



Selective extraction and preconcentration of chromium using *Moringa oleifera* husks as biosorbent and flame atomic absorption spectrometry

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ABSTRACT

In this study a new method for selective extraction and preconcentration of chromium in water using *Moringa oleifera* husks as the solid phase with a flow injection system and detection by flame atomic absorption spectrometry was developed. The behavior of Cr(III) and Cr(VI) adsorption onto *Moringa oleifera* husks allowed the selective separation of Cr(III) in the pH range of 7–9 and Cr(VI) in the pH range of 1–2. The operational variables of the preconcentration system were optimized through full factorial and Doehlert designs. The limits of detection for Cr(III) and Cr(VI) were 1.92 and 2.45 $\mu\text{g L}^{-1}$ and the precision were below 1.63% and 0.08%, respectively. Results for recovery tests using different water samples were higher than 88% for Cr(III) and 81% for Cr(VI).

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1. Introduction

Some metal species can exert high toxicity when present in their free ionic or combined forms. They can arise from natural or anthropogenic sources, the latter being responsible for high levels in various environmental compartments [1,2].

Among the metals largely used for industrial purposes, special attention should be given to chromium, which is used in a number of industrial processes such as stainless-steel production, leather tanning, electroplating and pigment fabrication. This metal is considered to be a serious environmental pollutant due to its poor storage conditions in some industrial activities and leakage to soils and waters [3].

In the environment, chromium is found in its two most stable oxidation states of Cr(VI) and Cr(III), which have different toxicity, mobility and bioavailability. Cr(VI) is known to be toxic to both plants and animals as well as potentially being carcinogenic, whereas Cr(III) is essential to human glucidic metabolism and exhibits much less toxicity and mobility [4,5].

Because of their widespread use in industry and the difference in toxicity, it is essential to develop analytical methods for quantifying the targeted two forms [6]. The determination of chromium species can be carried out using FAAS, GFAAS, ICP-OES and ICP-MS. However, the use of prior separation/preconcentration of the sample can aid in improving the determination of Cr(III) or Cr(VI) by these methods [7].

Techniques of sample preparation such as solid phase extraction (SPE) based on the selective or simultaneous retention of Cr(III) and Cr(VI) on sorbents is the most widely employed procedure for the

study of chromium speciation in water samples. Currently, one of the most important focuses in relation to studies on SPE for chromium speciation determination is the use of new solid sorbents.

Recently, our research group proposed new sorbent materials for SPE to determine heavy metals in aqueous and alcoholic samples, using natural adsorbents such as *Moringa oleifera* seeds [8–10]. As a continuation of these studies, the possibility of developing a sensitive and selective on-line FI-FAAS procedure for the preconcentration and separation of chromium species was investigated. The procedure is based on the selective retention of Cr(III) on *M. oleifera* husks at pH 7–9 and Cr(VI) at pH 1–2. It is worth noting the value of the development of analytical methods for the direct differentiate between trivalent and hexavalent species, especially due to the large difference in their toxicity. To date, there appears to have been no reports in the literature proposing the use of *M. oleifera* seeds without surface treatment in order to differentiate between these two species of chromium for analytical applications.

The multivariate optimization helped identify the variables that influence the separation system, quickly; reducing the number of experiments needed a relatively low cost. Full factorial designs are very useful for preliminary studies or in the initial steps of an optimization, while fractional designs are almost mandatory when the problem involves a large number of factors [11]. However, since only two levels are used, the models that can be fit to these designs are somewhat restricted. Consequently, if a more sophisticated model is required, as for the location of an optimum set of experimental conditions, then one must resort to designs for second-order models (response surface designs), which employ more than two factor levels to allow fitting of a full quadratic polynomial. In analytical chemistry, the response surface designs most used are symmetrical and describe a spherical experimental domain.

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The Doehlert design describes a spherical experimental domain and it stresses uniformity in space filling. Although this matrix is neither orthogonal nor rotatable, it does not significantly diverge from the required quality for effective use [12]. For two variables, the Doehlert design consists of one central point and six points forming a regular hexagon, and therefore situated on a circle. The number of levels is not the same for all variables. In a two-variable Doehlert design, for example, one variable is studied at five levels while the other is studied at only three levels. This property allows a free choice of the factors to be assigned to a large or a small number of levels. Different criteria can be used to assign the factors. As a general rule, it is preferable to choose the variable with the stronger effect as the factor with five levels in order to obtain most information of the system [13].

2. Experimental

2.1. Instrumentation

A Varian flame atomic absorption spectrometer, model SpectrAA 220 (Victoria, Australia), equipped with a chromium hollow cathode lamp and a deuterium lamp for background correction was used for the detection of chromium. The instrument was operated under the conditions recommended by the manufacturer: lamp current of 7 mA, wavelength of 357.9 nm, slit width of 0.1 nm, burner height of 17 mm, acetylene flow rate of 2.0 L min⁻¹, and air flow rate of 13.5 L min⁻¹. The absorbance reading mode was peak area.

The flow system for preconcentration was constructed using a Gilson Minipuls 3 peristaltic pump (Villiers Le Bel, France) equipped with eight channels and Tygon® and polyethylene tubes were used to pump the solutions through the mini-column (60 mm × 3 mm) in the elution and preconcentration steps. A Gehaka PG1800 pH meter was used to adjust the pH of the samples and the working solutions.

A Fourier Transform Infrared (FT-IR) spectrometer (Shimadzu, IRPrestige-21, Tokyo, Japan) was used to characterize the *M. oleifera* husks.

2.2. Reagents, solutions and samples

All working solutions were prepared with deionized water obtained from a Gehaka (São Paulo, Brazil) water purification system.

All reagents were analytical grade. Before use, laboratory glassware was kept overnight in 10% (v/v) nitric acid aqueous solution, followed by ultra-sonication for 1 h and finally rinsing with deionized water. The nitric acid solution used as the eluent was prepared through dilution in water of concentrated nitric acid obtained from Merck (Darmstadt, Germany).

Chromium(VI) and chromium(III) working standard solutions were all prepared by appropriate dilution of 1000 mg L⁻¹ K₂Cr₂O₇ (Carlo Erba) and 1000 mg L⁻¹ CrCl₃·6H₂O (Carlo Erba) stock solutions, respectively.

2.3. Preparation of the column

The Moringa seeds used were obtained from trees cultivated in the city of Uberlândia (Minas Gerais, Brazil) and collected in July 2010. The husks were separated from the seeds, washed with deionized water and dried at 25 °C. After drying, the husks were crushed in a blender (Black & Decker, São Paulo, Brazil) and passed through 850 μm sieves.

The mini-columns were comprised of polyethylene tubes with an inner diameter of 3 mm and were sealed at both ends with glass wool. The mini-column (60 mm × 3 mm) was filled with 30 mg of the husks and the performance was stable during all experiments.

2.4. On-line preconcentration system

The on-line flow system used for the development of the proposed method is shown in Fig. 1. The flow system consists of a peristaltic pump equipped with Tygon® tubes, four 3-way solenoid valves and a mini-column filled with biosorbent. The system was coupled to the FAAS instrument. During the preconcentration step (Fig. 1A) valve 1 is ON and the other valves remain OFF, the samples or working solutions are pumped through the mini-column and the effluent is discharged. In the elution step (Fig. 1B), valve 1 is OFF and valves 2, 3 and 4 are ON. The water flow is stopped and the eluent percolates through the mini-column in the opposite direction to that of the sample undergoing the preconcentration step. The eluate is carried directly to the nebulization system of the FAAS instrument.

2.5. Optimization for the chromium separation

The solution pH is a critical variable that directly affects the ion adsorption. *M. oleifera* husks can adsorb cations or anions depending on the solution pH. The effect of solution pH on the Cr(VI) and Cr(III) separation in the biosorbent was investigated by varying the pH from 1 to 9. Buffers were avoided because they lead to a significant reduction in the analytical sensitivity. The effect of various buffer systems was investigated to determine whether an increase would occur in the analytical signal. The presence of buffer significantly affects the efficiency of retention of chromium, probably due to competition for the cation or anion, present in the buffer, and the active sites. So, the pH was adjusted by adding 0.1 mol L⁻¹ HNO₃ or 0.1 mol L⁻¹ NaOH. Twenty-five milliliters of a solution containing separately each species were placed under stirring with 0.5 g of biosorbent for 20 min, after the filtration, the concentration of chromium species was measured in supernatant, and retained amount of chromium in biosorbent was calculated by the difference between the initial and final concentrations.

2.6. Optimization strategy for the Cr(III) preconcentration

In the first step, the effect of the eluent on the Cr(III) desorption was investigated to determine its influence on the analytical signal. The Cr(III) elution was studied using: HNO₃, HCl, Tris and NaOH at 0.5 mol L⁻¹.

The optimization of the parameters affecting the sorption of Cr(III) by the *M. oleifera* husks was performed using a two-level full factorial experimental design involving three factors (adsorbent mass, sample flow rate and eluent concentration) and a final optimization by Doehlert design. All experiments were carried out in duplicate using 15.0 mL of a 100 μg L⁻¹ Cr(III) solution at pH equal to 7.0.

2.7. Studies of interferent ions

In order to investigate the selective extraction and determination of Cr(III) ions in real samples containing different metal ions, 100 μg L⁻¹ of Cr(III) solution and increasing amounts of potentially interfering ions were submitted to the preconcentration procedure. In this study, interference was investigated using a 2⁷⁻³ fractional factorial experimental design including a central point, resulting in 17 experiments. The results were compared with Cr(III) preconcentration in the absence of the potentially interfering ions. Since the content of Ca²⁺, Na⁺ and Mg²⁺ is high in water samples, additional experiments were performed in order to evaluate the possible interference of these ions in high concentrations. Effect of interfering was verified in solutions containing the analyte and the interfering ions in concentrations 100 times higher than the analyte, by comparing the analytical signal of a solution containing only Cr(III) or Cr(VI) and a solution containing the analyte and interfering ion.

The effect of complexants in the Cr(III) and Cr(VI) retention was investigated. EDTA, citric acid and diphenylcarbazine were evaluated

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