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Cellulose microfiber functionalized with N,N′-bis (2-aminoethyl)-1,2-ethanediamine as a solid sorbent for the fast preconcentration of Cd(II) in flow system analysis

Fernanda Midori de Oliveira[a], Bruna Fabrin Somera[a], Marcela Zanetti Corazza[a], Maria Josefa Santos Yabe[a], Mariana Gava Segatelli[a,b], Emerson Schwingel Ribeiro[c], Éder Cláudio Lima[d], Silvio Luís Pereira Dias[d], César Ricardo Teixeira Tarley[a,*]

[a] *Universidade Estadual de Londrina (UEL), Departamento de Química, Centro de Ciências Exatas, Rodovia Celso Garcia Cid, PR 445 Km 380, CEP 86050-482 Londrina, PR, Brazil*
[b] *Universidade Tecnológica Federal do Paraná (UTFPR), Av. dos Pioneiros, 3131, CEP 86036-370 Londrina, PR, Brazil*
[c] *Universidade Federal do Rio de Janeiro (UFRJ), Instituto de Química, CEP 21941-909 Rio de Janeiro, RJ, Brazil*
[d] *Universidade Federal do Rio Grande do Sul (UFRGS), Instituto de Química, CEP 91501-970 Porto Alegre, RS, Brazil*

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ABSTRACT

The present paper describes the synthesis of a new chemically modified cellulose microfiber through oxidation with sodium periodate and functionalization with N,N′-bis (2-aminoethyl)-1,2-ethanediamine for the fast and selective preconcentration of Cd(II) ions in flow system analysis. The new sorbentsorbent was characterized by FTIR, SEM, and surface area values. The uptake behavior of Cd(II) ions onto this sorbent was evaluated from kinetic data, pseudo-first-order and pseudo-second-order models, as well as from Langmuir, Freundlich and Langmuir–Freundlich adsorption isotherms. The maximum sorption capacity of 4.59 mg g^{-1} was estimated by the Langmuir–Freundlich model with fast kinetics for the sorption of Cd(II) described by the pseudo-second-order kinetic model. After characterization, the sorbent was packed in a mini-column, and a fast flow injection preconcentration system for Cd(II) determination by FAAS was developed. The best Cd(II) preconcentration condition, obtained by means of factorial design and response surface methodology, was achieved at pH 9.36 and a flow rate of 10 mL min^{-1} followed by elution with 1.0 mol L^{-1} nitric acid. By using 78 s preconcentration time, fast and highly sensitive determination of Cd(II) ions could be achieved with a limit of quantification of 0.20 μg L^{-1}, preconcentration factor of 26, consumption index of 0.5 mL, concentration efficiency of 20 min^{-1}, and sample throughput of 39 h^{-1}. The repeatability for 10 replicate determinations was found to be 7.8 and 2.5% for Cd(II) ion concentrations of 5.0 and 100.0 μg L^{-1}, respectively. The new sorbent efficiency for the interference-free preconcentration of Cd(II) ions was assessed by analysis of tap, mineral and lake waters, as well as synthetic seawater and normal saline waters. Furthermore, complex samples, such as biological samples, could be analysed by the proposed method in accordance with the accuracy attested by analysis of certified reference materials, TORT-2 (lobster hepatopancreas), and DOLT-4 (dogfish liver).

1. Introduction

Solid phase extraction/preconcentration methods associated with spectroanalytical techniques, such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF-AAS) and inductively coupled plasma optical emission spectrometry (ICP OES), have been well-known as powerful tools for accurate and precise determination of metal ions at very low concentrations in the presence of complex matrix [1]. In view of its low cost, simplicity and fair detectability, FAAS is undoubtedly recognized as the most widely used technique in combination with solid phase preconcentration methods, mainly those based on flow injection analysis [2]. In such preconcentration methods, ideally carried out at high flow rates, a sorbent, packed in a mini-column, should present attractive properties, including high surface area, high sorption capacity, chemical stability, selectivity, fast sorption kinetics, low resistance to fluid passage, absence of swelling effect in different fluids and regeneration ability [3]. Many published studies have focused on the development of new sorbent materials, such as ion imprinted polymers [4], nanocomposites [5], ion imprinted hybrid polymers [6] and carbon nanotubes [7], as well as on functionalizing modifiers (chelating agents and inorganic oxides) onto the surface of conventional sorbent, such as supports, including hydrophobic polymers, silica gel and cellulose

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[*] Corresponding author. Tel.: +55 43 3371 4366; fax: +55 43 3371 4286.
E-mail address: tarley@uel.br (C.R.T. Tarley).

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[8,9]. Cellulose is recognized as a natural polymer, it presents, to some extent, the required features of a sorbent in flow analysis, and it is able to retain metal ions due to the presence of hydroxyl groups, but with very low reactivity and selectivity. Moreover, cellulose has drawbacks associated with swelling effect in different fluids [10,11]. Thus, several works have riveted on improvements of reactivity and physical properties of cellulose as a sorbent for metal ions by introducing chemical modifiers onto its surface [12]. For instance, the accessible hydroxyl group of cellulose makes it possible to be used for the preparation of functional polymers under its surface, leading to the formation of graft copolymers [13]. Other recent applications of the chemically modified cellulose sorbent could be found in literature. The manuscript published by Gong et al. [14] demonstrates the determination of Cu(II) by FAAS after preconcentration in a batch procedure using cellulose modified with citric acid. Soylak and Cay [15] developed a method for the preconcentration of chelates of Ag(I) and Pb(II) with ammonium pyrrolidine dithiocarbamate (APDC) onto a cellulose nitrate membrane filter, with subsequent determination by FAAS. In a similar way, Rajesh and Hari [16] proposed the preconcentration of Hg(II)–diphenylthiocarbazone complex onto cellulose, followed by elution with polyethylene glycol-400 and determination by visible spectrophotometry. Ethylenediamine was incorporated onto the surface of cellulose fibers for the retention of Cu(II), Ni(II) and Zn(II) [17]. Other chemical modifiers for cellulose, such as pyrocatechol violet, 8-quinolinol [18], 2,3-dihydroxypyridine [19] and quaternary ammonium groups [20], could be pointed out. The use of N,N′-bis (2-aminoethyl)-1,2-ethanediamine (triethylenetetramine, TETA) as a chemical modifier of cellulose may promote a high preconcentration factor, selectivity, high sorption capacity and fast kinetics. It presents acid–base constants ranging from 3.89 up to 9.99 and high values of the formation constant with cations of transition and near-transition elements [21]. Despite the attractive features of TETA as a chelator for metal ions, its application has been scarce, concerning both this subject and another one, not yet published, for the cellulose microfiber functionalization. Recently, Gurgel and Gil [22] performed the chemical modification of succinylated twice-mercerized sugarcane bagasse with TETA, using 1,3-diisopropylcarbodiimide or acetic anhydride as an activating agent for batch sorption studies of Cu(II), Cd(II), and Pb(II).

In the present study, a new approach to the cellulose microfiber functionalization, based on oxidation of cellulose with sodium periodate and subsequent functionalization with N,N′-bis (2-aminoethyl) ethane-1,2-diamine, is described. Morphological data of the sorbent material were obtained by scanning electron microscopy (SEM) and surface area data, whereas spectroscopy data were evaluated by FTIR. Sorption studies, comprising sorption kinetics and isotherms, were carried out for Cd(II) ions as a model. In addition, in order to assess the practical application of the modified cellulose microfiber, a fast flow sorbent preconcentration method for Cd(II) determination by FAAS was developed. The reliable determination of Cd(II) in water samples and biological materials is described.

2. Experimental

2.1. Reagents and instruments

Cellulose microfiber (Fluka, Buchs, Switzerland; fiber length: 0.02–0.15 mm), N,N′-bis (2-aminoethyl)-1,2-ethanediamine 98% (triethylenetetramine, TETA; Sigma–Aldrich, Steinheim, Germany), sodium periodate (Merck, Darmstadt, Germany), buffer solutions (phosphate, ammoniacal and borate), hydroxylamine hydrochloride, ethylene glycol (all from Merck) were used without prior purification. The desired pH was adjusted with 0.10 mol L^{-1} sodium hydroxide or hydrochloric acid solutions. All solutions were prepared in water purified with a Milli-Q purification system (Millipore, Bedford, MA, USA). Before use, all laboratory glassware was kept overnight in a 10% (v/v) HNO_3 solution, in order to avoid any metal contamination. After that, it was rinsed with deionized water and submitted to drying procedure. A standard Cd(II) solution of 40.0 $\mu g\,L^{-1}$ was prepared from a stock standard Cd(II) solution of 1000.0 mg L^{-1} (Merck) using appropriate dilutions. Concentrated HNO_3 (Merck) and 30% (v/v) H_2O_2 (Merck) were used for the certified reference material decomposition in the block digestor.

Absorption measurements were carried out by using a Shimadzu AA-6601 flame atomic absorption spectrometer (Shimadzu, Tokyo, Japan), equipped with a hollow cathode lamp for Cd(II) and a deuterium lamp for background correction. The hollow cathode lamp was operated at 8.0 mA and the wavelength was set at 228.8 nm. The flame composition was operated with acetylene flow rate of 1.8 L min^{-1} and air flow rate of 10.0 L min^{-1}. The flow sorbent preconcentration manifold was constructed by using a peristaltic pump from Ismatec, Model IPC (Ismatec IPC-08, Glattzbrugg, Switzerland) furnished with Tygon® tubes to propel all samples and reagent solutions. Preconcentration and elution procedures were carried out by using a home-made injector commutator made of poly(methylmetacrylate). Polyethylene tubes of 0.8 mm in diameter were used to transport both the sample and the eluent. Scanning electron microscopy (SEM) analyses were performed in a Model JSM 6360-LV JEOL scanning electron microscope. Prior to the analyses, the samples were coated with a thin layer of gold/palladium alloy, using a Bal-Tec MED 020 equipment, in order to minimize charging under the incident electron beam. The specific surface area value was determined from adsorption isotherms by using the Brunauer, Emmett and Teller (BET) multipoint method and submitting the sample to previous activation in a vacuum at 150 °C for 2 h by using an automatic nitrogen gas adsorption instrument (Micromeritics Flow Sorb 2300). A FTIR Shimadzu 8300 spectrometer operating in the transmission mode between 4000 and 400 cm^{-1} was used to elucidate functional groups present in the sorbent. Elemental analyses of organic groups, incorporated into the matrices, were carried out on a CHN PerkinElmer M CHNS/O Analyzer (Model 2400, Series II). The analyses were performed in triplicate. The digestion of certified reference materials was performed by using a block digestor (Marconi, Piracicaba, Brazil). About 150 mg of TORT-2 (lobster hepatopancreas) and 165 mg of DOLT-4 (dogfish liver) were predigested overnight with 20.0 mL of concentrated HNO_3 and 5.0 mL 30% (v/v) of H_2O_2. At the end of this procedure, the samples were digested in a block digestor for 4 h at 120 °C, transferred to a beaker, heated on a hot plate to near dryness, and then cooled at room temperature with further buffering at pH 9.36 with ammoniacal buffer. For data acquisition related to analysis of variance, the STATISTICA program (version 6.0) was used.

2.2. Preparation of dialdehyde cellulose (DAC)

About 10 g of cellulose microfiber were immersed into a reaction flask containing 15 g of sodium periodate in 500 mL of deionized water. The mixture was mechanically stirred in the dark for 72 h at room temperature. After the reaction, the remaining periodate was decomposed with an excess of ethylene glycol, the solid material was filtered off, washed thoroughly with deionized water and dried in an oven at 60 °C. The resulting material will hereafter be designated as DAC [23,24].

2.3. Determination of aldehyde content

The aldehyde content was determined by elemental analysis for nitrogen of oxime groups formed by the reaction of DAC with a

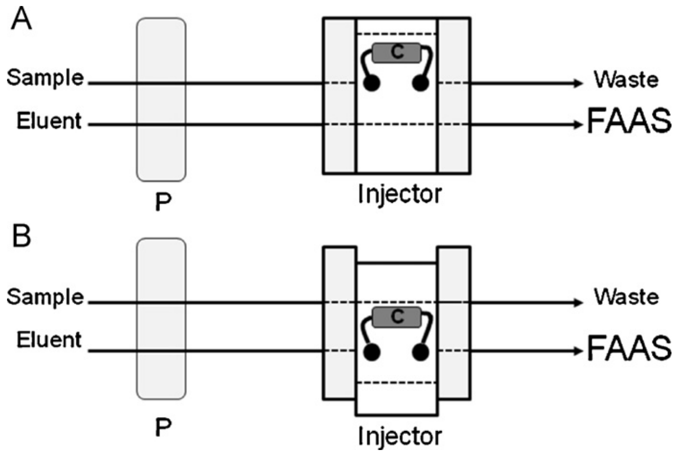

Fig. 1. Diagram of flow system for Cd(II) ions preconcentration onto DAC-TETA. (A) Preconcentration step, (B) elution step. P: peristaltic pump; C: column packed with DAC-TETA.

solution of hydroxylamine hydrochloride. In order to form the imine, 10 mL of the DAC suspension containing 0.1 g of solid was mixed with 0.4 g of hydroxylamine hydrochloride dissolved in 100 mL of 0.1 mol L^{-1} acetate buffer (pH 4.5) for 24 h at room temperature [25].

2.4. Functionalization of dialdehyde cellulose with triethylenetetramine

The DAC material was converted to a compound, containing nitrogen, through Schiff base formation reaction with triethylenetetramine. 5 g of DAC were added to 100 mL of an aqueous solution containing 2.37 g of triethylenetetramine (pH adjusted to 4.5). The mixture was stirred at room temperature for 24 h. The resultant solid was filtered, washed and dried in an oven at 60 °C for 2 h. The resulting material will hereafter be designated as DAC-TETA. The nitrogen content was determined by elemental analysis and converted to amino group per weight of cellulose.

2.5. Preconcentration of Cd(II) in flow system analysis

Based on the on-line solid phase preconcentration system as shown in Fig. 1, the DAC-TETA sorbent (195 mg) was packed in a mini-column (2.0 cm × 1.0 cm i.d.), made of polyethylene, containing fiberglass in its extremities to prevent possible losses of the sorbent during system operation [26]. Aliquots of 13.0 mL of the samples buffered with 0.266 mol L^{-1} ammoniacal buffer (pH 9.36) were percolated through the mini-column at a flow rate of 10.0 mL min^{-1}. Then, after the preconcentration procedure, the on-line desorption of Cd(II) ions towards the FAAS detector was accomplished with 1.0 mol L^{-1} HNO_3 at a flow rate of 5.0 mL min^{-1}.

2.6. Sorption isotherms

100 mg of DAC-TETA and 20.0 mL of Cd(II) solutions, with concentrations ranging from 1.0 to 60.0 mg L^{-1}, were agitated in polyethylene flasks at 25 °C for 15 min at pH 9.36 in 0.266 mol L^{-1} ammoniacal buffer. After this procedure, the suspensions were separated by centrifugation at 3000 rpm for 10 min. The amount of Cd(II) sorbed by DAC-TETA was determined according to the following equation:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{m} \qquad (1)$$

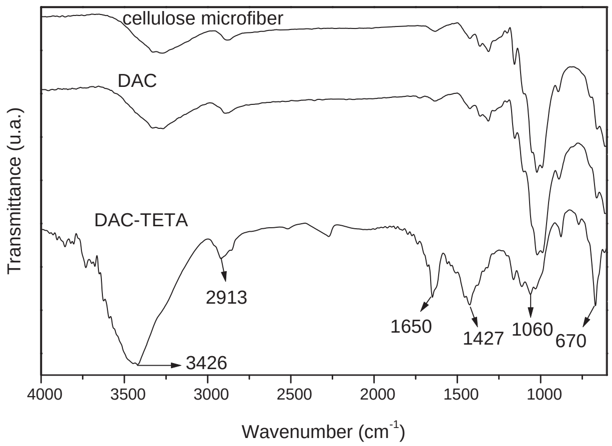

Fig. 2. FTIR spectra of pure cellulose microfiber, DAC, and DAC-TETA.

where q_{eq} is the amount (mg) of Cd(II) sorbed by DAC-TETA (g), C_0 and C_{eq} are, respectively, the initial and equilibrium concentrations (mg L^{-1}) of Cd(II) determined by FAAS, V is the volume of the solution (mL), and m is the mass (g) of DAC-TETA. The isotherm was made by plotting q_{eq} (mg g^{-1}) as a function of equilibrium concentration, C_{eq} (mg L^{-1}). In order to understand the distribution behavior of Cd(II) ions between the liquid and sorbent phases in the experimental isotherm, as well as to determine the maximum sorption capacity, different adsorption isotherm models, such as linear and non-linear Langmuir and Freundlich and non-linear Langmuir–Freundlich models, were investigated [27].

2.7. Sorption kinetics

Pseudo-first-order and pseudo-second order kinetic models are the most frequently used ones to evaluate time-dependent sorption dynamics [28]. The sorption kinetics data were obtained by shaking 100.0 mg of DAC-TETA with 20.0 mL of 1.10 mg L^{-1} Cd(II) solution in polyethylene flasks at room temperature for different periods of time (5, 15, 25, 35 and 45 min). The assays were performed at pH 9.36 in 0.266 mol L^{-1} ammoniacal buffer.

3. Results and discussion

3.1. Characterization of DAC-TETA

The nitrogen content, determined by elemental analysis and converted to amino group per weight of cellulose, resulted in 210 ± 3 μmol g^{-1}. The FTIR spectrum of DAC-TETA shows a band at 3426 cm^{-1}, which is attributed to the presence of hydroxyl groups. The absorption at 2913 cm^{-1} is related to the C–H bonds on carbons (Fig. 2). A band at 1650 cm^{-1} is referred to the N–H bond deformation in the plane, whereas at 1427 cm^{-1} it presents the corresponding absorption of the C–N stretching vibrations; at 1060 cm^{-1} it shows the absorption band due to the C–O–C bond stretching, whereas at 670 cm^{-1} it is possible to observe the C–OH out-of-plane stretching vibrations [29]. The FTIR data demonstrate that the proposed synthesis route for obtaining the DAC-TETA material is efficient. According to the SEM measurement, the cellulose microfibers present fibrous characteristics, and the functionalization has promoted a small roughness in the sorbent (Fig. 3B). Namely, it is observed that the fibrous structure of cellulose is maintained with little degradation after the DAC-TETA material synthesis, which is highly desirable for the proposed application of this solid sorbent in the flow preconcentration system for metal determination. The DAC-TETA surface area of 53.0 m^2 g^{-1} is a value very similar to those presented by some ion imprinted

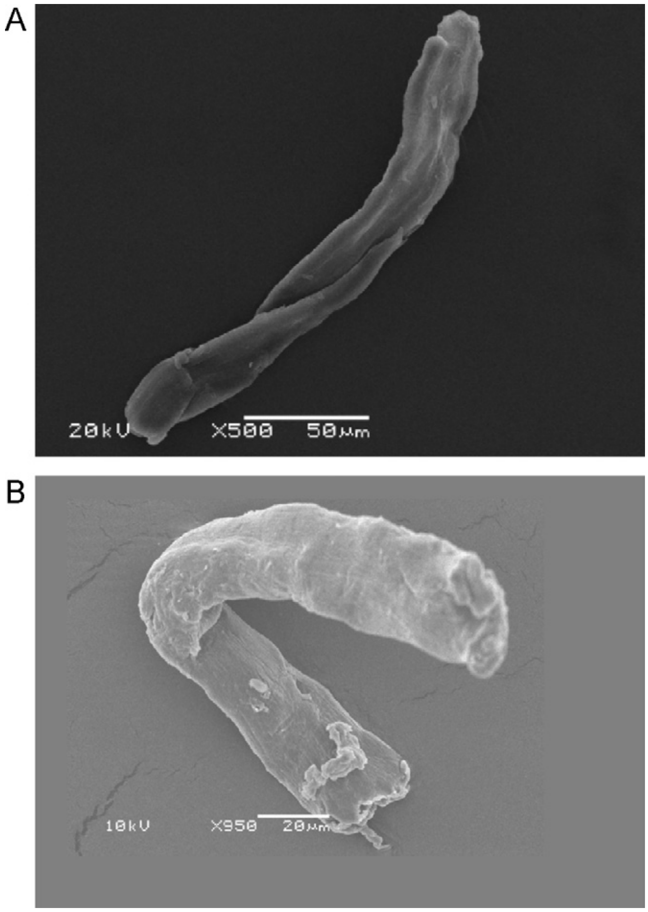

Fig. 3. SEM images of DAC (A) and DACT-TETA (B). The images are given with 500 and 950 times amplification, respectively.

polymers (58.0 $m^2 g^{-1}$) [30] and inorganic oxides, such as ZrO_2 (57.0 $m^2 g^{-1}$) [31].

3.2. Optimization study

The variables that play an important role in the solid phase preconcentration flow system, including sample pH, preconcentration flow rate, buffer concentration and eluent type, were evaluated by means of a 2^4 factorial design, as a screening assay, and a Doehlert matrix for the final optimization [32]. Table 1 presents the factors, their levels and the analytical results taken as peak height. The whole optimization process of the preconcentration system was performed by preconcentrating 13.0 mL of Cd(II) solution at a concentration of 45.0 $\mu g L^{-1}$ by setting HNO_3 as an eluent at 1.0 $mol L^{-1}$. All the assays were carried out randomly to avoid systematic errors and the data were processed by using the STATISTICAL (Version 6.0) software package. The effects of the factors, as well as their interactions, were compared to the standard error with a 95% confidence interval, according to literature [33]. As observed from Table 2, the higher effects, compared to the standard error, show the significance of the variables, as well as their interactions in the preconcentration system. Owing to the positive effect (0.0256), the amount of Cd(II) ions retained onto DAC-TETA increases with the sample pH increment. Such behavior could be rationalized on the basis of the deprotonation of nitrogen atoms present in the TETA structure at higher pH values, at which the Cd(II) sorption occurs more efficiently because of complex formation. The experimental domain, investigated for the preconcentration flow rate (4.5–10.0 $mL min^{-1}$), leads to slight effect on the analytical signal, thus proving the large accessibility of binding sites and quick mass transfer of Cd(II) towards the DAC-TETA surface. Therefore, in order to achieve a solid phase preconcentration flow system with high sample throughput and low sample consumption, without analytical signal losses, a preconcentration flow rate of 10.0 $mL min^{-1}$ was chosen for further studies. Taking into account the use of a single-line solid phase preconcentration system, where the sample is driven through packed mini-column followed by acid elution, the preconcentration pH after each preconcentration/elution cycle can be kept unchanged only by adjusting the pH of sample with buffer solution. As observed in the present study, the negative effect of −0.1779 for the buffer concentration demonstrates that at high ionic strength of phosphate buffer, the sorption rate of Cd(II) ions is seriously diminished. However, in addition to this study, the influence of Cd(II) sorption at pH 9.0 in the presence of different buffer solutions (borate and ammoniacal) at both low and high concentrations, 0.009 and 0.1 $mol L^{-1}$, respectively, was also examined. From the results (data not shown), it could be seen that Cd(II) was more efficiently sorbed onto DAC-TETA using ammoniacal buffer solution at a concentration of 0.1 $mol L^{-1}$, with around 30% improvement of

Table 1
Factors, design matrix, employed in the 2^4 design, and analytical results.

Variables	Levels	
	(–) Low	(+) High
pH[a]	7	9
Preconcentration flow rate (PFR) ($mL min^{-1}$)	4.5	10
Buffer concentration (BC) ($mol L^{-1}$)	0.009	0.1
Eluent type (ET)	HCl	HNO_3

Assays	pH	PFR	BC	ET	Absorbance (peak height)
1	–	–	–	–	0.2779/0.2693
2	+	–	–	–	0.2547/0.2543
3	–	+	–	–	0.2310/0.2276
4	+	+	–	–	0.2416/0.2446
5	–	–	+	–	0.0595/0.0636
6	+	–	+	–	0.0709/0.0683
7	–	+	+	–	0.0546/0.0544
8	+	+	+	–	0.0584/0.0612
9	–	–	–	+	0.3290/0.3280
10	+	–	–	+	0.2964/0.2734
11	–	+	–	+	0.2567/0.2688
12	+	+	–	+	0.2618/0.2634
13	–	–	+	+	0.0649/0.0696
14	+	–	+	+	0.0878/0.0817
15	–	+	+	+	0.0502/0.0567
16	+	+	+	+	0.2831/0.2653

[a] Note: Buffered with phosphate buffer solution.

Table 2
Effects and standard error calculated for the 2^4 factorial design.

Variables and their interactions	Effect ± standard error
pH	0.0256 ± 0.00153
PFR	0.0021 ± 0.00153
BC	−0.1779 ± 0.00153
ET	0.0462 ± 0.00153
pH × PFR	0.0343 ± 0.00153
pH × BC	0.0379 ± 0.00153
pH × ET	0.0236 ± 0.00153
PFR × BC	0.0381 ± 0.00153
PFR × ET	0.0203 ± 0.00153
BC × ET	0.0117 ± 0.00153
pH × PFR × BC	0.0152 ± 0.00153
pH × BC × ET	0.0332 ± 0.00153
pH × PFR × ET	0.0267 ± 0.00153
PFR × BC × ET	0.0284 ± 0.00153
pH × PFR × BC × ET	0.0241 ± 0.00153

PFR: preconcentration flow rate; BC: buffer concentration; ET: eluent type.

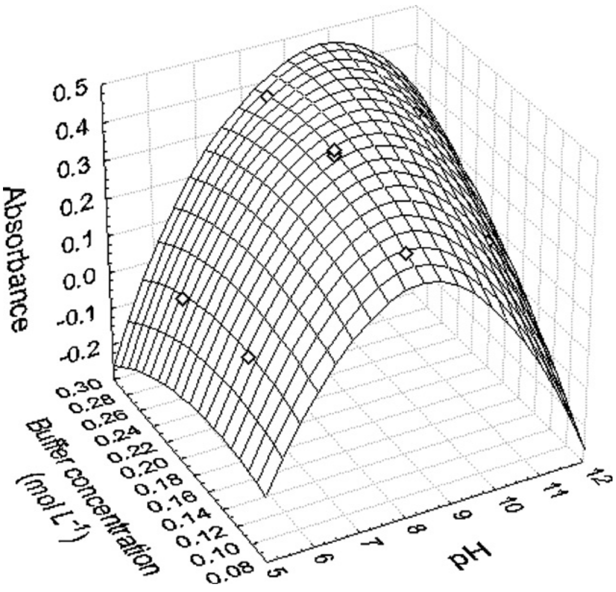

Fig. 4. Response surface relating pH, buffer concentration (mol L^{-1}), and absorbance.

the analytical signal, as regards measurements in the presence of 0.009 mol L^{-1} phosphate buffer. Finally, the eluent type selection (positive effect of 0.462) reveals that nitric acid is more efficient to strip off Cd(II) ions sorbed onto DAC-TETA.

Considering the above comments, it is possible to state that nitric acid, as an eluent, and ammoniacal solutions as buffers constitute the best set of conditions for the Cd(II) preconcentration in future experiments. Hence, the Doehlert matrix, comprising 7 assays that contained four replicates at the central point, was built for the final optimization of the sample pH and buffer concentration (Table 3). The greatest absorbance was verified at the central point, thus indicating the presence of positive curvature. So, the experimental data from the Doehlert matrix were modeled by the following quadratic model: $\text{Abs} = -2.0473 + 0.5614\text{pH} - 0.879BC - 0.0363\text{pH}^2 + 0.4451\text{pH}BC - 6.1828BC^2$, whose response surface is illustrated in Fig. 4. The values predicted by the quadratic model are shown in Table 3, and they are found to be very close to those experimental values. The maximum point under the response surface was obtained by solving the quadratic model as a function of pH and buffer concentration, with values of 9.36 and 0.266 mol L^{-1}, respectively.

3.3. Breakthrough curve

The influence of the sample volume, percolated through the mini-column packed with DAC-TETA (195 mg), was evaluated from breakthrough experiments. Under optimized conditions, aliquots of 5.0 mL of Cd(II) at 500 $\mu\text{g L}^{-1}$ were continuously percolated through the mini-column, where each aliquot was further collected, and the Cd(II) amount was determined by FAAS. It was observed that, using 40.0 mL of a standard solution, the Cd(II) amount is fully sorbed by DAC-TETA, resulting in a breakthrough capacity of 0.037 mg g^{-1}.

3.4. Sorption isotherms

Sorption capacity corresponds to the maximum amount of a sorbate that could be retained onto a sorbent under equilibration time. Thus, before the construction of adsorption isotherms, the time dependence of the binding amounts of Cd(II) onto DAC-TETA was evaluated using batch procedures. In order to achieve this aim, 100.0 mg of DACT-TETA were mixed with 20.0 mL of 1.1 mg L^{-1} Cd(II) solution at pH 9.36 and agitated during elapsed times varying from 5 to 45 min. These assays were carried out in closed polyethylene flasks at room temperature. It was observed that the rate, at which the quantitative sorption of Cd(II) ions occurs, was reached in 15 min, and after this period of time a further decrease in metal uptake was observed. A reasonable explanation for this behavior could be associated with the very fast kinetic transference of the Cd(II) onto the DAC-TETA surface, in agreement with the behavior seen in the solid phase preconcentration flow system previously mentioned. After equilibration for 15 min, the desorption process, more intense than the sorption, was observed, which promoted the stripping off of Cd(II) from the DAC-TETA surface. Thus, to determine the sorption capacity, the dispersions were agitated for 15 min. Figs. 5 and 6 show the experimental and theoretical isotherms constructed using linear Langmuir and Freundlich models and non-linear Langmuir, Freundlich, and Langmuir–Freundlich models. As can be seen from these figures, the linear Freundlich isotherm presents a reasonable fitting to the experimental data ($R^2 = 0.9848$), thus indicating that the Cd(II) sorption onto DAC-TETA possibly takes place by interaction with heterogeneous sorptive sites arranged in multilayers. However, considering that the empirical Freundlich isotherm does not provide the sorbent saturation condition, the estimated maximum sorption capacity was determined by the hybrid non-linear Langmuir–Freundlich model. In this sense, the sorption uptake was found to be 4.59 mg g^{-1}, with a very good regression coefficient ($R^2 = 0.9966$) (Fig. 6B and Table 4). On the other hand, the non-linear Langmuir model provided an overestimation of the maximum

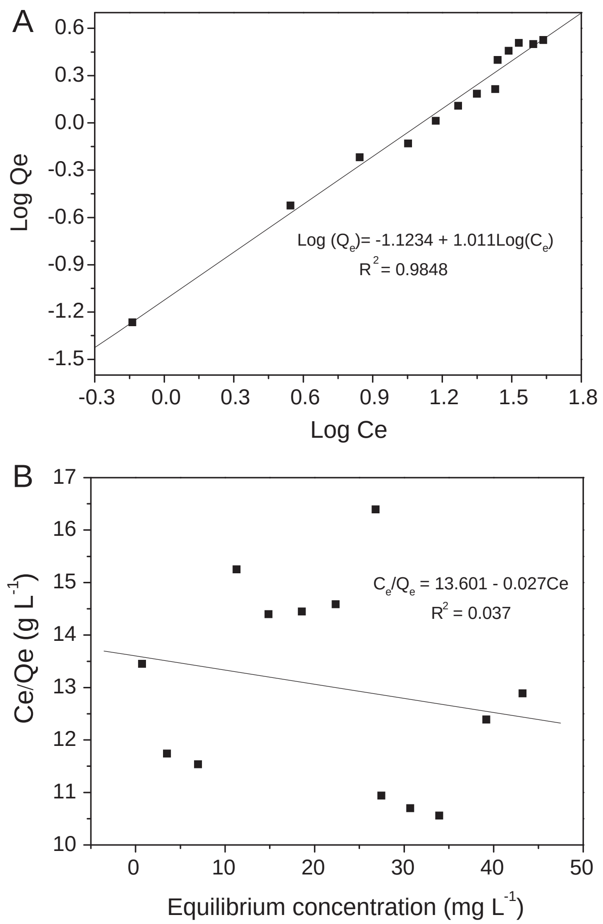

Fig. 5. Experimental isotherm and theoretical isotherms of Cd(II) ions onto DAC-TETA. (A) Langmuir and Freundlich; (B) Langmuir–Freundlich isotherm.

Table 3
Doehlert matrix used in the optimization of Cd(II) solid phase preconcentration using DAC-TETA as a sorbent.

Assays	pH	Ammoniacal buffer concentration (mol L^{-1})	Absorbance (peak height)	Value predicted by quadratic model
1	0 (8.3)	0 (0.1910)	0.4223/0.4293/0.4170/0.4310	0.4238
2	0 (8.3)	1 (0.2820)	0.4023	0.4140
3	0.866 (10.9)	0.5 (0.2365)	0.3673	0.3530
4	0 (8.3)	−1 (0.1000)	0.3451	0.3313
5	−0.866 (5.7)	−0.5 (0.1455)	0.0716	0.0836
6	−0.866 (5.7)	0.5 (0.2365)	0.0328	0.0200
7	0.866 (10.9)	−0.5 (0.1455)	0.1955	0.2060

The first number represents the Doehlert matrix coded values, whereas the values between parentheses stand for the real values.

Table 4
Isotherm parameters for Cd(II) sorption onto DAC-TETA.

Models	Equation	K[a]	b_1	n_1	R^2
Linear Langmuir	$C_e/Q_e = C_e/b_1 + 1/(n_1 b_1)$	1.98×10^{-3}	37.04	–	0.0370
Linear Freundlich	$\log(Q_e) = \log(n_1) + n_1 \log(C_e)$	7.53×10^{-2}	–	1.01	0.9848
Non-linear Langmuir	$Q_e = Kb_1 C_e/(1 + KC_e)$	8.03×10^{-3}	12.59	–	0.9205
Non-linear Freundlich	$Q_e = KC_e^{n_1}$	5.00×10^{-2}	–	1.10	0.9474
Non-linear Langmuir–Freundlich	$Q_e = Kb_1 C_e^{n_1}/(1 + (KC_e)^{n_1})$	2.19×10^{-2}	4.59	1.07	0.9966

[a] Note: K_L (Langmuir) (L g^{-1}); K_F (Freundlich) (mg g^{-1}) (L g^{-1}), b_1 (maximum sorption capacity, in mg g^{-1}), n_1 = empirical parameter related to the sorbent surface heterogeneity.

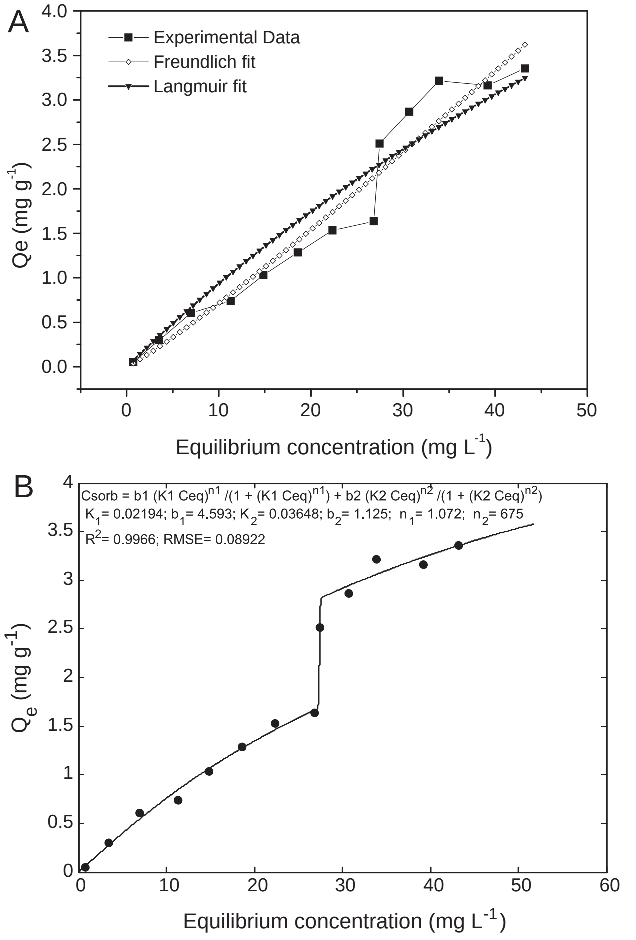

Fig. 6. Linear Freundlich (A) and Langmuir (B) isotherms of sorption of Cd(II) onto DAC-TETA.

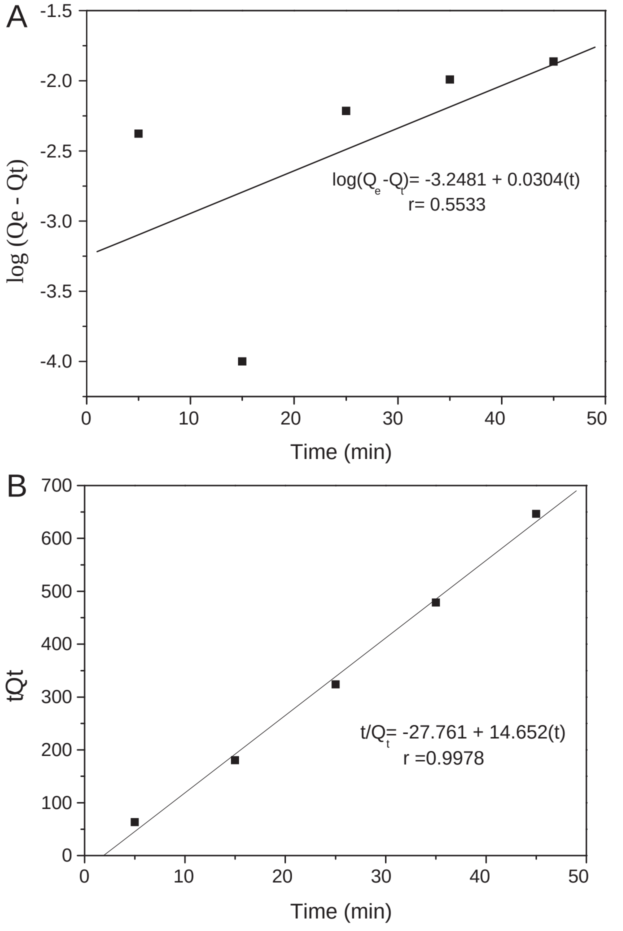

Fig. 7. Kinetic models of pseudo-first-order (A) and pseudo-second-order (B) for sorption of Cd(II) ions onto DAC-TETA.

sorption capacity of 12.59 mg g^{-1}. These findings demonstrate that DAC-TETA may assume, in fact, the existence of homogeneous and heterogeneous binding energy sites, which can be ascribed to dialdehyde and nitrogen groups present in TETA. Therefore, it appears that, at low concentrations, Cd(II) is retained mainly by interaction with nitrogen, but with negligible interaction with dialdehyde groups (heterogeneous binding), whereas at high concentrations, the sorption takes place on a completely homogeneous sorbent surface, *i.e.*, the dialdehyde groups. Such observations were further corroborated with the sorption kinetic data.

3.5. Sorption kinetics

The Cd(II) sorption dynamics was assessed as dependent on contact time, by employing the pseudo-first-order and pseudo-second-order models, Eqs. (2) and (3), respectively. Each model is characterized by its sorption rate (k) and it involves two variables, q_t and q_{eq}, namely, the sorbate amounts in relation to time (min) and equilibrium ($\mathrm{mg\,g^{-1}}$), respectively.

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303}t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \tag{3}$$

The pseudo-first-order kinetic model reports that the sorbate is bound to a single active site onto the sorbent surface. Additionally, it assumes that the rate of occupation of sorption sites is proportional to the square of the number of unoccupied sites [28]. On the other hand, the sorption kinetic data, modeled by the pseudo-second-order model, are characterized by the sorption process, where the sorbate is bound to two active sites onto the sorbent surface, and similarly to the previous model, this one also assumes that the rate of occupation of sorption sites is proportional to the square of the number of unoccupied sites. The results, obtained by the kinetic models (Fig. 7), demonstrate that the Cd(II) sorption onto DAC-TETA follows the pseudo-second-order kinetics ($r = 0.9978$). It means that two groups of sites with different energies are, in fact, responsible for the sorption of Cd(II) ions. Such sites are related to the dialdehyde function still present in the cellulose microfiber, as well as the nitrogen groups present in TETA.

3.6. Selectivity studies

The ability of DAC-TETA to enhance the preconcentration of Cd(II) ions in the flow system in the presence of other foreign ions was investigated. Foreign ions were added individually to 50 mL of 10.0 $\mu\mathrm{g\,L^{-1}}$ Cd(II) solution and submitted to the optimized preconcentration procedure. Satisfactory results were obtained for the Cd(II) preconcentration with high recovery in comparison with the Cd(II) solution in the absence of foreign ions (Table 5). Therefore, synthesized DAC-TETA is well suited for interference-free extraction and determination of Cd(II) ions with high sample throughput.

Table 5
Influence of foreign ions on solid phase preconcentration of Cd(II) using DAC-TETA as an sorbent.

Foreign ions	Proportion (analyte/interferent) (w/w)	Recovery of Cd(II) analytical signal (%)[a]
Co(II)	1:50	107.91
Se(IV)	1:50	106.36
As(III)	1:50	113.69
Sb(III)	1:50	100.05
U(IV)	1:50	110.56
Th(IV)	1:50	94.77
Ca(II)	1:100	104.17
Ba(II)	1:100	105.87
Mg(II)	1:100	100.00

[a] Results obtained from measurements performed in triplicates.

3.7. Figures of merit and analytical application

The parameters of the analytical performance of the solid phase preconcentration flow system using DAC-TETA as a sorbent are depicted in Table 6. The calibration curve for the proposed method was experimentally determined and found to be linear up to at least 140.0 $\mu\mathrm{g\,L^{-1}}$, described by the equation: Abs = 0.0452 + 0.0078[Cd(II)] ($R^2 = 0.9937$). The limits of detection and quantification of 0.069 and 0.20 $\mu\mathrm{g\,L^{-1}}$, were established in agreement with IUPAC, as three and ten times the standard deviation of ten blank solutions, respectively [34]. The parameters, consumption index (CI), preconcentration factor (PF) and concentration efficiency (CE) were calculated according to literature [26]. The precision of the overall preconcentration method, assessed by repeatability ($n = 10$) of 5.0 and 100 $\mu\mathrm{g\,L^{-1}}$ Cd(II) solutions, was found to be 7.78 and 2.53%, respectively. In view of the results shown in Table 6, it could be observed greater performance for the proposed method than for other previously and recently published solid phase preconcentration methods. Besides, it was revealed that the material appeared to be very stable for several measurements. In order to illustrate the practice analysis feasibility, the method was applied to the determination of Cd(II) in water samples from different sources, using external calibration curve. The tap water and mineral water samples were obtained from the Chemistry Department of the State University of Londrina and from a local supermarket, respectively. The lake water was collected in polypropylene bottles from Igapó Lake located in the city of Londrina. Normal saline, containing high salt content [0.9% of NaCl (w/v)], was acquired from a drugstore, and the synthetic seawater was prepared by previously published procedures [39]. Based on satisfactory recovery of spiked Cd(II), ranging from 94.92 up to 103.68% (Table 7), the method enables the adequate determination of this metal in water samples even at low levels. The accuracy was checked by analysis of certified reference materials. The certified contents of Cd(II) in TORT-2 and DOLT-4 were 26.70 ± 0.60

Table 6
Comparison of recently published methods for Cd(II) preconcentration based on on-line solid phase preconcentration coupled to FAAS.

Sorbent	PV (mL)	PF	LOD ($\mu\mathrm{g\,L^{-1}}$)	Sample throughput ($\mathrm{h^{-1}}$)	CE ($\mathrm{min^{-1}}$)	CI (mL)	Eluent	Ref.
Poly(divinylbenzene-N-vinylpyrrolidone) co-polymeric beads (Oasis HLB)	12	155	0.09	24.0	103	0.07	Methanol	[35]
$\mathrm{Cd^{2+}}$-imprinted poly(ethylene glycol dimethacrylate-co-vinylimidazole)	15	38.4	0.08	22.4	14.3	0.39	$\mathrm{HNO_3}$	[4]
Chloromethylated polystyrene functionalized with N,N-bis (naphthylideneimino)diethylenetriamine (NAPdein)	10	50	0.25	24.0	25	0.2	$\mathrm{HNO_3}$	[36]
Cadmium(II)-imprinted polymer	16	117	0.11	20	39.1	0.14	$\mathrm{HNO_3}$	[37]
Microcolumn of 1,10-phenanthroline immobilized on surfactant-coated alumina	20	41	0.14	14	27	0.48	Ethanol	[38]
DAC-TETA	13	26	0.069	39	20	0.5	$\mathrm{HNO_3}$	Present work

Note: PV, preconcentration volume; PF, preconcentration factor; LOD, limit of detection; CE, concentration efficiency; CI, consumption index.

Table 7
Evaluation of recovery values for Cd(II) ions determination in water samples.

Samples	Cd(II) ions added (μg L^{-1})	Cd(II) concentration found (μg L^{-1})[a]	Recovery (%)
Tap water	0	<ND	–
	3.00	3.10 ± 0.18	103.68
Mineral water	0	<ND	–
	3.00	3.12 ± 0.14	101.63
Lake water	0	0.75 ± 0.04	–
	3.00	3.55 ± 0.05	94.92
Synthetic seawater	0	<ND	–
	3.00	2.89 ± 0.01	96.97
Normal saline	0	0.27 ± 0.04	–
	3.00	3.31 ± 0.10	101.53

Not detected (ND) = below of limit of detection.

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

and 24.30 ± 0.80 mg kg^{-1}, respectively. Thus, the respective results, obtained by the method in authentic triplicates, were found to be 26.13 ± 0.68 and 21.95 ± 1.54 mg kg^{-1}, which are in good agreement (Student's *t*-test) with certified reference materials at the 95% confidence interval.

4. Conclusions

The aim of this work was to evaluate DAC-TETA as a new sorbent prepared by oxidation of cellulose with sodium periodate and subsequent functionalization with N,N′-bis (2-aminoethyl) ethane-1,2-diamine, and its application as an efficient solid phase extractor for the fast and sensitive determination of Cd(II) by FAAS in flow analysis. The functionalization of the cellulose microfiber with TETA was confirmed by FTIR spectroscopy and elemental analysis, whereas the SEM micrographs and surface area values reinforced the attractive properties of DAC-TETA as a solid sorbent for metal ion preconcentration. Some important features of the proposed method could be highlighted, including a very low limit of detection, reduced sample consumption, and, as a consequence, enhanced sample throughput. A detailed study related to the mini-column reusability was not carried out. However, considering that only the DAC-TETA mini-column was used in this manuscript, without losses in sorption capacity and selectivity, the material could be reutilized at least 100 times. Hence, DAC-TETA is a promising material for packing mini-columns, with a focus on the Cd(II) determination in routine analysis of biological and water samples.

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