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Ionic liquid mediated extraction, assisted by ultrasound energy, of available/mobilizable metals from sediment samples

Silvana M. Álvarez, Natalia E. Llamas, Adriana G. Lista, Mónica B. Álvarez *, Claudia E. Domini *

Departamento de Química, Universidad Nacional del Sur, Instituto de Química del Sur, INQUISUR (UNS-CONICET), Sección Química Analítica, Av. Alem 1253, (B8000CPB) Bahía Blanca, Argentina

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ABSTRACT

A new extraction method for metals from sediment samples was developed. In this procedure, the chelating agent EDTA was combined with a minimal amount of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (Bmim[BF_4]), assisted by ultrasound energy. The available analytes –Cd, Cr, Cu, Ni, Pb and Zn– were extracted under optimal conditions for a 12.5 ratio (extractant volume/sample mass) with 0.005 mol L^{-1} EDTA solution, 0.1 mol L^{-1} $NaHCO_3$, 5.0 mmol L^{-1} Bmim[BF_4] and 7.0 min of sonication time, using an ultrasonic bath (output power of 160 W). The best extractions were obtained with 100 W (power dissipated in the liquid). These conditions were obtained applying the univariate method. It is important to highlight that the conventional method (extraction with 0.05 mol L^{-1} EDTA solution only) consumes 6 h to extract available metals from sediment samples selectively, and with the proposed procedure the extraction time is noticeable reduced to 7.0 min. Extractable metal concentrations obtained were measured by flame atomic absorption spectrometry. The results showed good agreement with those obtained by the conventional method using a Student's paired *t*-test.

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1. Introduction

Heavy metals are natural constituents of the earth crust. Although they can be normally found in sediments, waters and even in living organisms, anthropogenic releases can increase their concentrations to unacceptable levels. Since heavy metals cannot be degraded they have become persistent environmental pollutants, producing acute or chronic toxicity problems [1,2]. Metals are distributed throughout the phases of the sedimentary material. They are associated by different mechanisms including ion exchange, adsorption/desorption, precipitation and complexation processes. The physicochemical variables, organic matter decomposition, leaching and ion exchange processes, affect the bonding forms under which those metals are linked and greatly influence metallic pollutants behaviour [3,4]. The most available/mobilizable form of metals corresponds to the exchangeable fraction that can be released by merely changing the ionic strength of the related aquatic medium. Thus, total metal concentrations sometimes are not useful to obtain information relevant to environmental studies aimed to evaluate the impact of anthropogenic or natural pollution sources.

In environmental sciences, selective leaching of sediments with chemical extractants (or mixtures) intends to establish which fractions of an element that, being previously held with a lower degree of mobility, have reached a more labile form by interaction with the aquatic/geochemical environment. The use of partial dissolution techniques has its genesis in geochemical exploration studies. Some extraction methodologies have been found in the literature to study metal mobility in sediments [5–7]. A single extraction procedure using 0.05 mol L^{-1} ethylenediaminetetraacetic acid (EDTA) has been proposed by the Standards, Measurements & Testing Programme (formerly BCR) of the European Commission in order to assess metal availability [8]. These methods are important to detect anomalous concentrations of metals and enable to perform a rapid assessment to check conformity to legislation [9].

EDTA is a weak organic acid with complexing/chelating ability to 'capture' divalent and trivalent cations. It is commonly used in soil analysis to determine micronutrients (Cu, Fe, Mn, Zn) available to plants. The EDTA extraction procedure removes metals associated with certain fractions of soils or sediments, which have been incorporated in various degrees through specific adsorption mechanisms. EDTA mainly takes away metals from the exchange sites of both organic and inorganic complexes in soils or sediments, without attacking the crystal structure of the silicate mineral [9–11].

In selective chemical extractions, high concentrations of matrix components are co-extracted at the same time that the

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* Corresponding authors.
E-mail addresses: malvarez@criba.edu.ar (M.B. Álvarez), cdomini@criba.edu.ar (C.E. Domini).

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target metals. Separation and preconcentration steps are often required prior to the determination of trace metals in environmental samples, taking advantage of the lower final extractant volumes to improve the analyte detection limit [12]. These pretreatment steps in order to remove matrix components from the trace metals have been reported in the literature [13,14]. Recently, Bagheri et al. [15] developed a solid phase extraction method to separate and concentrate trace amount of Cd(II) and Cu(II) from environmental samples, Zhao et al. [16] presented a dual-cloud point extraction procedure for simultaneous preconcentration and separation of heavy metal ions such as Cd(II), Co(II), Ni(II), Pb(II), Zn(II) and Cu(II) in water samples by using inductively coupled plasma optical emission spectrometry (ICP-OES) as detection technique.

Classical methods used to extract metals from complex solid samples are often tedious, labour intensive and time-consuming. Therefore, microwave extraction [17,18] and ultrasonic assisted extraction [18–21] have been used for the last years to accelerate these processes successfully.

In addition, a conflicting situation came out because the majority of the analytical methods also generate environmental pollutants. Green chemistry associated with metal extraction focuses on minimizing the environmental impact caused by the nature and quantity of extractants, as well as, the energy used in the process [22]. In this sense, it is desirable to design methods and chemical products that reduce or eliminate the use and generation of hazardous substances. In recent years, ionic liquids (ILs) have been used instead of organic solvents in extraction and micro-extraction procedures [23–26]. ILs constitute a group of organic salts consisting of a combination of different anions and organic cations, liquid at room temperature. The physicochemical properties of the ILs depend on the nature and size of the cation and the anion, which confer unique characteristics, thus these reagents are also termed 'designed extractants' [27]. The most important characteristics include their low vapour pressure, good thermal stability, high viscosity, dual natural polarity and a wide range of miscibility with water and other organic solvents [24]. Martinis et al. [26] affirmed that several parameters (e.g. partition coefficient, diffusion coefficient of solute, solubility of extraction solvent, liquid viscosity among others) are involved in the metal extraction mechanisms. The metal-ion partitioning process is based on the nature of the IL, metal ion and ligand. For example, IL structural variations (lengths of alkyl groups) would greatly influence in the selectivity and efficiency of the process. Both partition and ion-exchange mechanisms play important roles in the extraction process. These two mechanisms may generally work together to enhance IL's selectivity and efficacy for metal extraction.

To the best of our knowledge, up to present, there are no reports in which ILs were applied to evaluate metal speciation or fractionation in sediment samples.

Atomic spectrometric techniques are appropriate for the determination of metals at trace and sub-trace levels. The determination by flame atomic absorption spectrometry (FAAS) has a number of advantages including high selectivity, speed and fairly low operational cost [28].

The primary aim of this work was to test and evaluate a new mild extraction methodology combining ionic liquids and ultrasound energy to rapidly assess availability of cadmium, chromium, copper, nickel, lead and zinc in sediment samples. The proposed procedure constitutes a simpler, faster and efficient analytical method. It reduces significantly the extraction time of the available metal forms. In this way, a rapid evaluation of the trace elements associated to mobilizable fraction in sediments is achieved, mainly to check compliance to legislation [9].

2. Experimental

2.1. Reagents and instrumentation

All chemicals and reagents were of analytical grade. Doubly distilled water was used throughout. All glass and plastic ware was soaked in 10% HNO_3 for 24 h before use. The washing was completed with doubly distilled water. The ionic liquid 1-butyl-3-methyl-imidazolium tetrafluoroborate (Bmim[BF_4]) was purchased from Merck. Carlo Erba (Erbatron RSE) HF, HCl and HNO_3 were employed. Stock solutions of the analytes (1000 mg L^{-1}) were obtained from Carlo Erba Normex Standards. Multielement calibrant solutions of Cd, Cu, Ni, Pb and Zn were prepared in 0.5 mol L^{-1} HNO_3. A single element solution was employed for Cr analyses because instability of the signals was verified if this analyte is included in the multielement solution [29].

Atomic absorption measurements were performed with a Perkin-Elmer AAnalyst 200 spectrometer, equipped with single element hollow-cathode lamps for Cr, Cu, Ni and Pb. For Cd and Zn electrodeless discharge lamps were used. The instrument was operated at maximum sensitivity with an air-acetylene flame. Analytical lines (nm) and determination limits (μg mL^{-1}) were: Cd 228.8/0.02; Cr 359.3/0.15; Cu 324.8/0.08; Ni 341.5/0.12 Pb 283.3/0.34 and Zn 213.9/0.01.

Determination limits for the atomic spectrometric procedure were estimated from solutions containing the matrix components, i.e. simulating the composition of the solutions from each extraction step. Practical values were calculated as three times the IUPAC detection limit (defined as the ratio between three times the standard deviation of the blank signal (for $n = 10$) and the slope of the calibration line).

Co-extraction of elements in the leaching solutions may be a source of error due to inter-element interference effects. Analyte spiked samples of the digests, equivalent to sediment concentrations of 25 mg kg^{-1} and 50 mg kg^{-1}, were employed to evaluate possible matrix and inter-element interferences. No significant effects were observed at the concentration levels tested.

An ultrasonic bath, TESTLAB model TB 04 TA, 160 W ultrasonic power, 40 kHz frequency was employed. Three reference materials, certified for total metal concentrations, were used. MURST-ISS-A1, an Antarctic bottom sediment provided by the Italian Research Program in Antarctica, and two soils supplied by the National Institute of Standards & Technology (NIST), NIST-SRM-2709, a San Joaquin Valley soil, providing basal concentrations of the elements of interest and NIST-SRM-2711, a Montana soil with moderately high trace metal concentrations. Even though the NIST standard reference materials are not sediments, they were used to test the ability of the proposed method to deal with samples of different composition and larger concentration ranges.

2.2. Collection and pre-treatment of sediment samples

Metal extraction tests were conducted on sediment samples from the Bahía Blanca Estuary, located at the southern coast of the Buenos Aires province, in Argentina. The coastal-marine area comprises several ports and towns exceeding 300,000 inhabitants. The zone is constituted by several channels and is characterized by the presence of fine sand, silt and clay surface sediments. Tidal fluctuations of 4 m and the prevailing northwest winds created a strong current. Water exchange is influenced by a system of semidiurnal tides and freshwater contribution is limited to many small streams and the run-off water from an agricultural area (4200 km^2) as well as the input of municipal wastewater and direct industrial discharges [6].