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Determination of cadmium in alcohol fuel using *Moringa oleifera* seeds as a biosorbent in an on-line system coupled to FAAS

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ABSTRACT

In this study a new method for determination of cadmium in alcohol fuel using *Moringa oleifera* seeds as a biosorbent in an on-line preconcentration system coupled to flame atomic absorption spectrometry (FAAS) was developed. Flow and chemical variables of the proposed system were optimized through multivariate designs. The limit of detection for cadmium was 5.50 $\mu g\,L^{-1}$ and the precision was below 2.3% (35.0 $\mu g\,L^{-1}$, $n = 9$). The analytical curve was linear from 5 to 150 $\mu g\,L^{-1}$, with a correlation coefficient of 0.9993. The developed method was successfully applied to spiked alcohol fuel, and accuracy was assessed through recovery tests, with recovery ranging from 97.50 to 100%.

1. Introduction

In Brazil, the oil crisis in the 1970s contributed to the implementation of a government program called Proálcool (National Alcohol Program) in 1975 to stimulate the production of ethanol from sugar cane [1,2]. Ethanol is a renewable fuel that contributes significantly to the energy independence of Brazil, attracting interest from several countries. However, for Brazilian ethanol to be introduced successfully in the international market it is extremely important to develop methods of analysis to ensure its quality. During the processes of production, transport and storage of alcohol fuel, several sources of contamination are present, including by metal ions. The presence of metal ions, even at low concentrations can adversely affect the performance of the engine [3,4], intensify the corrosive properties of ethanol and increase the emission levels of pollutants generated and the consequent environmental pollution [5–7].

Flame atomic absorption spectrometry (FAAS) has been extensively used for the determination of several metal species [8–11]. However, detection limits in the order of mg L^{-1} prevent the use of this technique in the analysis of samples containing low concentrations of analytes, requiring preconcentration steps to improve the sensitivity [12–16].

Among the existing preconcentration techniques, solid phase extraction has some advantages such as simplicity, high analytical frequency and enrichment factors, besides reducing the matrix effects [16–18].

Many studies involving metal preconcentration have been reported, mostly with the use of commercially available sorbents. However, other materials known as 'natural adsorbents' have recently been successfully employed in metal adsorption processes [19–21]. The term 'natural adsorbent' is assigned to any material that is not synthetically produced and has adsorptive properties in terms of chemical species of inorganic and organic origins.

The use of natural adsorbents in procedures for solid phase extraction becomes more attractive when coupled on-line with the detection system and when using an adsorbent with high adsorptive capacity, such as the seeds of *Moringa oleifera*. Table 1 lists various biosorbents and their applications in solid phase extraction procedures as well as their limits of detection.

M. oleifera is the best known species of the Moringaceae family. It is a plant native to northwest India but has spread all over the world, mainly in tropical countries. *M. oleifera* seeds have been used for the treatment of turbid water due to their flocculation properties. A flocculating protein from the seeds of *M. oleifera* Lam. was isolated by Gassenschmidt et al. [29] and its molecular mass was found to be around 6.5 kDa and the isoelectric point was above pH 10. Flocculation activity could be explained by the charge-patch mechanism due to low molecular weight and high charge den-

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Table 1
Use of bioadsorbents in solid phase extraction systems.

Bioadsorbent	Sample	Detection	LOD	Ref
Agrobacterium tumefaciens immobilized in Amberlite XAD-4	Water, baby food and certified samples	FAAS	3.6 ng mL^{-1} Fe(III) 3.0 ng mL^{-1} Co(II) 2.8 ng mL^{-1} Mn(II) 3.6 ng mL^{-1} Cr(III)	[22]
Pilayella littoralis immobilized in silica	Drinking water	ICP-OES	0.6 ng mL^{-1} Cu(II) 11 ng mL^{-1} Fe(III) 8 ng mL^{-1} Al(III) 0.4 ng mL^{-1} Co(II)	[23]
Penicillium italicum immobilized in Sepabeads SP 70	Natural waters	FAAS	0.41 μg L^{-1} Cd (II) 1.60 μg L^{-1} FeIII	[24]
Pseudomonas aeruginosa immobilized in Chromosorb 106	Natural waters and food	GFAAS	30 ng L^{-1}	[25]
Bacillus sphaericus immobilized in Diaion SP-850	Certified water samples and foods.	FAAS	Water samples: 0.20 μg L^{-1} Cu(II) 0.75 μg L^{-1} (PbII) 0.25 μg L^{-1} Fe(III) 0.30 μg L^{-1} Co(II) Solid samples: 2.5 ng L^{-1} Cu(II) 9.4 ng L^{-1} Pb(II) 3.1 ng L^{-1} Fe(III) 3.8 ng L^{-1} Co(II)	[26]
Saccharomyces cerevisiae	River water	ICP-OES	0.1 μg L^{-1} Cd(II)	[27]
Bacillus subtilis immobilized in Amberlite XAD-4	Certified water samples and foods.	FAAS	0.0297 mmol L^{-1} Cu(II) 0.035 mmol L^{-1} Cd(II)	[28]

sity. The amino acids detected were mostly glutamic acid, proline, methionine and arginine. However, the mechanism of coagulation by polypeptides is still unknown. The shelled and non-shelled seeds contain approximately 37 and 27% of protein, respectively. Studies involving the use of natural adsorbents for the treatment of industrial effluents in terms of the removal of heavy metals have been published [30–32]. However, the use of this material in the preconcentration of metals in alcohol fuel has not been reported in the literature.

Thus, due to the possible sources of contamination by metal ions, such as cadmium, during the production of alcohol, the objective of this study was to develop a methodology for an on-line preconcentration system, using *M. oleifera* seeds as a biosorbent, coupled to flame atomic absorption spectrometry, for the determination of cadmium in alcohol fuel.

2. Experimental

2.1. Instrumentation

A Varian SpectrAA 50 (Victória, Australia) flame atomic absorption spectrometer (FAAS), equipped with a cadmium hollow cathode lamp and a deuterium lamp for background correction, was used for the detection of cadmium. The instrument was operated under the conditions recommended by the manufacturer, as shown in Table 2.

The pH value of the point of zero charge of the proposed biosorbent was measured over the pH range of 3–12 using a Microelectrophoresis Apparatus Mk II (Cambridge, UK).

Table 2
Operating parameters employed in Cd(II) determination by FAAS.

Parameters	
Wavelength (nm)	228.8
Lamp current (mA)	4
Burner height (mm)	17
Acetylene flow rate (L min^{-1})	1
Air flow rate (L min^{-1})	10
Aspiration flow rate (mL min^{-1})	5

A Fourier Transform Infrared (FT-IR) spectrometer (Shimadzu, IRPrestige-21, Tokyo, Japan) and a thermogravimetric analyzer (TA Instruments TGA 2950, New Castle, USA) were used to characterize the *M. oleifera* biosorbent.

A Mettler Toledo 320 pH meter was used to adjust the pH of the samples and working solutions. An Ismatec-IPC (Zurich, Switzerland) peristaltic pump equipped with eight channels and Tygon® and polyethylene tubes were used to pump the solutions through the mini-column (60 mm × 0.2 mm) in the elution and preconcentration steps. The mini-column was filled with 200 mg of seeds in the size range of 140–850 μm.

2.2. Reagents and solutions

All working solutions were prepared with ultrapure water obtained from a Milli-Q system (Millipore, Bedford, MA, USA). All reagents were analytical grade. All laboratory glassware was washed with a neutral detergent and then kept overnight in 10% nitric acid aqueous solution, followed by ultra-sonification for 1 h and finally rinsed with deionized water.

Working solutions were prepared daily through dilution of a 2000 mg L^{-1} stock solution of cadmium in a hydro-alcoholic solution containing 80% (v/v) of alcohol fuel and 20% (v/v) of water with a tris(hydroxymethyl)aminomethane buffer.

The nitric acid solution used as the eluent was prepared through dilution in water of concentrated nitric acid obtained from Merck (Darmstadt, Germany).

The 10^{-3} mol L^{-1} potassium chloride solution was adjusted within a pH range of 3–12 for the determination of the point of zero charge of the *M. oleifera* biosorbent.

2.3. Preparation of the biosorbent

The Moringa seeds used to construct the mini-column were obtained from trees cultivated in the city of Uberlândia (Minas Gerais, Brazil) and collected during September–November 2007. The seeds were separated from the pods, washed with deionized water and dried at 25 °C. After drying, the seeds were crushed in a blender (Black & Decker, São Paulo, Brazil) and passed through 850 μm sieves.