochemical sensors for determination of metallic cations. The use of biochar prepared in a narrow temperature range (300–350 °C) as electrode modifier promoted high selectivity and sensitivity for preconcentration and determination of cadmium and lead ions in industrial effluents samples. At the same way, Oliveira et al. [35] related the determination of Cu(II) ions on spirit drinks samples and Kalinke et al. [36] described a method for paraquat determination in coconut water and natural water samples. Moreover, the use of biochar as support material for preparation of mercury, antimony and bismuth nanostructures was reported. Those methodologies were applied for determination of zinc ions in pharmaceutical formulations [37], paraquat in fruit juices [38] and lead ions in ceramic dishes [39], respectively. Although biochar has called attention for development of electroanalytical methods, there are no information about a systematic study using a voltammetric technique for evaluation of biochar adsorption capacity.

Based on the above-cited works, which have explored successfully the quantitative aspects in the use of biochar on electroanalytical applications, the main goal of the present work is the use of voltammetric tools to verify the effect of pyrolysis temperature of biochar samples prepared from castor oil cake and develop a protocol to investigate the mechanisms involved in the interaction between biochar surface and metallic ions (Pb(II), Cd(II) and Cu(II)) by using of kinetic models of pseudo-first and pseudo-second order.

2. Materials and methods

2.1. Apparatus

Differential Pulse Adsorptive Stripping Voltammograms (DPAdSV) measurements were performed in a potentiostat/galvanostat μAUTOLAB Type III (EcoChemie) connected to a microcomputer controlled by software (NOVA1.10.4®) for data acquisition and experimental control. All the voltammetric measurements were carried out in a 10 mL glass cell at 25 °C, with a three-electrode configuration: carbon paste modified electrode as the working electrode, Ag/AgCl KCl 3.0 mol L^{-1} as the reference electrode and platinum wire auxiliary electrode.

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 and solutions containing different concentrations of Pb(II), Cd(II) and Cu(II) ions were prepared by dilution.

2.3. Biochar preparation and characterization

Biochar samples were obtained from biomass pyrolysis, utilizing castor oil cake feedstock. First, the material was sieved to obtain particle size between 177 to 420 μm, and then was subjected to the pyrolysis process in a EDG FT-40 tubular furnace, with conditions programmed of heating rate of 5 °C min^{-1}, during 60 min and final temperatures ranging between 200 and 600 °C.

The material characterization was realized using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC), performed on a Netzsch STA 449F3, under nitrogen flow, until 1000 °C. 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 400 cm^{-1} with a resolution of 4 cm^{-1} and Boehm titrations [40] using a Metrohm 780 pH meter. Elemental composition was determined using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. Surface area and pore size distribution of samples was performed on a Quantachrome porosimeter, New 1200 model, with sorption of nitrogen gas, using the B.E.T. method (Brunauer, Emmett and Teller).