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Investigation on the Performance of Chemically Modified Aquatic Macrophytes—*Salvinia molesta* for the Micro-Solid Phase Preconcentration of Cd(II) On-Line Coupled to FAAS

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Abstract In this study, a new method for the preconcentration of cadmium ions using modified aquatic macrophytes – *Salvinia molesta* as biosorbent in an on-line preconcentration system coupled to flame atomic absorption spectrometry (FAAS) was developed. The method is based on preconcentration of 20.0 mL sample at pH 3.75 through 35.0 mg of biosorbent at 10.0 mL min^{-1} and subsequent elution with 0.5 mol L^{-1} HNO_3. A preconcentration factor of 31-fold, linear dynamic range from 5.0 to 70.0 µg L^{-1} ($r = 0.9996$) and detection and quantification limits of 0.15 and 0.51 µg L^{-1} were obtained. The characterization of the biosorbent chemically modified with NaOH and citric acid, was performed through FTIR and SEM measurements. The method precision was found to be 3.97% and 1.48% for 5.0 and 60.0 µg L^{-1} Cd(II) solutions, respectively. The applicability of method was checked by analysis of different kind of water samples and certified reference material.

Keywords Biosorption · Atomic spectrometry · Flow injection analysis and water

Currently, contamination of aquatic environments by low concentrations of potentially toxic metals is a major global concern, especially in countries with emerging and developing economies (Harguinteguy et al. 2015). The main sources of metals pollution in environmental samples comes from industrial and anthropogenic activities (Ozdemir et al. 2012) giving rise to accumulation of metals ions in the food chain causing serious problems due to high solubility and mobility of metals (Modenes et al. 2013; Mishra and Tripathi 2008; Espinoza-Quinones et al. 2009). According to International Agency for Research on Cancer (IARC 1993), cadmium has been classified as carcinogenic metal and it is commonly found in effluents from industries and activities of metallurgical and mining. Its maximum levels allowed in drinking water have been established by government agencies as USEPA (US Environmental Protection Agency) and WHO (World Health Organization 2004) with values of 5.0 and 3.0 µg L^{-1}, respectively, whereas for effluents discharged into aquatic bodies, the National (Brazilian) Council for the Environment (CONAMA, resolution no. 357, 2005) establishes a maximum level of 0.2 mg L^{-1}. In the sense, several conventional methods, that involves physical, chemical and biochemical processes have been applied in order to remove or reduce heavy metals in environmental samples (Miretzky et al. 2004; Fu and Wang 2011; Davis et al. 2003). The adsorption has been pointed out as highly effective and inexpensive among the various treatments to

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remove heavy metal ions. From the analytical point of view, the monitoring of cadmium at trace levels requires the use of well-known sensitive analytical techniques such as, ICP-MS and GF AAS (Corazza and Tarley 2016). However, due to high cost of acquisition and maintenance of these techniques, the use of FAAS associated with preconcentration procedure has been mandatory to reach high detectability (Diniz et al. 2014). Therefore, the use of biosorbents, such as aquatic macrophytes, has currently attracted the attention of researchers as alternative adsorbent for the preconcentration of heavy metals from aqueous solutions due to their low cost, easy availability and high reusability (Miretzky et al. 2004; Anayurt et al. 2009; Munagapati et al. 2010; Li et al. 2007; Tuzen et al. 2007, 2009; Soylak et al. 2006). One should note that the type of aquatic macrophytes used for the adsorption of metals may significantly influence on the performance of pollutant removal, due to presence of functional groups on their surface (carboxyl, hydroxyl, carboxylic acid, amine, and others) (Mishra and Tripathi 2008; Mazej and Germ 2009; Kumar et al. 2006). Moreover, some studies have reported that chemical modification of biosorbents improves the adsorption capacity towards the metal ions (Santos et al. 2010; Souza et al. 2012). Although many species of aquatic macrophytes have been used for the removal heavy metals, there is no report in the literature regarding the use of aquatic macrophytes *Salvinia molesta* as adsorbent in the field of separation science. Thus, in this work, we describe the development of a new preconcentration method for on-line Cd(II) determination by FAAS using *Salvinia molesta* as adsorbent packing material in micro-column. Additionally, in order to improve its adsorption performance, the biosorbent was chemically modified with sodium hydroxide and citric acid in similar way to previous study reported by our research group (Souza et al. 2012).

Materials and Methods

A flame atomic absorption spectrophotometer (Shimadzu, Kyoto, Japan) equipped with a hollow cathode lamp as radiation source (Hamamatsu Photonics, K.K) and deuterium lamp as background source correction was used in all measures of cadmium. The hollow cathode lamp was operated at 8.0 mA and the wavelength was set at 228.8 nm. For characterization studies, a Shimadzu FT-IR 8300 Fourier transform spectrometer operating in transmission mode (4000–400 cm^{-1}), at 4 cm^{-1} resolution and conventional KBr pellet technique was used, whereas the surface morphology was evaluated by a scanning electron microscopy (SEM) using a Philips FEI Quanta 200 (Amsterdam, The Netherlands). A flow injection system was constructed from an Ismatec IPC-08 peristaltic pump (Glattzbrugg, Switerland) and Tygon® tubing for propelling samples and reagents to the detection system. 35 mg of the biosorbent (*Salvinia molesta*) was packed into a homemade mini-column, made of polyethylene (2.0 cm in length and 1.0 cm at the top internal diameter) with each one extremities sealed by a small piece of cotton tissue. The mini-column was coupled in a homemade injector commutator for preconcentration and elution procedure. The pH of the solutions was measured with a Metrohm 826 mobile digital pH meter (Herisau, Switzerland). Ultrapure water from a Milli-Q purification system (Bedford, MA, USA) was used to prepare all the solutions. Certified reference material (Dolt-4) was decomposed in a microwave oven Milestone Ethos One (São Paulo, Brazil). In order to prevent metals contamination, all glassware was kept overnight in a 10 % (v/v) HNO_3 solution and rinsed with deionized water before use. Cd(II) working solution of 50 $\mu g\ L^{-1}$ were prepared from a 1.0 $mg\ L^{-1}$ standard solution by making appropriate dilutions. The solution pH was adjusted with sodium citrate, acetate and ammonia buffer solutions prepared from the respective salts without any purification (Merck), whereas the Tris(hydroxymethyl) aminomethane hydrochloride (Tris–HCl) was obtained from Sigma-Aldrich (Steinhein, Germany). Solutions of 0.1 $mol\ L^{-1}$ NaOH and 1.2 $mol\ L^{-1}$ citric acid, acquired from Vetec-Brazil, were used for performing the chemical modification.

Species of aquatic macrophytes – *Salvinia molesta* were collected in spring water during 2 months and prepared according to Verma et al. (2008). Part of the biomass was reserved for chemical modification with sodium hydroxide and citric acid as described by Souza et al. (2012). The on-line preconcentration system was performed percolating aliquots of 20.0 mL of the samples or Cd(II) standard solution, buffered with 0.01 $mol\ L^{-1}$ acetate/acetic acid buffer (pH 3.75) through 35.0 mg of *Salvinia molesta* packed into a mini-column at 10.0 $mL\ min^{-1}$. After the preconcentration step, the Cd(II) ions adsorbed on the biosorbent were eluted with 1.5 $mol\ L^{-1}$ HNO_3 through the mini-column toward the FAAS detector. To evaluate the applicability of this method, tap water was collected in the laboratory of the State University of Londrina (Londrina, Brazil) whereas the mineral water was acquired at a local supermarket. Lake water was collected from Igapó Lake in the city of Londrina-PR, acidified until pH 2.0 and then filtered through a 0.45 µm cellulose acetate membrane before use. All the samples had the pH adjusted to 3.75 using 0.01 $mol\ L^{-1}$ acetate buffer. The accuracy of the proposed method was evaluated by addition and recovery test using an external calibration curve and by analysis of certified reference material. In addition, analytical blanks were used to confirm the absence of interfering in the analytical system.

Results and Discussion

FTIR spectroscopy of the unmodified and chemically modified *Salvinia molesta*, was used to obtain information about the functional groups on the biosorbent, as demonstrated in Fig. 1.

As can be seen, the spectra are similar each others with respect to functional groups, differing only by the increase in the intensity of N–H bending from amide (1539 cm^{-1}) (Khosa et al. 2013), which may be attributed to the formation of amide from the reaction of citric acid with amines groups bounded to the biosorbent. The broad band at 3408 cm^{-1} can be attributed to the stretching of hydroxyl from protein groups, lignin, cellulose of the modified biomass and to adsorbed waters or amine (–NH) groups bounded to the biosorbent. The intense band at 1643 cm^{-1} can be attributed to the stretching vibration of carbonyl, while intense peak at 1067 cm^{-1} is assigned to C–O stretching of alcohols and carboxylic acids presents in the biosorbent and from the addition of citric acid. In addition, the peaks observed at 1246 and 1426 cm^{-1} can be assigned to the C–H groups whereas the bands below 800 cm^{-1} are attributed to finger print zone of phosphate and sulphur functional groups (Santos et al. 2011; Anayurt et al. 2009). Figure 2 shows the SEM images of modified and unmodified biosorbent. As one can see, even using an image with low magnification (×6000), it is possible to observe multicellular complex hairs on the surface of unmodified biosorbent, in the form of wax crystals that create a nanoscale roughness. Upon modification, it is observed an increase on the roughness of surface and the absence of wax crystals, which most likely were removed by the treatment with NaOH. From the results, the decrease on the hydrophobicity and increase on the roughness of biosorbent upon modification is highly desirable considering the application of biosorbent in flow systems for the preconcentration of metal ions in aqueous medium.

The pH dependence on the biosorption of Cd(II) onto *Salvinia molesta* was studied for the following values: pH 3.00; 3.75; 4.50; 5.75; 7.00 and 8.50. The maximum biosorption of Cd(II) ions onto *Salvinia molesta* surface was observed at pH 3.75 (Fig. 3).

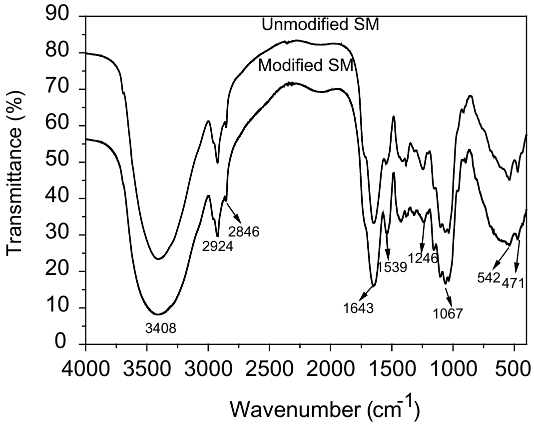


Fig. 1 FTIR spectrum of modified aquatic macrophyte (*Salvinia molesta*)

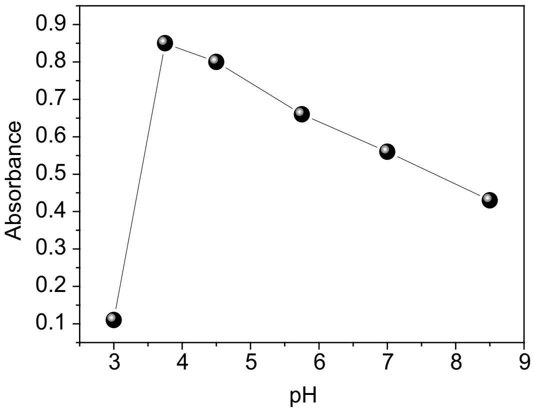
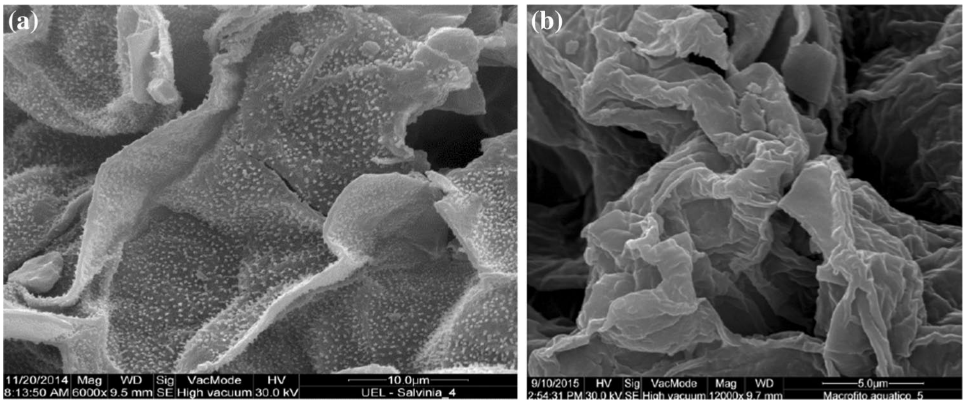


Fig. 3 Effect pH in the biosorption of Cd(II) onto modified aquatic macrophyte (*Salvinia molesta*). Conditions: mass of biosorbent: 35.0 mg; concentration of Cd(II) 50.0 µg L^{-1}; preconcentration volume: 20.0 mL; preconcentration flow rate: 4.0 mL min^{-1}; buffer concentration: 0.01 mol L^{-1}; eluent: 1.5 mol L^{-1} HNO_3

Fig. 2 SEM image of **a** unmodified *Salvinia molesta* with magnification of 6000 times and **b** modified *Salvinia molesta* with magnification of 12,000 times



This result can be rationalized bearing in mind the presence of functional groups with low pKa values on the biosorbent, which justify the higher adsorption of Cd(II) even at low pH medium. Thus, the further experiments were carried out at pH 3.75, since at higher pH values there is possible formation of soluble species of Cd(II), such as $Cd(OH)^+$, decreasing the interaction of biosorbent by surface. Due to use of dilute mineral acid as eluent in the flow preconcentration system, the influence of buffer concentration on the solution of Cd(II) was studied in the domain experimental of 0.005–0.20 mol L^{-1} using acetate/acetic acid buffer. It was possible to observe that an increase of buffer concentration reduced significantly the analytical response, due to a competitive effect between Cd(II) and ions from the buffer. Thus, acetate/acetic acid buffer at 0.01 mol L^{-1} was chosen for the further experiments. Regarding the eluent concentration on biosorbent preconcentration system, it is very well-known that the use of higher eluent concentration provides higher desorption of metals giving rise to a high and narrow peak profile (Tarley et al. 2015; Corazza et al. 2014). Thus, the effect of eluent was studied in domain experimental of 0.5–2.0 mol L^{-1}. It was observed that higher HNO_3 concentrations were able to elute the ions without memory effect and with high and narrow peak profile, so 1.5 mol L^{-1} HNO_3 was chosen as eluent for the further experiments. The influence of preconcentration flow rate has been investigated in the range of 2.0–10.0 mL min^{-1}. According to obtained results, there was no significant difference on the analytical response when flow rates above 4.0 mL min^{-1} were used and, thus, the flow rate of 10.0 mL min^{-1} was chosen for the further experiments, yielding a high sample throughput of 30 h^{-1}. The applicability of the proposed method in the presence others cations in different proportions (1:1 and 1:50 m/m) was investigated under the optimized conditions using the flow injection system. As can be seen in Table 1, the presence of 50.0 µg L^{-1} of foreign ions leads to recovery results for the Cd(II) varying from 99.5 % to 104.0 %, whereas in the presence of 2.5 mg L^{-1} of foreign ions the recovery of the analyte varied from 91.5 % to 111.4 %, demonstrating good tolerance and high selectivity to the Cd(II) determination. All results were compared with the results of Cd(II) preconcentration in the absence of the potentially interfering ions and the tolerance limit for each ion was taken as the amount that produced error not exceeding ±10 % regarding the Cd(II) determination alone.

The optimized method by loading 20.0 mL of Cd(II) solution through micro-column provided a calibration curve (Abs = 0.0094 [Cd^{2+}] (µg L^{-1}) + 0.0030), varying from 5.0 up to 70.0 µg L^{-1} with good correlation coefficient (r = 0.9992). In addition, a calibration curve without preconcentration step was obtained (Abs = 0.0003 [Cd^{2+}] (µg L^{-1}) + 0.0027) (r = 0.9996). From the ratio between the slopes of calibration curves built with and without preconcentration method, a preconcentration factor of 31 was obtained, attesting the improvement in the detectability of cadmium determination by FAAs using the modified aquatic macrophyte *Salvinia molesta*. The detection (LOD) and quantification (LOQ) limits, defined as 3 *std* (standard deviation for 10 blank measurements) $slope^{-1}$ and 10 *std* $slope^{-1}$, were found to be 0.15 µg L^{-1} and 0.51 µg L^{-1}, respectively (IRMM 2009). The precision of the method was evaluated in terms of repeatability by determining Cd(II) concentrations of 5.0 and 60.0 µg L^{-1} for n = 10, resulting of relative standard deviations (RSD) of 3.97 % and 1.48 %, respectively. The accuracy of the proposed method was estimated by analysis of

Table 1 Influence of foreign ions in the preconcentration of 50.0 µg L^{-1}Cd(II) solution

Foreign ions	Cd(II): interferent (m/m)	Cd(II) analytical signal recovery (%)
Ni(II)	1:1	102.4
	1:50	91.9
Co(II)	1:1	103.9
	1:50	109.9
Zn(II)	1:1	99.5
	1:50	105.4
Hg(II)	1:1	101.2
	1:50	108.7
Cu(II)	1:1	103.9
	1:50	91.5
Pb(II)	1:1	104.0
	1:50	101.0
Ca(II)	1:50	91.8
Mg(II)	1:50	105.2
Ba(II)	1:50	111.4

Table 2 Application of proposed method for Cd(II) ions preconcentration in water samples and validation from spiked samples

Samples	Cd(II) (µg L^{-1})		
	Amount added	Amount found[a]	Recovery (%)
Tap water	0	ND	–
	3	2.66 ± 0.04	92.7
	10	8.20 ± 0.04	90.6
Mineral water	0	ND	–
	3	2.66 ± 0.09	92.7
	10	8.51 ± 0.05	94.1
Igapó Lake water	0	ND	
	3	3.30 ± 0.03	110
	10	9.78 ± 0.09	97.8

ND below of detection limit

[a] Results are expressed as mean value ± standard deviation based on three replicates (n = 3)

Table 3 Comparison of the analytical performance of different adsorbents used for the Cd(II) preconcentration with posterior determination by FAAS

Adsorbent	Samples	Mode	LOD (μg L^{-1})	VP (mL)	Linear Range (μg L^{-1})	PF	Ref
Moringa oleifera seeds	Alcohol	On-line	5.5	10	5.0–150.0	–	Alves et al. (2010)
Bacillus subtilis immobilized in Amberlite XAD-4	River and well water	On-line	40	250	–	50	Dogru et al. (2007)
Bacillus thuringiensis var. israelensis on Chromosorb 101	Water and urine	On-line	0.37	250	20.0–2000	31	Mendil et al. (2008)
Poly-chlorotrifluoroethylene(PCTFE-beads)	Natural waters	On-line	0.3	2.4	0.8–40.0	39	Anthemidi and Karapatouchas (2008)
1,5-diphenylthiocarbazone immobilised on naphthalene	Vegetables	On-line	1.23	25	0.2–1.0	20	Chandio et al. (2013)
[A336][TS]-modified Fe_3O_4	Tap water and fruit	Batch	0.5	50	2.5–260	50	Mehdinia et al. (2015)
IIP—poly(ethylene glycol dimethacrylate-co-vinylimidazole)	Water and urine	On-line	0.11	15	1.0–50.0	38.4	Segatelli et al. (2010)
Sisal fiber with Tiazolylazo-Resorsinol (TAR)	Mineral water	Off-line	0.08	50	0.1–800	30	Dias et al. (2013)
Chemically modified aquatic macrophytes—*Salvinia molesta*	Water and certified reference material	On-line	0.15	20	5.0–70.0	31	This work

LOD limit of detection, *VP* volume preconcentration, *PF* preconcentration factor, *[A336][TS]* Aliquat 336 thiosalicylate

different kind of water samples using addition and recovery test, whose recovery values were varied from 90.6% up to 110.0% (Table 2). The accuracy of method was also attested by analysis of certified reference material (DOLT-4) (Dogfish liver). The microwave-assisted mineralization was performed according to literature (Diniz et al. 2013). From the achieved results, the cadmium content obtained by proposed method (23.33 ± 0.84 μg L^{-1}) ($n = 3$) was statistically equal to that certified value (24.3 ± 0.8 μg L^{-1}), by applying *t* test at 95% confidence level.

The present method introduces a new approach for improving the detectability of Cd(II) by FAAS using chemically modified aquatic macrophytes – Salvinia molesta as alternative biosorbent. The reusability of the aquatic macrophytes has been estimated as being approximately 165 times, since the same material packed in the micro-column was employed in all studies without any loss of adsorption capacity. As can be seen in Table 3, in general, when compared to other preconcentration methods, the analytical performance of the proposed preconcentration method using *Salvinia molesta* proved to be highly efficient owing to the low sample consumption, high chemical stability, satisfactory preconcentration factor and low limit of detection. These features are highly desirable in flow injection systems, which make the method very economical and environmentally friendly, since no organic solvent and any chelating agents were employed in the desorption of the Cd(II) ions. In addition, the accuracy was attested by analysis of certified reference material (Dogfish liver), which confirms the applicability of method for more complexes samples.

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