Analytica Chimica Acta 809 (2014) 82–87

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Assessment of cadmium and iron adsorption in sediment, employing a flow injection analysis system with on line filtration and detection by flame atomic absorption spectrometry and thermospray flame furnace atomic absorption spectrometry

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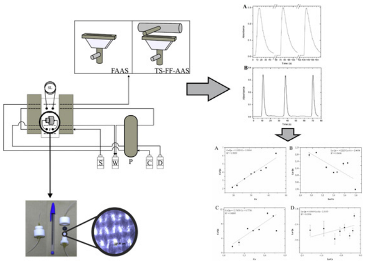
HIGHLIGHTS

- A FIA system with on-line filtration for isotherms adsorption studies was proposed.
- Isotherms for iron and cadmium elements in bottom lake sediment were done.
- Inferences about adsorption/desorption mechanisms were feasible.
- The proposed method turns the isotherm studies fast and reliable.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 August 2013
Received in revised form
19 November 2013
Accepted 23 November 2013
Available online 1 December 2013

Keywords:
Lake sediment
Adsorption isotherm
Cadmium
Iron

ABSTRACT

This work presents an evaluation of iron and cadmium adsorption in sediment of the Furnas Hydroelectric Plant Reservatory located in Alfenas, Minas Gerais (Brazil). The metal determination was done employing a flow injection analysis (FIA) with an on-line filtering system. As detection techniques, flame atomic absorption spectrometry (FAAS) for iron and thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) for cadmium determinations were used. The developed methodology presented good limits of detection, being 190 $\mu g\,L^{-1}$ for iron and 1.36 $\mu g\,L^{-1}$ for cadmium, and high sampling frequency for both metals 144 and 60 readings h^{-1} for iron and cadmium, respectively. Both metals obey the Langmuir model, with maximum adsorptive capacity of 0·169 $mg\,g^{-1}$ for iron and 7·991 $mg\,g^{-1}$ for cadmium. For iron, a pseudo-first-order kinetic model was obtained with a theoretical $Q_e = 9{\cdot}8355\ mg\,g^{-1}$ (experimental $Q_e = 9{\cdot}5432\ mg\ \ g^{-1}$), while for cadmium, a pseudo-second-order kinetic model was obtained, with a theoretical $Q_e = 0.3123\ mg\,g^{-1}$ (experimental $Q_e = 0{\cdot}3052\ mg\,g^{-1}$).

1. Introduction

The contamination of water resources due to population and industrial growth has worried the scientific community as well as governments around the world. Cadmium is a toxic element and iron can be both toxic and an essential element, depending on its concentration [1].

Iron is a haemoglobin constituent and its lack can lead to anaemia [2,3]. It also participates in several biogeochemical processes that can shift the ecosystem equilibrium [2,4]. Cadmium can be bioaccumulated in living organisms and through the food chain can reach humans and provoke deleterious effects, mainly to the liver and kidneys [5,6].

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http://dx.doi.org/10.1016/j.aca.2013.11.048

An interesting study field is the adsorption of metals in lacustrine system's bottom sediments. The sediments can act as a source of these elements when concentrations in water decrease. On the other hand, when the concentrations increase, it can act as an accumulator [7,8]. In this context, some research had been done to determine metals in sediment, as well as to understand their adsorption mechanisms.

The adsorptions isotherms are well known tools to study the adsorptions mechanisms [9]. The Langmuir and Freundlich models are examples of commonly used isotherms [10]. When the system obeys the Langmuir model, it can be inferred that the adsorption occurs in monolayer, and in the case of Freundlich model, it indicates a case of multilayer adsorption.

Inferences about bound type (chemical or physical sorption) between adsorbent and adsorbate, as well as kinetic features of adsorption processes, are also possible [11]. The physical–chemical parameters such as pH, redox potential, temperature and ionic strength cause strong influence on adsorption processes [12].

Usually, isotherms are performed by cumbersome process that consists in preparing suspensions with different adsorbent/adsorbate concentrations, followed by agitation during a predefined time. After it is filtrated, the adsorbate (metal) is finally determined [13]. Atomic absorption stands out among other techniques to determine metals and it is very fast; therefore, in isotherm studies, most of the time is spent at the previous steps, mainly in the filtration step. In this work a flow injection analysis (FIA) system is being proposed to execute filtration/separation and determination of metal in samples for adsorption studies. For iron determination the flame atomic absorption spectrometry (FAAS) technique was adequate, while for cadmium, due to this element's low concentration, a thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS) was needed. The system was applied to construct isotherms and the results were satisfactory.

2. Experimental

2.1. Adsorbent–adsorbate preparation

The bottom sediment samples (adsorbent) were collected with Ambühl & Bührer collector [14] in the Furnas Reservatory, Alfenas city, Brazil. The samples were dried at 60 °C, macerated and sieved to obtain particles at a size of 180 μm, and then stored. To determine total metal concentration, the samples were digested in microwave oven (ETHOS PLUS, Milestone, Sorisole, Italy) as described by the USEPA Method 3052, and determined using FAAS for iron, and inductively coupled plasma mass spectrometry (ICP-MS) for cadmium [15]. Standard solutions for iron and cadmium were prepared by dilution in water of 1000 mg L^{-1} stock solution (Merck, Darmastadt, Germany). For adsorption studies, the concentrations of 200 up to 900 μg L^{-1} for cadmium and 15–30 mg L^{-1} for iron were used. The concentrations of adsorbent (sediment) were 2·5 g L^{-1} for iron and 1.0 g L^{-1} for cadmium. To characterize the adsorbent an infrared spectroscopy (BOMEM, B100) was used with transmission between 4000 and 400 cm^{-1} and 4 cm^{-1} resolution, and the sample preparation was carried out with 0·1 g of sediment mixed with 1·0 g of KCl and then compacted.

2.2. FIA system manifold

The FIA system has an eight channel peristaltic pump (Ismatec IPC-08, Glattzbrugg, Switzerland) provided with Tygon®tubes to propel the flow, and polyethylene tubes of 0·8 mm of internal diameter (i.d.) to conduct the fluids. The commutator and all connections are acrylic lab-made. An atomic absorption spectrometer (Thermo Scientific, iCE 3000) was used to measure the absorbance. For the TS-FF-AAS setup a nickel tube (J&J Ethen, 52070, Aachen, Germany) was used with 6 cm length and 2·5 cm i.d., containing six 2·5 mm i.d. holes, and also a ceramic capillary (Friatec, Mannhein, Germany) made of non-porous Al_2O_3 ceramic (10 cm in length, 0·5 mm i.d. and 2·0 mm o.d.) for transporting samples towards the nickel tube.

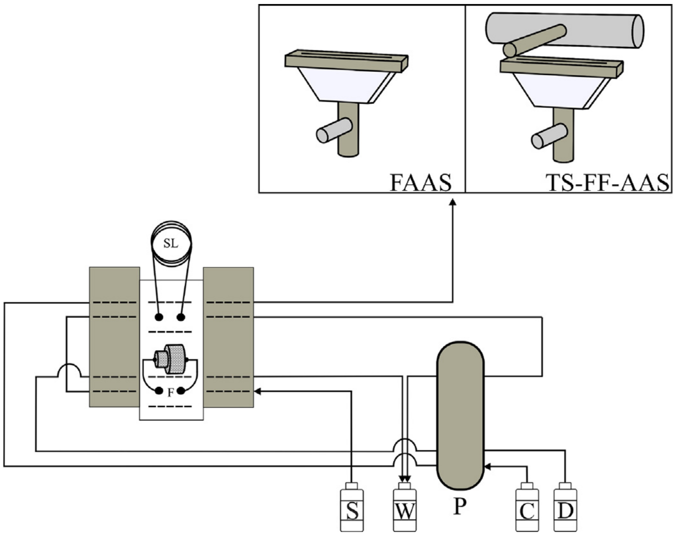

Fig. 1. FIA manifold used for both iron and cadmium determinations on sampling position. S: sample; W: waste; P: peristaltic pump; C: carrier fluid; D: washing solution; F: filter; SL: sample loop.

Fig. 1 displays the FIA system manifold for the determination of iron and cadmium. During the online filtering/sampling step, the sample in suspension form is propelled towards the filtering membrane, and afterwards it is conducted to the sample loop. In the following tread, the sample loop is inserted on the carrier fluid and conducted to the detection system. For the iron determinations the FIA system was coupled directly into the spectrometer for the FAAS determination [16], and to determine cadmium, a TS-FF-AAS was used [17]. Table 1 shows the parameters to iron and cadmium determinations. The filtration system used was described elsewhere [18]. For the porous size determination, a Zeiss (AXIO) with image acquisition was used. A polyester membrane with the mean pore size was measured, being 100·55 ± 10·02 μm (Fig. 2), and largest pore size of 110·25 μm was used for filtration.

2.3. Desorption and adsorption experiments

To perform desorption curves for iron, 2·5 g of adsorbent (sediment) was mixed with one liter of deionized water and submitted to a shaker in an agitator table (Quimis, Q225 M, Brazil). At the first 30 min, aliquots of 5 mL were collected and led to measurements in FIA-FAAS system. The measurements were carried out with 30 min of time increment each until the signal turned constant. It is important to stress that in these experiment**s** we study desorption of

Table 1
Instrumental parameters for the iron and cadmium determinations.

Variable	Iron	Cadmium
Flow rate (mL min^{-1})	4.8	0.72
Sample volume (μL)	100	40
Flame type	Air/acetylene	Air/acetylene
Fuel flow (L min^{-1})	1.2	1.2
Measurement time (s)	100	100
Spectral resolution (nm)	0.2	0.5
Lamp current (mA)	6	8
Wavelength (nm)	248.3	228.8
Carrier fluid	HCl 0.5%(v/v)/KCl 0.05 mol L^{-1}	HNO_3 1% (v/v)