Evaluation of the capacity of copper(II) adsorption on surface functional groups of natural materials using carbon paste electrodes

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Abstract. A methodology was developed to evaluate the capacity of heavy metal ions adsorption on particulate samples using carbon paste electrodes. These were prepared by mixing spectroscopic grade graphite powder, the sample and using silicon oil as a binder. Diatomite and compost samples were used as a model of inorganic and organic natural product, respectively. In order to probe the methodology, copper(II) was used as cation model. The protocol involves the in situ monitoring of copper(II) adsorption using temporary open-circuit potential measurements. Copper(II) adsorbed on each sample dispersed in carbon paste was determined in 0.1 mol L⁻¹ Na₂SO₄ by cyclic voltammetry. Functional groups of diatomite and compost responsible of adsorption were determined by Fourier-transform infrared spectroscopy. Besides, adsorption capacity of diatomite was exploited to electrochemical determination of copper(II) by differential pulse anodic stripping voltammetry.

1. Introduction
Owing to heavy metal contamination of the environment, sustainable materials have been used to mitigate their impact through adsorption process. Natural or agricultural products and their wastes have been used as low-cost adsorbents [1]. These adsorbents contain in its surface a diversity of functional groups that allow the binding and retaining of many heavy metal ions. The adsorbent materials that have been studied most extensively include the following: activated carbon, agricultural solid wastes (e.g. fruit cortex), clay minerals, compost, oxides, textile fibers and zeolites [1-3]. The surface properties of adsorbents vary considerably according to origin and method of making or handling [3]. Hence, it is necessary to evaluate the performance of the adsorption process of metal cations for each material. In comparison with various conventional spectroscopic methods which require periodic determination of ions, solid state electrochemical methods can provide an alternative approach. Since a decade ago [4], carbon paste electrodes has been proposed as a method for study the
ion-exchange phenomenon in zeolites. This phenomenon is a form of sorption along with adsorption and absorption processes. Thus, taking advantage of carbon paste electrodes for the study of the interactions of powder solids with soluble species, herein, its use is proposed to study adsorption of copper(II) on natural adsorbents. Experimental

1.1. Chemicals, solutions and samples
All reagents (analytical grade) were used as received. All solutions were prepared with deionized water (DI, 18.2MΩcm) and oxygen was removed by bubbling nitrogen gas through the solutions. Diatomite sample was obtained from a Colombian mine in Valle del Cauca, and compost sample, composed by chicken manure and sawdust in a proportion of 3:1, was obtained from Biorgánicos S.A Company, Antioquia, Colombia. Both samples were sieved through Tyler screens.

1.2. Preparation of electrodes
Modified carbon paste electrodes were prepared by mixing of graphite powder (99.9995%, APS 2-15 micron) with diatomite or compost samples and silicon oil (C7H8OSi, d25°C = 0.963gcm⁻³) until obtaining a uniformly paste. The solids/binder ratio was 70/30 and the sample/graphite ratio was ¼. The amount of silicone oil binder in the paste has been used previously [4, 5], because it produces a suitable consistency of peanut butter that allows its handling. Unmodified carbon paste electrode (UCPE) was prepared in the above way but without adding sample to the mixture. Each paste was packed into a insulin syringe, and the electrodes were used 1 day after their preparation. This protocol has been found to be useful to obtain reproducibility and repeatability because it ensures a stabilization of the paste due to its self-homogenization [5]. Prior to each experiment, the electrode surface was renewed by pushing out of some of paste and smoothing the surface on a paper sheet.

1.3. Characterization of samples
The morphology of the diatomite sample was observed by a scanning electron microscope (SEM) FEI Quanta 650 FEG coupled with Energy Dispersive Spectroscopy (EDS), an accelerating voltage of 10keV was used. Quantitative X-ray fluorescence (XRF) analysis of diatomite sample was carried out in a sequential WD spectrometer S8 Tiger, Bruker. The surface functional groups of diatomite and compost samples were characterized by a Bruker Tensor 27 infrared spectrometer (FTIR).

1.4. Electrochemical experiments
The electrochemical measurements were performed in a three-electrode cell. Modified and unmodified carbon paste electrodes were used as working electrode, a graphite rod (99.9995%) and Ag|AgCl|3molL⁻¹ KCl were used as counter and reference electrode, respectively. Electrochemical measurements were carried out using a Metrohm Autolab PGSTAT302N potentiostat/galvanostat controlled by Nova 1.11™ software. All experiments were performed in a 60mL cell at room temperature.

1.5. Adsorption tests
Methodological steps followed for evaluating copper(II) adsorption properties of the diatomite and compost samples dispersed in carbon paste electrodes are given as follows. First, to simulate metal adsorption, CPE was dipped in a copper(II) aqueous solution under stirring, then CPE was removed from the solution and rinsing with DI to remove the excess of copper(II) solution from electrode. The time to reach the maximum adsorption capacity was evaluated by open-circuit potential measurements, i.e., measuring the potential of electrode against the reference electrode using the electrometer of potentiostat. Afterwards, CPE was transferred to an electrochemical cell containing supporting electrolyte and it was characterized by cyclic voltammetry.
2. Results and discussion

2.1. Copper(II) adsorption on diatomite and its quantification

Figure 1(a) shows a typical SEM micrograph of diatomite sample used to modify CPE for metal sensing application. It exhibits highly porous cylinder-like shape with an average pore size of 1μm. Hollow cylindrical structures with diameters in the range of 15-20μm, and height between 20 and 40μm were observed. These specimens were identified taxonomically belonging to Aulacoseira granulata species [6]. The main oxides of sample, analyzed by XRF, were 85.0% SiO₂, with 7.4% Al₂O₃ and 3.6% Fe₂O₃.

To ensure an appropriate contact time for equilibrium adsorption, UCPE and CPE-diatomite were immersed in 10⁻³ molL⁻¹ copper(II) solution for 30 min under stirring. Once completed, each electrode was rinsed with DI and transferred into a new solution containing 0.1 molL⁻¹ Na₂SO₄. In order to evaluate the adsorption capacity of diatomite towards copper(II), a potentiostat was used to linearly vary the potential from OCP in negative-going direction at a constant scan rate, and the resulting current was measured (Figure 1(b)). Background current was negligible in the absence of diatomite. Conversely, current was progressively increased from OCP for diatomite dispersed in carbon paste. A cathodic peak (C₁) appeared as a result of the copper(II) reduction

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\text{Cu}^{II}_{\text{(ads)}} + 2e^- \rightarrow \text{Cu}^0
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where subscript (ads) means the adsorbed species on the diatomite surface. On reverse scan, an anodic stripping peak (A₁) was observed, which corresponds to metallic copper oxidation [7]. To determine surface functional groups responsible of copper(II) adsorption, an infrared analysis was performed. FTIR spectrum (Figure 1(c)) shows absorption bands at (3391, 1637, 1041, 791 and 451) cm⁻¹. Both stretching and bending vibrations of the −OH at (3391 and 1637) cm⁻¹ are due to the formation of hydrogen bonds between the −OH group and the H₂O molecules [8,9]. Peaks at (1041 and 451) cm⁻¹ were assigned to siloxane (−Si−O−Si−) group stretching, and the peak at 792 cm⁻¹ was ascribed to silanol (SiO−H) vibration. Hence, copper(II) adsorption properties of diatomite can be attributed to silanol groups [9].

Figure 1. (a) Typical SEM image and the corresponding EDS analysis of diatomite. (b) Cyclic voltammograms (v=0.10 Vs⁻¹) of both (i) UCPE and (ii) diatomite dispersed in carbon paste obtained in 0.1 molL⁻¹ Na₂SO₄ at pH 3 after adsorption test in 10⁻³ molL⁻¹ copper(II). (c) FTIR spectrum of diatomite.

Above result is applicable to trace copper determination by differential pulse voltammetry taking advantage of copper(II) accumulation capacity on CPE-diatomite. Accumulation step was performed without agitation in different acid media. Figure 2(a) shows stripping peaks obtained from pH 2 to 6. The stripping peak currents increase from pH 2 to 4, at lower acidity the peak current decreases significantly. This behavior can be attributed to the different speciation of functional groups formed on
the surface of diatomite and the competitive absorption of protons. Figure 2(b), (c) shows the stripping voltammograms of the copper(II) in range from 1 to 10ppm and the respective calibration curve. The peak current increases proportionally with the concentration of copper(II) with a linear regression equation of $I_{pa}(\mu A) = -0.1582 + 1.0762$ copper(II)(ppm), correlation coefficient of 0.9981. The detection and quantification limits were 0.35 and 1.07ppm, respectively.

![Figure 2. Differential pulse voltammograms of (a) 5ppm copper(II) obtained at different pH values, and (b) in different copper(II) concentrations at pH 3, as indicated in the figure legends. (c) Calibration curve for copper(II) concentration between 1 to 10ppm. Supporting electrolyte: 0.1molL$^{-1}$ Na$_2$SO$_4$; preconcentration time: 120s, amplitude: 0.050V.](image)

2.2. Compost properties in sorption of copper(II)
Compost samples from various composting time periods were dispersed in carbon paste. Samples were taken at 0, 20, 43 and 91 day intervals of composting. Open-circuit potential measurements were used to determine the time needed to reach complete adsorption of copper(II) on the surface of compost samples. These measurements were compared to the response of UCPE in 10$^{-3}$molL$^{-1}$ copper(II). Figure 3(a) shows the OCP evolution upon immersion of each electrode in copper(II) aqueous solution. A sudden variation of OCP to less positive values was observed upon UCPE interaction with the solution during the first 30s. Conversely, OCP shifted progressively towards more positive values for all compost samples. The stable state was reached around 500s. This indicates the elapsed time to complete copper(II) adsorption on samples. Monitoring was repeated 3 times for each one of the electrodes, with a variation of ± 0.003V. It is worth noting that OCP values increases as the composting time increases.

![Figure 3. OCP measurements of UCPE and compost samples of (i) 0, (ii) 20, (iii) 43 and (iv) 91 days of composting dispersed in carbon pastes in 10$^{-3}$molL$^{-1}$ copper(II).](image)
Therefore, the capacity of copper(II) adsorption on compost samples was evaluated after 500s of immersion in $10^{-3}\text{molL}^{-1}$ copper(II). Figure 4(a) shows the cyclic voltammograms of adsorbed copper on compost samples. The electrochemical behavior of copper adsorbed on compost samples is similar to that on diatomite, however, background current is higher in the former. Current peak decreases as the composting time of samples increases until reach 43 days, to then increase slightly for the sample of 91 days of composting. The magnitude of current peak is related to the adsorption capacity, as has been proposed elsewhere [10]. In order to investigate the cause of this behavior, infrared spectra of compost samples were obtained. FTIR absorption spectra in the range of 2000 to 4000cm$^{-1}$ are given in Figure 4(b). The broad band in the range of 3000 to 3690cm$^{-1}$ corresponds to vibrations of adsorbed OH groups, while the peak at 2920cm$^{-1}$ is assigned to the asymmetric and symmetric aliphatic C–H stretching of CH$_2$ groups ascribed to humic acids [11]. Surprisingly, the intensity of this last band varies in the same way as the stripping current peak. The higher anodic current peak for copper oxidation, the higher FTIR band is achieved (Figure 4). Hence, depending on the time composting, compost showed ability to adsorb copper(II) in different degrees, which was high for the compost with high hydroxyl and humic acids content. A detailed investigation of interaction or bonding of metal ion with the functional groups formed on the surface of natural samples here studied is beyond the aim of this work. Nonetheless, a paper describing the adsorption of silver ions on different functional groups like amino and carboxyl using carbon paste electrodes has been published recently [12].

**Figure 4.** (a) Cyclic voltammograms ($v=0.10\text{Vs}^{-1}$) of compost samples dispersed in carbon pastes obtained in 0.1molL$^{-1}$ PBS at pH 7 after immersion of compost in $10^{-3}\text{molL}^{-1}$ copper(II) for 500s. b) FTIR spectra at different composting times: (i) 0, (ii) 20, (iii) 43 and (iv) 91 days.

3. Conclusions
A methodology was developed to study adsorption of metal ions on both inorganic and organic surface functional groups, by using carbon paste electrodes. Diatomite and compost samples were used as models of inorganic and organic compounds to illustrate the methodology. The results showed that the method is able to evaluate the capacity of adsorption of heavy metal ions such as copper(II). In-situ open-circuit potential measurements allow rapid estimates of the adsorption equilibrium time. On the other hand, voltammetry provides experimental data (e.g. current peak or charge) that can be used to measure quantitatively the degree of adsorption of metal ions.

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