Composite materials based on hybrid mesoporous solids for flow through determination of ultratrace levels of Cd(II)

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In this work we present a solid phase extraction (SPE) flow through system coupled to graphite furnace atomic absorption spectrometry (GFAAS) for the determination of Cd(II) at ultratrace levels. The flow system holds a minicolumn which was filled, one in turn, with three different lab made materials: a) mesoporous silica functionalized with 3-aminopropyl groups from 3-aminopropyl triethoxysilane (HMS); b) HMS with a resin, Amberlite IR120; c) HMS-Amberlite IR120 and polyvinyl alcohol (PVA). All the solids were characterized by FTIR and SEM. Batch experiments were performed in order to study the optimum adsorption pH, the adsorption kinetics and the maximum adsorption capacity.The materials were compared in terms of their aptitude for the pre-concentration of the analyte under dynamic conditions. Microvolumes of HCl were employed for the release of cadmium and its introduction into the electrothermal atomizer.

The operational variables of the flow system were also tested and optimized. The comparison of the figures of merit revealed HMS-A-PVA as the best option from an analytical point of view: limit of detection= 4.7 ng L^{-1}, limit of quantification= 16 ng L^{-1}, RSD %= 4 (n =6, 100 ng L^{-1}), linear range: from LOQ up to 200 ng L-1 and a lifetime over 600 cycles with no obstructions to the free movement of fluids, material bleeding or changes on the analytical sensitivity. The proposed method was shown to be tolerable to several ions typically present in natural waters and was successfully applied to determination of trace of Cd(II) in real samples. A full discussion of the main findings with emphasis on the interaction metal ion/fillings will be provided.

1. Introduction

Cadmium is a persistent pollutant of high toxicity for animals and human beings even at extremely low concentrations and even act as human carcinogen.[1]   It is easily accumulated in living organisms and concentrated through the food chain. The appropriate guideline values for cadmium content for drinking water by WHO[2] and USEPA[3] are 3.0 µg L^{-1} and 5.0 µg L^{-1}, respectively. Since human activities have increased its use, it is mandatory to develop reliable analytical methodologies able to determine cadmium at trace levels in all kind of samples.

As reviewed by Plotka-Wasylka et al.,[4] monitoring of compounds present in complex samples at trace or ultratrace levels usually requires a preliminary step of isolation and/or pre-concentration. Solid phase extraction (SPE) [5, 6] can meet these requisites, becoming of great value for analytical chemists.

Consequently, SPE has been widely used either in batch or in column with the aim of retaining compounds, elements or species onto different solid materials, being the elution of the analytes performed with suitable chemical reagents.[4-8] Main features of the preconcentration/elution cycles are quantitative retention and quantitative elution of the analyte, together with a high preconcentration factor.[4-9]

Minicolumn SPE has proven to be advantageous when properly managed. It allows improving the analytical performance of a given methodology, including the reduction of costs understood as high sample throughput, low amounts of reagents, reduction of wasting, environmental safety, etc.[4-12] Even though the use of SPE has been improved in the past few years through the development and refinement of new supporting formats and stationary phases (e.g. activated carbon, amorphous silica, clays, zeolites, organic chelating resins, ion-imprinting polymers, etc.), many of these materials suffer from problems such as low retention capacity, low selectivity, long equilibrium times, mechanical and/or thermal instability, etc. On this subject, several studies devoted to the design of new supports and new synthetic sorbents have been reported in the literature.[8-19] For example, resins based in styrene–divinyl benzene have been used mostly for removal of contaminants. Approaches involving surface modification, impregnation or grafting have been reported in the literature.[20-22]

Silica based mesoporous materials synthesized via the templating function of surfactant micelles[4,6,8,19,23] yield organic–inorganic hybrid with a pre-designed structure. From an ana-

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lytical point of view hybrid mesoporous silica (HMS) present good adsorption capacities; high reproducibility of the retention step; large lifetimes; and excellent perspectives for specificity.[19, 23, 27] The latter, mainly due to their high flexibility for functionalization.[4-11,19,23-27] Moreover, polymeric composites consisting of HMS and organic polymers represent a new class of materials that exhibit improved performance compared to their isolate components.[28] As a result, amino-functionalized porous hybrids and polymer composites have been fully investigated as potential adsorbents of heavy metal cations[10, 11, 25, 29-36] or organic molecules [37] demonstrating the combined advantages of the developed porous framework and the functional groups.[23-38] Nonetheless, most work on the literature highlights the physical and chemical interaction of the compound under study and the synthetized solid [12,19,23,24] leaving apart the quantitative release of the retained compound, which is mandatory for analytical purposes.

Finally, there is an important development of SPE sorbents derived from the combination of different compounds since they allow: high selectivity, easiness of use, simplicity of synthetic procedure, less consumption of organic solvents, reduction of dangerous wastes, all in agreement with principles of green chemistry.[4, 19-24]

According to this, we present the synthesis of mesoporous silica functionalized with 3-aminopropyl groups, and its combination with two new composite materials, one blended with the resin Amberlite™ IR120 (HMS-A) and the other blended with the same resin and the polymer polyvinyl alcohol (HMS-A-PVA)

The resin blended composite was thought as a way of obtaining a greater tortuosity of the pathway within the column and thus, to increase the exposure of the analyte to the amino groups of the HMS and, possibly, the number of chelating groups.

Regarding the HMS-A-PVA, it was considered that the incorporation of a water soluble polymer in a proportion that ensures adherence but not complete coverage of the original material (HSM-A) could impose a synergic effect on the chelating properties.

The structure and morphology of the sorbents were characterized by Fourier transform infrared (FT-IR), scanning electron microscope (SEM) and Brunauer–Emmett–Teller (BET) for HMS mesoporous.

The operational conditions for the adsorption/desorption of Cd(II) were optimized under static and dynamic experiments. These three sorbents were used for the preconcentration of Cd by flow through minicolumn SPE coupled to GFAAS. Figures of merit of the three approaches will be presented and compared to each other and to other alternatives recently reported in the literature, showing HMS-A-PVA the best analytical performance. Finally, the proposed methodology was applied successfully for cadmium preconcentration in real samples. As far as we know this is the first time that a blend between a resin and a hybrid mesoporous material modified with PVA has

been used for flow through preconcentration in a minicolumn coupled to GFAAS for the determination of ultratrace levels of Cd (II).

2. Experimental

2.1. Reagents

Standard solutions of Cd(II) were prepared by proper dilution of 1,000 g L^{-1} stock solutions (Merck Darmstadt, Germany) with double deionized water, DDW, (18MΩcm^{-1}, MilliQ Water System, Millipore, Bedford, MA, USA). The pH of the solutions was changed through the addition of suitable quantities of HCl or NaOH solutions (Merck) (1 mol L^{-1}).

Tetraethylorthosilicate (TEOS) 98%, cetyl trimethylammonium bromide (CTAB) (M = 364.46 g mol^{-1}) and 3-aminopropyltriethoxysilane (APTES) from Sigma–Aldrich, (Steinheim, Germany) were employed for the synthesis of the organic–inorganic mesoporous solids.

For solid-phase modification the cationic resin Amberlite™ IR120 and polyvinyl alcohol (PVA) polymer powders (Sigma-Aldrich, 99% hydrolysed, M_{av} = 89-98000 g mol^{-1}) were used.

All operations were performed in a laminar flow hood.

Nalgene glassware (Nalge, Rochester, NY, USA) was washed with a nitric acid solution (50:50 HNO$_3$: DDW) and rinsed with DDW, ethanol and acetone.

2.2. Apparatus

A pH-meter (Boeco BT-500, Germany) with a glass working electrode and a reference electrode of Ag/AgCl was used for pH measurements. FTIR spectra were collected using a NICOLET 8700 20 SXC spectrometer (Thermo Fisher). SEM micrographs were taken using a Zeiss DSM 982 Gemini (Carl Zeiss, Jena, Germany) coupled with an Energy dispersive X-ray analyzer (EDX) probe. N$_2$ adsorption–desorption analysis was performed by ASAP 2020 system (Micromeritics, USA).

Surface areas were obtained using the Brunauer–Emmentt–Teller (BET) method and pore size calculated using the Barrett–Joyner–Halenda (BJH) model.

The flow-through measurements were performed using a peristaltic pump (IPC, Ismatec, Glattbrugg-Zürich, Switzerland), 0.5 mm i.d. PTFE® tubings (Cole Parmer, Chicago, IL, USA), and acrylic minicolumns (MC) fixed to the PFTE® tubings through 0.25-28 female connectors.

FAAS determinations of cadmium in batch experiments were carried out by running the standard program of the spectrome
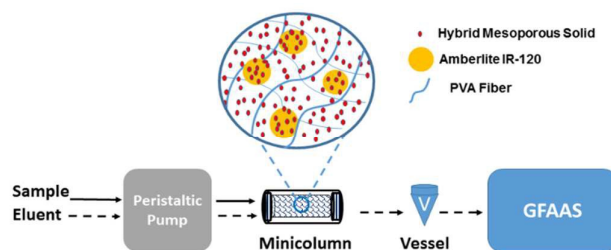

Fig.1 SPE system. GFAAS: Graphite furnace atomic absorption spectroscopy. Zoom view of minicolumn filling shows: HMS in red circles; Amberlite in yellow circles and PVA fibers in blue strings.

ter Shimadzu AA 6800 (Shimadzu, Kyoto, Japan). A Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory GFA 6000 and an autosampler ASC-6000 was used for the determination of Cd(II) after preconcentration. Cadmium hollow cathode lamp (Hamamatsu Photonics, Japan), deuterium lamp background correction and pyrolytic graphite furnaces were employed throughout the measurements. Temperature programs were those provided by the manufacturer.

2.3. Sample preparation
Tap water from our laboratories and osmosis water samples provided by dialysis treatment centers from Argentina were analyzed without pretreatment.

2.4. Procedures

2.4.1. Synthesis of the mesoporous solids
One-pot synthesis of mesoporous aminopropylfunctionalized silica was performed similarly as that described previously for mercaptopropylfunctionalized silica by Kim et al. and Walcarius and Delacôte [10,11]. The procedure involves the hydrolysis and co-condensation of TEOS and APTES in hydroalcoholic medium using CTAB as template, and ammonia (28% aqueous) as a catalyst. CTAB (2.4 g) was dissolved in 50 mL DDW, 45 mL ethanol (95–96%) and 13mL of 28% aqueous ammonia. To obtain a 20% m/m APTES/TEOS, both components were mixed in proper amounts in 5mL of ethanol as reported elsewhere.[10,11] The mixture was then added to the "surfactant + catalyst" solution and stirred for 2 h at room temperature.
The obtained solid was filtrated and washed several times with DDW and ethanol and then, it was dried in a vacuum desiccator during 10 h at 100ºC. For the surfactant extraction, the solid was refluxed with HCl 1 mol L^{-1} in ethanol at 75 ºC for 24 h. Finally, it was washed again with ethanol and DDW and dried in the vacuum desiccator for 10 h at 100 ºC.

2.4.2. Preparation of HMS-A and HMS-A-PVA composite material
After three preliminary washings with 1M HCl and NaOH solutions in order to remove chemicals residues (solvents, functionalizing agents) eventually trapped in the resin matrix, it was converted into the hydrogen form by 1M HCl and finally, washed with DDW to remove all the excess acid. After drying at 70 ºC, it was ready for further experimental work.
The HMS-A composite material was prepared by simple mixing of different amounts of the resin to the HMS, leading to composite materials with different proportions HMS-A.
To prepare the HMS-A-PVA composite, the HMS-A mixture that yielded the best analytical behaviour (details are given below) was impregnated with 1% PVA aqueous solution. Solutions of 1 % PVA were prepared by dissolving 1 g of PVA in 100 mL of DDW and then refluxing at 80 ºC for 4 h until complete dissolution.

2.4.3. Batch sorption experiments

Batch adsorption experiments were carried out by soaking 25 mg of the different composite materials: HMS, HMS-A (90/10 proportion) and HMS-A-PVA (HMS-A plus 15μL of PVA 1%), in 10 mL of a Cd solution at room temperature with magnetic stirring. In all cases, suspensions were filtered with a syringe filter of 0.22 μm. Cadmium in the filtered solutions was determined by FAAS. The standard program recommended by the manufacturer was run in all cases.
With the aim of evaluating the influence of pH on the sorption of Cd, HCl, NH_3 or NaOH solutions were employed for pH conditioning (pH 1 to 8). Suspensions were agitated during 24 h, filtered and measured.
For determining the effect of the contact time analyte/composite material, the experiments were carried out at the optimum pH, room temperature and definite intervals. Results were modelled with pseudo first order (PO1) and pseudo second order (PO2) models, accordingly to Chiron et al.[38] For pH sorption and kinetic studies the Cd(II) concentration was 5mg L^{-1}.
For adsorption isotherms, the experiments were carried out at initial Cd concentrations in the range 5–1000 mg L^{-1} at the optimum pH. The well-known adsorption isotherm model namely Langmuir was selected to analyze the equilibrium data of cadmium sorption onto the composites.[38]
The amount of cadmium sorbed (q (mg/g)) was calculated by the following expression:

$$q_e = \frac{(C_O - C_e)V}{1000\, m} \quad (1)$$

where qe is the sorption capacity in mg g^{-1}, C_0 and C_e are the initial and equilibrium concentrations of Cd in mg L^{-1}, V is the volume of the solution in mL and m is the weight of the sorbent (HMS, HMS-A, HMS-A-PVA) expressed in g.

2.4.4. Analytical procedure for Cd(II) determinations in mini-columns (MC)
The preconcentration system is shown in Fig. 1. The MC was constructed from an acrylic cylinder (3.0 cm long, 1.6 cm diameter). The inner part was drilled to obtain inner dimensions equal to 10 mm long, 0.5 mm id. The aspect ratio (length to diameter) was adjusted to keep minimal dispersion in the system together with lower resistance to the flow stream. The MC was slurry loaded with the solids (0.015 g) one in turn, by means of a syringe and used for over 500 enrichment cycles before repacking. Two plugs of polystyrene foam were placed at both sides of the filler in order to retain the solid.
In a typical experimental procedure under optimized conditions, the sample was introduced in the MC filled with each one or the three composite materials, at a flow rate of 1.0 mL min^{-1} and a pH value equal to 7.0. The preconcentration time was 10 minutes. 0.5 mL of HCl 0.5 M was employed for elution at a flow rate of 0.5 mL min^{-1}. An aliquot of 50 μL was injected into the graphite furnace and the analytical signal thus obtained.
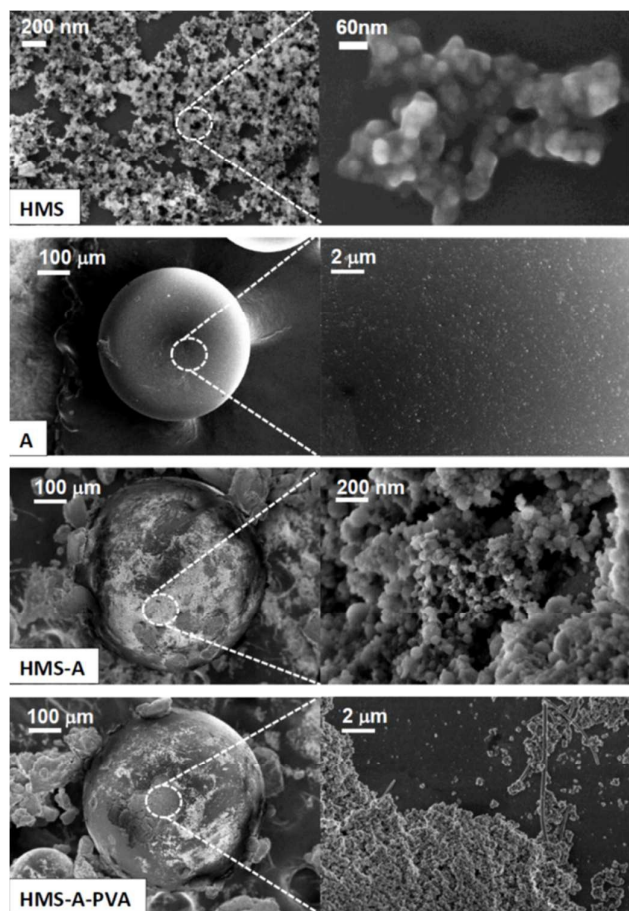
Fig. 2 SEM micrographs of HMS, Amberlite (A), HMS-A and HMS-A-PVA. On right side: magnification of the micrographs.

3. Results and discussion

3.1 Characterization

3.1.1. HMS

SEM micrographs of the solid HMS show the morphology of the synthetized material and reveal a spheres-like shape with diameters of 30 +/- 3 nm (Fig.2).

The BET measurement shows a surface area of 681 m^2 g^{-1} and a narrow pore size distribution around 3.5 nm, revealing the presence of mesopores in the solid structure.

The FTIR spectrum of the solid HMS (Fig.3) shows a broad absorption band in the region 3765–3055 cm^{-1} attributed to the stretching of the framework Si–OH group with physically adsorbed water molecules. The features around 1084.2 and 964.5 cm^{-1} indicate Si-O-Si and Si-O-H stretching vibrations, respectively. The bands around 794.7 and 462.1 cm^{-1} result from Si-O vibrations.

The absorption peaks obtained at 1635.7, 1706.8 and 1418.15 cm^{-1} could be attributed to N-H groups and/or to the v_{OH} vibration of adsorbed water, while N–H stretching (3200–3500 cm^{-1}) and C–N
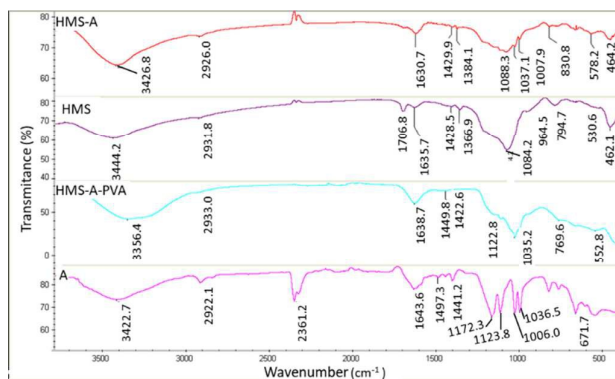

Fig. 3 FTIR spectra of (A): Amberlite, (HMS): Hybrid mesoporous solid, (HMS-A): Hybrid mesoporous solid 90%-10% Amberlite, and (HMS-A-PVA): HMS-A-1% PVA.

stretching (1030–1230 cm^{-1}) overlap with the broad absorption band of the silanol group and the Si–O–Si vibrations.[29, 31] On the other hand, the FTIR spectra reveals characteristic peaks from aliphatic C-H bond and CH_2-N bond at 2931.8 cm^{-1} and at 1366.9 cm^{-1}, respectively.[31]

Since the evaluation of the tempalte removal was difficult to follow through the IR spectraof the positive counter ion CTA^+; we studied the elimination of CTAB by the EDX determination of elemental bromine. Experiment performed EDX analysis to test this (see ESI Fig.S1). Experiments performed in the HMS showed that elemental bromine was completely removed after the HCl/ethanol treatment.

3.1.2 HMS-A and HMS-A-PVA

In order to know more about the interaction between the composite material and the analyte, a study of their composition and morphology was also performed by FTIR and SEM. SEM micrographs reveal that the HMS on the surface of the resin preserves the morphology in both cases: with or without PVA (Fig. 2). As expected, it is also observed that the polymer fibers in the solid HMS-A-PVA cover partially the resin and the HMS.

On the other hand, the FTIR spectra (Fig. 3) reveals the characteristics peaks around 1400 cm^{-1} for amino groups, vibrations bands around 1100 for the Si-O-Si and 1000 cm^{-1} for Si-OH groups, that are present in HMS-A and HMS-A-PVA.

It is needless to say that the deformation of some of these peaks can be attributed to the overlapping of other major peaks and to the interaction resin-solid (SO_3 symmetric stretching band at 1006.0, 1036.5, 1123.8 and 1172.3 cm^{-1}, SO_2 asymmetric stretching at 1411.2 cm^{-1} and C=C aromatic nucleus skeletal vibration band at 1643.6 cm^{-1}).[39] In the case of HMS-A-PVA, the broader bands assigned to Si–O–Si and Si–OH at 1084.2 and 1005.9 and in the frequency range from 3000 to 3650 cm^{-1} mainly related to hydroxyl groups, were correlated to TEOS sol–gel reactions. They could be responsible for the alteration of the three-dimensional structure of the PVA chains.[35, 40]

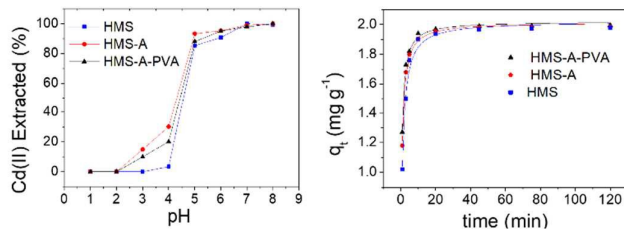### 3.2. Optimization of pH for sorption of Cd(II)

Fig.4 Effect of pH on the adsorption of Cd (II)(a) and adsorption kinetics (b) for the three sorbents.

Fig.5 Adsorption isotherms for Cd(II) onto the three solids: qe= equilibrium adsorption capacity (mg g^{-1}); Ce=equilibrium concentration (mg L^{-1}).

With the aim of modifying the surface charge of the three sorbents –one in turn- and thus, its aptitude for retaining the analyte, changes on the pH of the solutions in contact with the solid were performed in batch (see Fig.4 (a)). Results show that the percentage of extracted cadmium increases with the pH up to a value of 7 where a 99% recovery of the analyte is observed. From pH= 7 onwards no differences were observed. Lower sorption values at pHs below 3 were attributed to electrostatic repulsion between cationic cadmium -as $Cd(H_2O)_4^{2+}$ and or $CdCl^+$ [41]- and the silanols and amino groups, both protonated. [29-31] At pH above 5 the efficiency of extraction increases mainly due a combined effect of adsorption, electrostatic attraction (the surface charge of silica is negative and cadmium speciation is mainly $Cd(H_2O)_4^{2+}$ and chelation via the deprotonated amino groups. Consequently pH= 7 was selected as the best option for further experiments. Alkaline media was no assayed in order to prevent HMS dissolution or $Cd(OH)_2$ precipitation .

The three composite materials evidenced the same behaviour with respect to pH. This behaviour is not surprising since the same results are reported in the literature for similar composite materials (PVA-mesoporous silanes nanofiber and membranes).[35,36] Moreover the small amount of resin present in the lab-made sorbents aids on this assumption that no changes on pH should be expected.

3.3. Kinetic studies on the adsorption of Cd(II) onto HMS, HMS-A and HMS-A-PVA

Sorption kinetics experiments were performed in order to optimize the design of the flow through arrangement. The initial sorption velocities studies were of particular relevance due to their influence on the efficiency of SPE at short contact times analyte/filler (which is our case). Results show that Cd(II) retention at optimal pH and Cd(II) concentration of 5 mg g^{-1} increases with time during the first
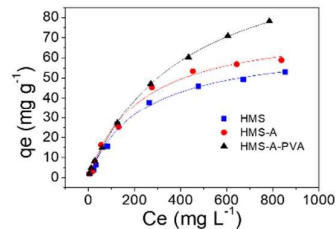
10 min and then an equilibrium value is reached. It is reasonable to assume that

this fast retention equilibrium could be attributed to strong chelation. Experimental data were modelled by means of different kinetic models according to Chiron et al., namely pseudo-first-order and pseudo-second-order.[38] Table 1 summarizes the calculated parameters qe$_1$, qe$_2$, K$_1$ and K$_2$ for each one of the composite materials. Pseudo second order (PO2) showed the best correlation to the experimental data for all the cases (See Fig.4 (b)).
These results suggest that the adsorption data of all sorbents could be chemical sorption or chemisorption.[35]
Experiments performed for both, the bare resin and the bare PVA, showed adsorption for times beyond 60 minutes. Since our experimental conditions consider contact times sample/filling of 10 minutes, the influence of the bare resin and the bare PVA resulted negligible.

3.4. Cadmium Adsorption isotherm

Langmuir isotherm plots for cadmium sorption onto HMS, HMS-A and HMS-A-PVA are shown in Fig. 5. Non-linear regression fittings were employed to calculate the maximum adsorption capacity of Cd ions onto the thee sorbents obtaining: 67 mg g^{-1} for HMS; 77mg g^{-1} for HMS-A and 111 mg g^{-1} for HMS-A-PVA. The synergy between the chelating groups could be responsible for the increment of the adsorption capacity of the different sorbents.[14, 35, 36]

3.5. Optimization of dynamic conditions for the determination of Cd(II) using minicolumn-GFAAS with the three different sorbents

3.5.1 HMS

Dynamic SPE experiments were assayed in order to reach the best conditions for sorption of the analyte onto the filled MC and its

Table 1 Kinetic adsorption parameters calculated using Pseudo-first-order and Pseudo-second-order models for the three filling materials. Concentration of Cd(II) = 5 mg L−1; Cd(II) volume= 10 ml; sorbent dosage= 0,025 g.

Filling composite material	Pseudo-first-order (PO1)			Pseudo-second-order (PO2)		
	q_{e1} [a](mg g^{-1})	K_1 [b](min^{-1})	R^2	q_{e2} [c](mg g^{-1})	K_2 [d](g mg^{-1} min^{-1})	R^2
HMS	1.93	0.61	0.93296	2.02	0.52	0.98585
HMS-A	1.93	0.85	0.92253	2.01	0.75	0.99296
HMS-A-PVA	1.94	0.98	0.90568	2.01	0.88	0.99303

[a] q_{e1} = sorption capacity for PO1 ; [b] K_1 =Kinetic constant for PO1; [c] q_{e2} =sorption capacity for PO2; constant forPO1; [d] K_2 = Kinetic constant forPO2
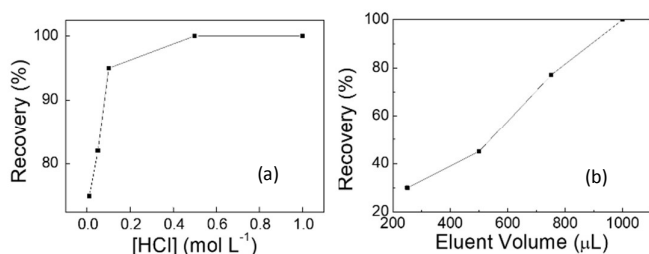
Fig.6 (a)Percent of recovery for different HCl concentrations. Sample volume: 10 mL of [Cd(II)]: 0.1 ng mL^{-1}, sample flow rate: 1 mL min^{-1}, elution flow rate: 1 mL min^{-1}, eluent volume: 1 mL, PCF: 10. (b) Optimization of elution volume. [HCl]: 0.5 mol L^{-1}, [Cd(II)]: 0.1 ng ml^{-1}, Sample volumen: 10 mL, Adsorption flow rate: 1 mL min^{-1}, Desorption flow rate: 0.5 mL min^{-1}.

Fig.7 Shows the effect of sample flow rate on preconcentration of Cd by passing through 10 mL of 0.1 µg L^{-1} Cd (II) at pH=7.

release (see Fig.1). Since the one variable at a time (OVAT) approach was employed, the loaded mass of cadmium was kept constant by passing through 10 mL of 0.1 µg L^{-1} Cd (II) at pH=7 and thus, the best conditions for elution were tested.As mentioned above, Cd(II) is not retained under high acidic conditions, so it was assumed that a high concentration of acid could be useful for elution. HCl was preferred instead of nitric acid as it prevents oxidation of the amine groups of the filling –enlarging its lifetime- and, it is more suitable for GFAAS operation. The effect of HCl concentration on the recovery of Cd(II) was studied from 0.1 to 1 M. Fig.6 (a) shows that from 0.5 M onwards, a quantitative recovery (>98%) of the analyte was observed. Consequently, HCl concentration was fixed at 0.5 M as a compromise between maximum recovery of the analyte and minimal amount or acid inside the graphite furnace. The sample flow rate and eluent flow rate were kept constant at 1mL min-1 for this preliminary experiment. The effect of the eluent volume on the recovery of Cd(II) was also study. As shown in Fig.6 (b) the minimum volume of eluent required for quantitative desorption (>98%) was found to be 1.0 mL.After fixing the eluent conditions, the sample and elution volumetric flow rates were optimized once at a time (OVAT). Both variables were changed between 0.5 and 3 mL min^{-1}. As stated above, the selected values need to comply with: no filler compaction, no internal pressure increment and maximum preconcentration factor (PCF). Values above 3 mL min^{-1} were not employed for sample introduction as the solids suffer compaction with the development of internal pressures and thus, leaking of the flowing solutions. Values below 0.5 mL min^{-1} were not compatible with the proper operation of the peristaltic pump. It can be seen that a sample flow rate of 1 mL min^{-1} was the most advantageous for preconcentration. Lower values produce a low sample throughput and higher values decrease the time of contact between the filling and the analyte and thus, the efficiency of retention. Regarding the eluent flow rate, any value below 2 mL min^{-1} allowed full recovery (>98%). However, an elution flow rate of 0.5 mL min^{-1} was selected in order to ensure maximum contact time analyte/eluent.

To summarize, the optimal dynamic conditions using HMS as sorbent and 10 mL of sample were: sample flow rate 1 mL min^{-1}, HCl 0.5 M at an elution flow rate of 0.5 mL min^{-1} with an elution volume of 1 mL. Under these conditions, the PCF was 10.
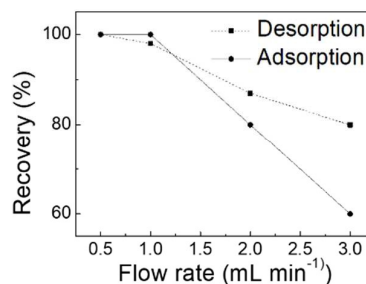
3.5.2 HMS-A and HMS-A-PVA

In order to improve the analytical sensitivity of the proposed methodology, two new composite materials were designed using the HMS synthetized in the laboratory and tested as fillers of the MC. The mass of HMS employed for the three fillers was kept constant as stated above. The first and simpler strategy was to incorporate an exchange resin (Amberlite™ IR120) with the idea of obtaining a greater tortuosity of the pathway within the column and thereby increasing the exposure of the analyte to the amino groups of the solid

and/or adding chelating groups provided by the resin. The second design, adds to the previous a polymer with chelating groups in such concentration that ensures adherence but not full coverage. Considering the dimensions of the MC (45 µL bed volume), 10 µL of PVA 1% w/w were chosen as the best option to fulfil these conditions. So, no other amounts of PVA were assayed.

For testing the first design, different blended sorbents were obtained by mixing different quantities of resin and HMS. From here, the solids will be identified with HMS-A, 0-100 indicating the proportion of HMS/ resin in each particular case. In order to compare the behaviour of the resin alone and its mixtures with different proportions of the resin, all experiments were performed under the same optimized operational conditions. Taking into account the results for the different proportions of resin (ESI Table S1) HMS-A 90-10 was chosen as the best option (Cd(II) recovery >98%). Studies involving Cd(II) recovery for the optimized proportions HMS-A and HMS-A-PVA as fillers showed the same performance that HMS alone under the conditions described above.

At this point, the reduction of the elution volume becomes the obvious step to test differences on the behaviour of the solids. To study this, the same experiment was performed by decreasing the elution volume. Results for 750 µL and 500 µL elution volumes showed 97 and 75% of Cd(II) recovery respectively for HMS-A filling, and almost > 99% for HMS-A-PVA. In the case of HMS alone, the reduction of the elution volume seriously jeopardizes the analyte recovery which is decreased up to 50% for 500 µL of eluent. These results are in agreement with the hypothesis that, under the optimal dynamic conditions, the exposure of the functional groups
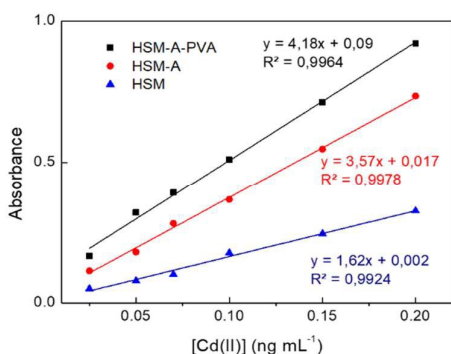
Fig.8 Working curves for Cd (II) determination. Sample volume: 10 mL, eluent [HCL]: 0.5 mol L^{-1}, eluent volume: 0.5mL.

of HMS could be the main responsible for the greater adsorption in HMS-A. In the case of HMS-A-PVA, the addition of chelating groups provided by hydroxyls could explain the findings.

If the goal is to find the best PCF, the elution volume needs to be reduced and thus, HMS-A-PVA seems the best option.

3.6 Analytical performance of HMS, HMS-A and HMS-A-PVA MC fillers

For comparison, calibration curves were constructed by concentrating 10 mL of standard solution of Cd (0.02-0.20 ng mL^{-1}) during 10 minutes at a flow rate of 1.0 mL min^{-1}, and 0.5 mL of elution volume. 50 µL of the eluent were then injected into the furnace. The results of the three different MC fillings employed with the same amount of active solid HMS and under the same experimental conditions are shown in Fig. 8. The fillings are named HMS (only the synthetized solid), HMS-A (solid + resin, 10-90) and HMS-A-PVA (solid+ resin and 1% PVA), respectively. Table 2 shows the figures of merit obtained with the three different solids as MC fillers. To notice, the three materials could be reused more than 500 cycles without significant losses in analytical sensitivity (no changes in the slope of the working curve). Note that the extremely low concentration of cadmium and the short times of contact under dynamic conditions (no need to reach equilibrium), allow this remarkable

reuse of the filling. Table 3 shows some figures of merit of the proposed methodology in comparison to others recently reported in the literature.[16-18, 30]

Amongst the numerous studies, the references selected are those where the instrumental detection (GFAAS) is not a variable. It can be observed that dynamic linear range and precision expressed as RSD %, are similar. Regarding limits of detection, they are also similar except for reference 16, which seems rather optimistic considering a limit of quantification (LOQ) equal to 0.01 ng ml^{-1} (see reported linear range which is assumed takes its lower value as equal to LOQ). Also it is important to note that the proposed method does not require matrix modifiers[15] for the GFAAS operation (adding steps even in the case of permanent`s) or the employment of strong magnetic fields that conspire with the possibility of automation.[16]

It is worthy to notice that the best performance in terms of number of cycles of sorption/desorption without significant losses of sensitivity is obtained with the procedure presented here. Also a lower sample consumption and higher sample throughput is attained.

3.7 Interferences study

Since the ultimate objective of this work is its further application to the determination of Cd(II) in natural waters, the effect of potential ions of usual occurrence in these samples was also carried out. Employing the best performance filling, HMS-A-PVA, in a minicolumn for SPE, different concentrations of Pb(II), Ni(II), Co(II), Zn(II), Na(I), chloride and nitrate ions, one in turn, were added to Cd(II) solutions. It was shown that no interference of the analytical signal was observed for concentrations up to 10 times higher than those typically present in river waters, which makes this approach able to perform the determination in such kind of samples (Table 4).

3.8 Applications to real samples.

The suitability for the analysis of real samples with HMS-A-PVA filler under optimal conditions was applied to Cd determination in osmosis and tap water, as shown in Table 5. As Cd concentration in the analysed samples was below the detection limit achieved here (See Table 3), known amounts of traces of Cd were spiked to the samples and recovery values ranging between 99-103% were obtained.

Table 2. Figures of merit for Cd(II) determination: Comparison of performance for HMS, HMS-A and HMS-A-PVA.

MC filler	LOD [a](ng mL^{-1})	LOQ[b](ng mL^{-1})	RSD %(n=6; 0.1 ng mL^{-1})[c]	%Recovery	Max Nº cycles[d]
HMS-A-PVA	0.0047	0.016	4	100	>600
HMS-A	0.0055	0.018	6	85	500-600
HMS	0.0121	0.040	11	39	500

[a] LOD is defined as 3Sb/m and [b] LOQ as 10Sb/m, respectively, where Sb is the SD of ten measurements of a procedural blank and m is the slope of the calibration graph. [c] Obtained with solid synthetized in different days, [d] Max N° cycles: Maximum number of cycles. Cycle: sorption/desorption in optimal conditions. [Cd (II)]: 0.1 ng mL^{-1}, sample volume: 10mL, eluent [HCL]: 0.5 mol L^{-1}, eluent volume: 0.5mL, maximum PCF in optimal conditions: 20.

Table 3 Comparison of the analytical performance of the presented method with recently reported nanomaterial-based methods for preconcentration of cadmium

Method	Sorbent	V_s[e]	ST[f] (h⁻¹)	LOD (ng mL⁻¹)	Linear range (ng mL⁻¹)	RSD (%)	Max Nº cycles	Reference
MSPE[a] –	MMCN[b]	10	4	0.0012	0.01-10	2.3	100	16
MSPE[a] -	II-MMS[c]	25	2	0.0061	0.01-0.20	4	8	30
SPE-GFAAS	NH2-IL/	50	3	0.0089	0.05-0.20	2.3	53	17
MSPE[a]-GFAAS	MAC[d]	100	10	0.0040	0.01-0.70	3.5	5	18
SPE-GFAAS	HMS-A-PVA	10	5	0.0047	0.02-0.20	4	>600	This work

[a] Magnetic solid phase extraction; [b] Magnetic Multiwalled carbon nanotubes; [c] Cd(II)-ion imprinted magnetic mesoporous material. IL/SG: Ionic liquid /Silica gel; [d] Magnetic Activated Carbon nanocomposite; [e] V_s= Sample volume; [f] ST= Sample throughput

Table 4 Maximum tolerable concentrations (MTC) of interferences in the determination of Cd (II) under optimized conditions. FPC: 20, [Cd (II)] = 0.1 ng mL⁻¹.

Interference	MTC (ng mL⁻¹)	Recovery (%)
Pb(II)	100	99±1
Zn(II)	75	100±1
Ni(II)	50	99±2
Co(II)	50	97±2
Na(I)	20000	100±1
Cl⁻	50000	98±2
NO₃⁻	50000	99±2

Table 5 Analysis of Cd(II) ions in different real samples (mean ± Sd, n = 3).

Sample	C_{added} (ng L-1)	C_{found} (ng L-1)	Recovery%
Osmosis water	0	N.D.	-
	50	49.7±3.2	99,3
	100	100.5±2.0	100.5
Tap water	0	N.D.	-
	50	50.2±2.5	100.3
	100	103.3±3.0	103.3

4. Conclusions

This work shows an easy way to improve the analytical performance of cadmium determination via a rational design of composite materials for preconcentration purposes that combine the complexing ability of the different components of the filling together with the dynamic conditions imposed by a flow through system holding a packed minicolumn. Overpressure was prevented and bleeding of the solid as well. As described above, HMS-A-PVA proved to be the best option for these purposes. Moreover, the proposed methodology does not require toxic organic solvents show slow sample consumption, high sample throughput, similar LOD as methods already

reported and excellent reusability. It was applied to real water samples with good percentages of recovery after the addition of ultratrace amounts of cadmium.

Conflicts of interest

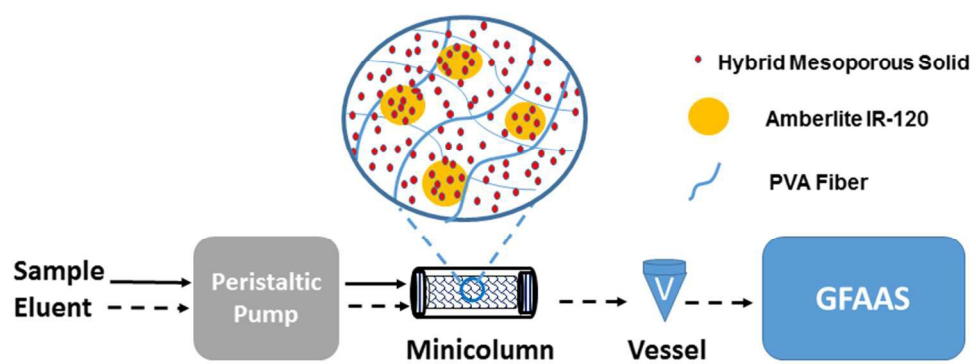The authors declare no conflicts of interest in this article

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References

1 International Agency for Research on Cancer (IARC) 1993, 19, 360–374.
2 World Health Organization (2006). Guidelines for drinking-water quality (3rd ed., Vol. 1). Geneva: Recommendations.
3 Unites States Environmental Protection Agency (2003). National primary drinking water standards, June 2003.
4 J. Płotka-Wasylka , N. Szczepańska, M. de la Guardia, J. Namieśnik, *TrAC - Trends Anal. Chem.*, 2016, **77**, 23–43.
5 http://www.waters.com/waters/en_PL/Beginner's-Guide-to-SPE-[Solid-Phase-Extraction]/nav.htm?locale=en_PL&cid=134721476 (2015)
6 B. Buszewski, M. Szultka, *Crit. Rev. Anal. Chem.*, 2012, **42**, 198–213.
7 A.R. Türker, *Sep. Purif. Rev.*, 2012, **41**, 169–206.
8 B. Hu, M. He, B. Chen, *Anal. Bioanal. Chem.,* 2015, **407**, 2685–2710.
9 R. Clough, C.F. Harrington, S.J. Hill, Y. Madrid, J.F. Tyson, *J. Anal. At. Spectrom.,* 2013, **28**, 1153.
10 M.L. Kim, M.B. Tudino, *Talanta*, 2010, **82**, 923–930.
11 A. Walcarius, C. Delacôte, *Anal. Chim. Acta,*2005, **547**, 3-13
12 V. Valtchev, L. Tosheva, *Chem. Rev.*, 2013, **113**, 6734–6760.
13 K. Pyrzynska, *TrAC - Trends Anal. Chem.*, 2010, **29**, 718–727.
14 S. Kocaoba, *J. Hazard. Mater.*, 2007, **147**, 488–496.
15 A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, *J. Colloid Interface Sci.*, 2005, **282**, 20-25.

16 L. Wang, X. Hang, Y. Chen, Y. Wang, X. Feng, *Anal. Lett.*, 2016, **49**, 818-830.

17 S. Wen, X. Zhu, Q. Huang, H. Wang, W. Xu, N. Zhou, *Microchim. Acta*, 2014, **181**, 1041-1047.

18 S. Mohajer, M. Chamsaz, M.H. Entezari *Anal. Methods*, 2014, **6**, 9490-9496.

19 F. Augusto, L.W. Hantao, G.S. Noroska, S.C.G.N. Braga, *TrAC - Trends Anal. Chem*., 2013, **43**, 14–23.

20 T. Prasada Rao, R. S. Praveen, Sobhi Daniel, *Crit. Rev. Anal. Chem.,* 2004, **34**, 177-193.

21 Setapar, A. Khatoon, R. A. Shiekh, *J. Environ. Sci.,* 2015, **31**, 104-123.

22 N.S harma, S.Tiwari, R. Saxena, *RSC Advances,* 2016, **6**, 10775-10782

23 A. Walcarius, M.M. Collinson, *Annu. Rev. Anal. Chem*., 2009, **2**, 121–143.

24 F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chemie - Int. Ed.*, 2006, **45**, 3216–3251.

25 S. Hamoudi , A. El-Nemr, K. Belkacemi, *J. Colloid Interface Sci.,*2010, **343**, 615-621.

26 K.M. Parida, D. Rath, *J. Mol. Catal A-Chem*., 2009, **310**, 93-100.

27 I. Sierra, D. Pérez-Quintanilla, *Chem. Soc. Rev*., 2013, **42**, 3792–3807.

28 S. Moulay, *Polymer Plast. Technol. Eng*., 2015, **54**, 1289-1319.

29 Y. Yu Zhao, S. Zhai, B. Bin Zhai, Q. An, *J Sol-Gel Sci Techn.,* 2012, **62**, 177–185

30 B. Zhao, M. He, B. Chen, B. Hu, *Spectrochim. Acta - Part B At. Spectrosc.*, 2015, **107**, 115–124.

31 M. Imamoglu, D. Pérez-Quintanilla, I. Sierra, *Microporous Mesoporous Mater.,* 2016, **229**, 90–97.

32 A. Heidari, H. Younesi, Z. Mehraban, *Chem. Eng. J.,* 2009, **153**, 70–79.

33 L.C.C.D. Silva, L.B.O.D. Santos, G. Abate, I.C. Cosentino, M.C.A. Fantini, J.C. Masini, J.R. Matos*, Microporous Mesoporous Mater*., 2008, **110**, 250–259.

34 Y.K. Lu, J. Tan, X.P. Yan, *Anal. Chem*., 2004, **77**, 453–457.

35 M. Irani, A.R. Keshtkar, M.A. Moosavian, *Chem. Eng. J.*, 2012, **200**, 192–201.

36 M. Irani, A.R. Keshtkar, M.A. Mousavian, *Chem. Eng. J.*, 2011, **175**, 251–259.

37 J. Ganan, S. Morante-Zarcero, D. Perez-Quintanilla, I. Sierra, *Anal. Methods*, 2015, 7, 4740– 4749.

38 N. Chiron, R. Guilet, E. Deydier, *Water Res.*, 2003, **37**, 3079–3086.

39 P.U. Singare, R.S. Lokhande, R.S. Madyal, *Open J. Phys. Chem.,* 2011, **1**, 45–54.

40 H.S. Mansur, R.L. Oréfice, A.A.P. Mansur, *Polymer,* 2004, **45**, 7193–7202.

41 W. Stumm, J.J. Morgan, *Aquatic Chemistry*, (3er Ed) Wiley &Sons, New York, 1995.

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