



## Preconcentration and determination of Cu(II) in a fresh water sample using modified silica gel as a solid-phase extraction adsorbent

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### ABSTRACT

A method was developed to attach 4-amino-2-mercaptopyrimidine (AMP) onto silica gel surface and to determine trace metals. The surface functionalization reaction was performed with a silylant agent, chloropropyltrimethoxysilane (Si-CPTS), and the product, Si-AMP, was characterized by FT-IR and elemental analysis to evaluate the surface modification. The functionalized silica was applied in the sorption of Cu(II) ions from an aqueous medium. The series of adsorption isotherms were adjusted to a modified Langmuir equation and the maximum number of moles of adsorbed copper was  $0.447 \text{ mmol g}^{-1}$ . The modified material was placed in a preconcentration system, where it reached an approximately 20-fold enrichment factor using 5 mg of Si-AMP. The proposed method was applied in the preconcentration and determination of Cu(II) in a fresh water sample from the Paraná river and was validated through a comparative analysis of a standard reference material (1643e).

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### 1. Introduction

In the last two decades, metal ions have been the focus of numerous studies of contaminants in aquatic environments. Their occurrence has raised major public health concerns due to their increasing presence in aquatic compartments and organisms [1–3]. Numerous harmful health effects, such as high blood pressure, and kidney and nervous system impairment, have been imputed to metal ions such as cadmium and lead, and all these metals, including copper, are considered toxic to aquatic biota [3]. In response to these concerns, several research groups have focused on the development of adsorbent materials that can be applied in combination with techniques such as atomic absorption spectrometry (AAS) and inductively coupled plasma optical emission (ICP OES) [4–10]. In general, these materials must be susceptible to surface modifications through chemical reactions with silica, cellulose, etc. Among the many types of solid phases used in solid-phase extraction (SPE), silica gel is the most common due to its advantageous characteristics of thermal stability, no swelling and hydroxyl reactive

groups [11,12]. To achieve considerable metal sorption capacity, molecules with basic centers are attached onto the surfaces of materials directly or through a silylant agent [13–16]. The basic centers consist of oxygen, nitrogen, sulfur, and other atoms that can act as electron-pair donors to coordinate metals ions in solution. The selectivity of the modified surface toward metal ions depends on several factors such as the size of the modifier, activity of the loaded group, and the characteristics of soft and hard acids and bases [4,14,15,17–19].

In this work, the chelating molecule 4-amino-2-mercaptopyrimidine (AMP) was attached onto a silica gel surface through an organosilane reaction, and characterized by FT-IR spectroscopy and elemental analysis. The material was applied in the extraction and preconcentration of Cu(II) in a fresh water sample taken from the Paraná river, Ilha Solteira, SP, Brazil. The sampling point was chosen taking into account the high Cu(II) concentration in surface sediment determined in previous work [20]. The accuracy of the proposed method was evaluated by comparison against a certified reference material (SRM 1643e).

### 2. Materials and methods

#### 2.1. Preparation of 4-amino-2-mercaptopyrimidine modified silica gel

Silica gel (Merck-60,  $\text{Ø} = 40 \mu\text{m}$ ) was previously activated at 423 K under vacuum for 24 h. 5 g of activated silica gel

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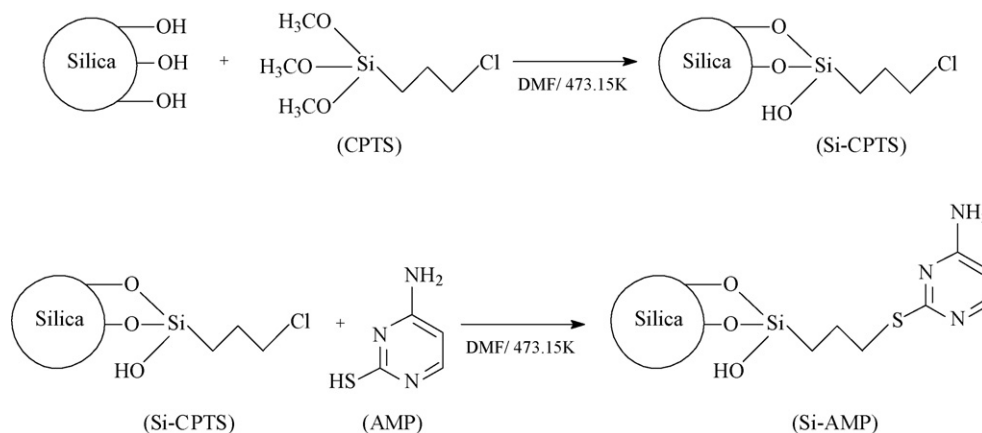


Fig. 1. Two-step functionalization reaction of silica gel with 4-amino-2-mercaptopyrimidine molecule ligand.

was suspended in 30 mL of dimethylformamide (DMF) under reflux, mechanical stirring and nitrogen atmosphere. 3.4 mL of 3-chloropropyltrimethoxysilane (Aldrich – Analytical grade) was then added to this suspension and the mixture was kept under reflux for 72 h. The reaction product was filtered, washed with acetone and ethanol and then dried.

The resulting solid, called Si-CPTS, was suspended in 30 mL of DMF under reflux, mechanical stirring and nitrogen atmosphere. 2.4 g of the 4-amino-2-mercaptopyrimidine molecule ligand was added to this mixture and the reaction was performed for 72 h at 423 K. The resulting product, called Si-AMP, was washed with acetone and ethanol. The two-step reaction is depicted in Fig. 1.

## 2.2. Instrumentation

The amount of molecule ligand (AMP) attached to the silica surface was determined using a Thermo Finnigan Flash 1112 Series EA CHNS elemental analyzer. Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were recorded on a Nicolet Nexus 670 spectrometer equipped with a Smart Collector, using 200 scans and  $4\text{ cm}^{-1}$  resolution. The metals were determined using a Perkin Elmer Analyst 700 atomic absorption spectrometer in the flame mode (FAAS).

## 2.3. Batch procedure

An aliquot of metal salt solution ( $5.0 \times 10^{-3}\text{ mol L}^{-1}$ ) and 0.05 mg of Si-AMP were placed in a 250 mL conical flask and the mixture was kept under mechanical stirring. This batch procedure was performed using different stirring times (1–40 min), pH (1–6) and different aliquots of metal salt solution (5–50 mL). The supernatant concentration of Cu(II) was determined directly by FAAS after stepwise dilution, and the number of divalent metal moles separated by unit mass of Si-AMP,  $N_f$  ( $\text{mmol g}^{-1}$ ) was calculated based on the following equation:

$$N_f = \frac{n_i - n_s}{m}, \quad (1)$$

where  $n_i$  is the initial mole number of the metal ion in solution phase,  $n_s$  is the metal mole number at equilibrium after adsorption, and  $m$  is the mass (g) of adsorbent (Si-AMP).

## 2.4. Preconcentration procedure

Before placing the sample in the system, it was subjected to an optimization procedure, in which the investigated parameters were eluant concentrations ranging from 0.5 to 2.0  $\text{mol L}^{-1}$  of chloric acid, and sample and eluant flow rates of 0.5–3.0  $\text{mL min}^{-1}$ . All

the parameters were optimized using 1.0 mL of eluant, and the preconcentration volume was 20.0 mL of Cu(II) solution at  $0.05\text{ mg L}^{-1}$ . The eluate was collected in polyethylene flasks, followed by Cu(II) determination by flame atomic absorption spectrometry. The Si-AMP column was prepared by packing 5.0 mg of material in a tygon tube with 2.86 mm of internal diameter.

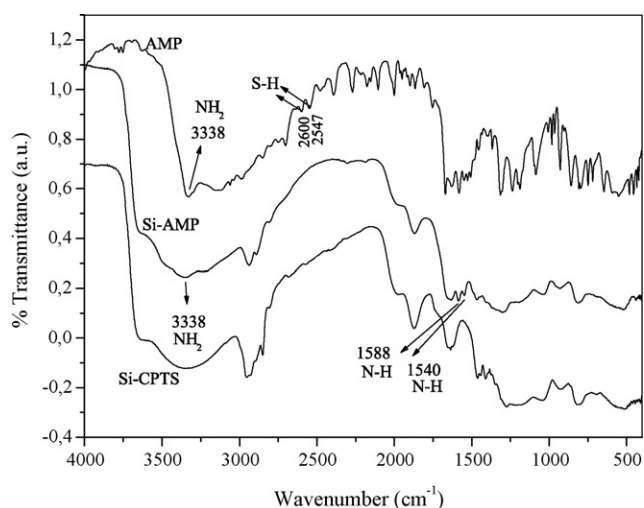
## 2.5. Preparation of fresh water sample and certified reference material

The river water sample was previously filtered through a  $0.45\text{ }\mu\text{m}$  membrane, after which 50 mL was transferred to a conical flask and kept on a hot plate until it dried. The resulting residue was then dissolved in a solution prepared with 5 mL of concentrated nitric acid and 500  $\mu\text{L}$  of hydrogen peroxide kept at  $100^\circ\text{C}$  for 30 min. The digested water sample was adjusted to pH 5 by adding a sodium hydroxide solution, after which the extract was transferred to a 50 mL volumetric flask. The results were compared with those obtained by graphite furnace atomic absorption spectrometry (GFAAS) to estimate the contribution of dissolved organic substances that can be associated with copper ions [21]. In addition, to certify the method using a continuous flow, aliquots of 20.0 mL of SRM material were subjected to the preconcentration system and the eluates collected were analyzed by flame atomic absorption spectrometry.

## 3. Results

### 3.1. Characterization

The 4-amino-2-mercaptopyrimidine compound was chosen for anchorage onto the silica surface due to the potential evidenced by its nitrogenated and sulfurated groups. The percentage of nitrogen determined by elemental analysis for Si-AMP was found to be 1.03. Based on this value, the concentration of molecule ligand anchored to the silica surface was calculated as  $0.245\text{ mmol g}^{-1}$  of material. The infrared spectra of solid samples shown in Fig. 2 confirmed the functionalization reaction of the silica surface by the AMP molecule ligand. The main changes observed in the Si-AMP spectrum in the region of  $3338\text{ cm}^{-1}$  were attributed to the N–H stretching mode from primary amine bonded to a carbon atom in the aromatic ring, while those at  $1588$  and  $1540\text{ cm}^{-1}$  were attributed to the N–H bending (scissoring) vibrations of primary amines. C–N stretching vibration from nitrogen atom in the aromatic ring could not be detected due to silica matrix absorption. Other absorption bands, which appeared in the region of  $2900$  and  $2850\text{ cm}^{-1}$ , were attributed respectively to asymmetrical ( $\nu_{\text{as}}\text{CH}_2$ ) and sym-



**Fig. 2.** Infrared spectra of Si-CPTS, Si-AMP and AMP molecule (4-amino-2-mercaptopyrimidine).

metrical ( $\nu_s\text{CH}_2$ ) stretching of methylene groups from silylant agent.

An analysis of the infrared spectra led to the conclusion that the covalently bond established between the Si-CPTS and 4-amino-2-mercaptopyrimidine occurred via thiol groups in response to the presence of the  $\text{NH}_2$  stretching mode at  $3338\text{ cm}^{-1}$  which was visible in the Si-AMP spectra. In some cases infrared spectroscopy can be incapable to show the correct side of the immobilization due to the fact that amine and thiol groups are good nucleophiles, which react with chloride groups. This behavior has been observed previously with other related materials and detailed explanations have been given based on FT-Raman spectroscopy [22,23].

### 3.2. Experiments in batch mode

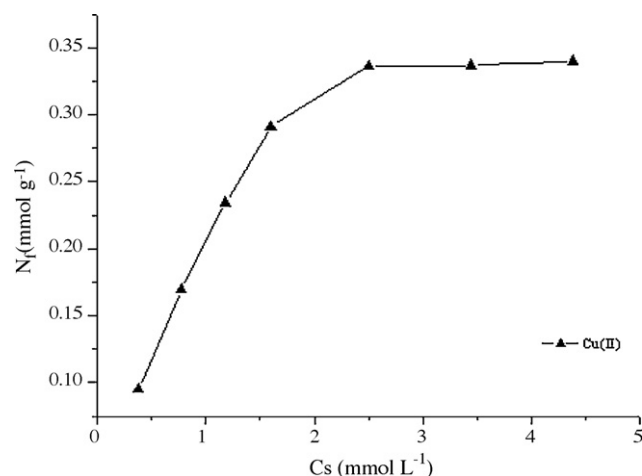
The adsorption kinetics of Cu(II) in aqueous medium reached equilibrium after 10 min of stirring. This fast kinetics may be ascribed to the availability of adsorption sites (mainly nitrogen atoms) in the chain. The influence of pH was investigated in the range of 1–6 and the optimum adsorption capacity was attained with pH 5 and 6.

The adsorption capacity of Si-AMP was determined based on increasing metal ion concentrations in solution and 10 min of stirring until the adsorption sites became saturated. The equilibrium value for the adsorption capacity ( $N_{f\text{max}}$ ) of Cu(II) was  $0.34\text{ mmol g}^{-1}$  and is depicted in Fig. 3. The results are consistent with those of other studies, in which Cu(II) demonstrated affinity for amino groups, an intermediate base [24,19].

To evaluate the maximum adsorption capacity of Si-AMP ( $N_s$ ), the experimental adsorption data were applied to the modified Langmuir equation [25,26].

$$\frac{C_s}{N_f} = \frac{C_s}{N_s} + \frac{1}{N_s b}, \quad (2)$$

where  $C_s$  is the concentration of the solution ( $\text{mmol L}^{-1}$ ),  $N_f$  is defined as the concentration of metal ions extracted from the solution per gram of material ( $\text{mmol g}^{-1}$ ),  $N_s$  is the maximum amount of metal ions extracted from the solution ( $\text{mmol g}^{-1}$ ), and  $b$  is a constant. The  $N_s$  value for Cu(II),  $0.447\text{ mmol g}^{-1}$ , was calculated based on the linearization of adsorption isotherms (Fig. 4) derived from  $C_s/N_f$  as a function of the  $C_s$  plot.



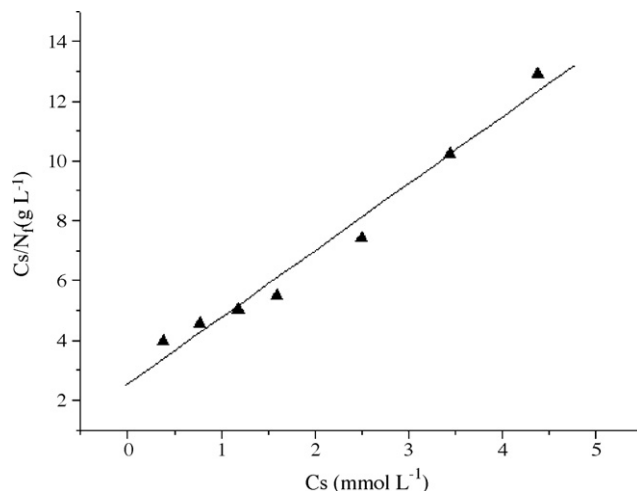
**Fig. 3.** Adsorption isotherm for Cu(II) in aqueous medium. Mass of Si-AMP = 0.05 g.

### 3.3. Preconcentration system

The preconcentration system was tested for Cu(II) ions in aqueous medium with a synthetic solution before analyzing the fresh water sample. Initially, the sample and eluant flow rate were tested by percolating 20 mL of Cu(II) stock solution at  $0.05\text{ mg L}^{-1}$ , using as eluant 1 mL of  $2.0\text{ mol L}^{-1}$  HCl solution. The results, which are depicted in Fig. 5, indicate that the load capacity depends on the sample flow rate, and that the signal declines sharply above  $1.0\text{ mL min}^{-1}$ . This decline is likely a consequence of the shorter contact time between the metal species and the adsorption sites. Thus, a preconcentration flow rate of  $1.0\text{ mL min}^{-1}$  was adopted for further experiments, since the previous rate,  $0.5\text{ mL min}^{-1}$ , would have required long periods of sample preconcentration. The eluant flow rate did not significantly affect the measured signal, so the flow rate adopted was also  $1.0\text{ mL min}^{-1}$ .

The eluant concentration was investigated in a range of  $0.5\text{--}2.0\text{ mol L}^{-1}$  of HCl solution. As can be seen in Fig. 6, when concentrations of less than  $1.5\text{ mol L}^{-1}$  were used, the measured signal declined, while higher concentrations caused the measured signal to increase. Because the desorption process was favored at higher concentrations, the value of  $2.0\text{ mol L}^{-1}$  was adopted in subsequent experiments.

Thinking about the possibility that some ions that are found naturally in river water might cause a decrease in extraction efficiency, experiments to evaluate the influence of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$



**Fig. 4.** The linear form of adsorption isotherm of Cu(II).

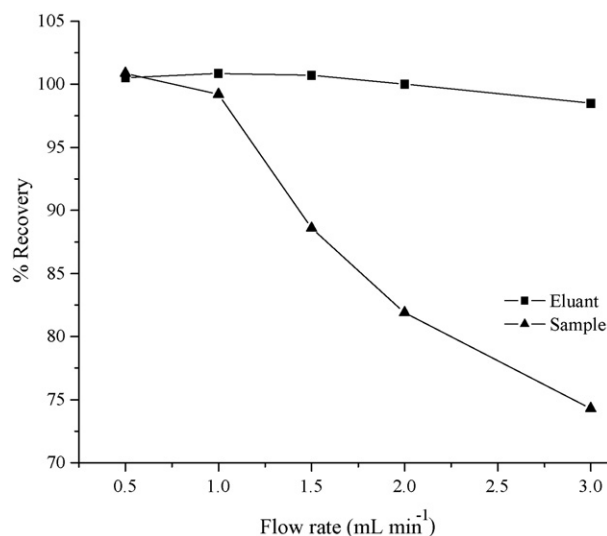


Fig. 5. Effect of sample (▲) pre-concentration and eluant (■) flow rate on the signal measured by atomic absorption spectrometry in the flame mode.

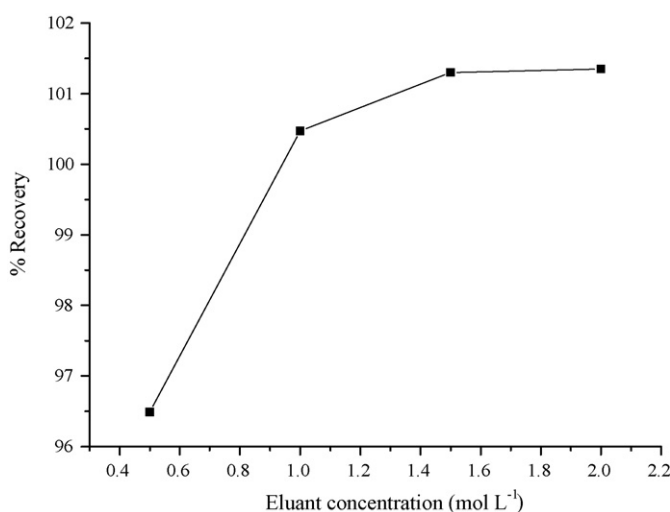


Fig. 6. Effect of eluant concentration on the signal measured by atomic absorption spectrometry in the flame mode.

and  $Mg^{2+}$  ions were performed through the percolation of 20 mL of  $0.05 \mu g L^{-1}$  of Cu(II) containing each interfering ion. The interfering ions salts used were nitrate or sodium salts and their behavior were studied in a concentration range from 10 to  $500 mg L^{-1}$ . The results are shown in Table 1.

The results showed that  $SO_4^{2-}$  ions did not interfere on the pre-concentration and determination of Cu(II) ions in a concentration range from 10 to  $500 mg L^{-1}$ ,  $Ca^{2+}$  interfered at  $100 mg L^{-1}$  and  $Cl^-$  and  $Mg^{2+}$  ions interfered at  $500 mg L^{-1}$ . The results indicated that high concentration of  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Cl^-$  interfere with the pre-concentration of Cu(II) ions.

Table 2  
Comparison of Cu(II) ions pre-concentration in solid support materials.

Type material	Mass used (g)	Volume pre-concentrated (L)	Enrichment factor	Reference
Amidoamidoxime silica	0.04	0.10	20.0	[27]
Modified activated carbon	–	0.25	25.0	[28]
<i>p</i> -Aminobenzoic modified cellulose	1.00	0.05	10.1	[29]
Activated carbon	–	0.025	30.0	[30]
AMP modified silica	0.005	0.020	20.0	<sup>a</sup>

<sup>a</sup> Data presented by the developed silica.

Table 1  
Influence of interfering ions on the Cu(II) pre-concentration.

Interfering ions	Concentration ( $mg L^{-1}$ )		
	10	100	500
$SO_4^{2-}$	$101.6 \pm 2.5$	$105.0 \pm 2.0$	$97.2 \pm 1.6$
$Cl^-$	$100.7 \pm 1.8$	$99.3 \pm 1.9$	$77.4 \pm 3.5$
$Mg^{2+}$	$98.4 \pm 3.5$	$103.6 \pm 3.2$	$79.8 \pm 2.2$
$Ca^{2+}$	$99.7 \pm 2.9$	$72.4 \pm 0.4$	$42.0 \pm 2.8$

After optimization of the parameters of the pre-concentration system, the enrichment factor, which reached about 20-fold, was calculated from the following equation:

$$Ef = \frac{Ec}{Sc}, \quad (3)$$

where  $Ec$  represents the eluant concentration and  $Sc$  the sample concentration.

Through the comparison between the proposed material Si-AMP with other solid supports applied in the Cu(II) sorption and pre-concentration, presented in Table 2, is possible to infer its advantages. Si-AMP showed similar enrichment factor compared with several materials, which is related to the sorbent mass used and taking this parameter into account the Si-AMP enrichment factor could be enhanced. Despite this, experiment with mass above 0.005 g of modified silica was not performed due to clog possibility.

### 3.4. Pre-concentration of fresh water

After the mineralization procedure, aliquots of 20 mL of fresh water samples were subjected to the pre-concentration system at  $1.0 mL min^{-1}$ . The metal ions were eluted with a  $2.0 mol L^{-1}$  HCl solution percolated at  $1.0 mL min^{-1}$ , after which the eluate was poured into a flask and analyzed by flame atomic absorption spectrometry. The Cu(II) in the fresh water sample was determined by electrothermal atomization in a graphite furnace atomic absorption spectrometer, and the results are presented in Table 3.

The results achieved with the pre-concentration system are congruent with the 20-fold enrichment factor, as indicated by the copper concentration found in the fresh water sample analyzed by GFAAS and with FAAS, after the pre-concentration. The difference between the mineralized and non-mineralized samples can be attributed to the copper ion complex formed with organic matter, which prevents the copper ions from being available at the Si-AMP adsorption sites. The analysis of water SRM was also in agreement with the enrichment factor, demonstrating that the system can be applied easily in the determination of trace copper in fresh water samples.

The method sensitivity used to quantify Cu(II) ions in the eluate was evaluated by the detection and quantification limit determination without the pre-concentration system [31]. The value found was  $7.9$  and  $26.2 \mu g L^{-1}$  for detection and quantification limit respectively, taking into account 15 blank measures. Through the analysis of Table 3 can be observed that without the pre-concentration procedure Cu(II) ions only could be determined safely



**Table 3**

Levels of trace copper determined in fresh water samples and water SRM with (PS) and without (NPS) the preconcentration system.

Metal	Sample (NPS) ( $\mu\text{g L}^{-1}$ ) <sup>a</sup>	Mineralized sample (PS) ( $\mu\text{g L}^{-1}$ ) <sup>b</sup>	Non-mineralized sample (PS) ( $\mu\text{g L}^{-1}$ ) <sup>b</sup>
Copper	4.45 ± 0.32	97.0 ± 4.2	38.0 ± 2.0
Metal	SRM ( $\mu\text{g L}^{-1}$ )		SRM PS ( $\mu\text{g L}^{-1}$ ) <sup>b</sup>
Copper	22.76 ± 0.31		457.15 ± 7.46

<sup>a</sup> Analyzed by GFAAS.

<sup>b</sup> Analyzed by FAAS.

by GFAAS, once the metal ions concentration in natural water sample is approximately six times lower than the method quantification limit. Through this comparison is possible to understand the importance of solid-phase extraction procedures on the analytical determination of trace metal ions in environmental samples when sophisticated equipments are not available.

#### 4. Conclusions

The covalent bond of the molecule ligand via chloropropyltrimethoxysilane reaction resulted in a hybrid material with good separation and preconcentration capacity. Solid-phase extraction with Si-AMP can be applied in the determination of trace metals in fresh water samples using flame atomic absorption spectrometry, which reduces the cost of an analysis. The Si-AMP was used over 60 cycles of adsorption/desorption without any loss in its properties, demonstrating the stability of the covalent bond between the organic molecules and inorganic matrix. The difference observed in the preconcentration values of mineralized and non-mineralized fresh water samples suggests that the material can also be applied in an environmental study involving metal lability.

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#### References

- [1] L.Y.L. Zhao, R. Schulin, B. Nowack, Cu and Zn mobilization in soil columns percolated by different irrigation solutions, *Environ. Pollut.* 157 (2009) 823–833.
- [2] M. Maanan, Heavy metal concentrations in marine mollusks from the Moroccan coastal region, *Environ. Pollut.* 153 (2008) 176–183.
- [3] S.E. Manahan, *Environmental Science and Technology*, CRC Press, Boca Raton, USA, 2000.
- [4] I.L. Alcântara, P.S. Roldan, M.A.L. Margionte, G.R. Castro, C.C.F. Padilha, A.O. Florentino, P.M. Padilha, Determination of Cu, Ni and Pb in aqueous medium by FAAS after preconcentration on 2-aminothiazole modified silica gel, *J. Braz. Chem. Soc.* 15 (2004) 366–371.
- [5] G.R. Castro, J.D. Oliveira, I.L. Alcântara, P.S. Roldan, C.C.F. Padilha, A.G.S. Prado, P.M. Padilha, Application of cellulose modified with p-aminobenzoic groups in preconcentration system for determination of Cu, Fe, Ni, and Zn in fuel ethanol samples by flame atomic absorption spectrometry, *Sep. Sci. Technol.* 42 (2007) 1325–1340.
- [6] A. Goswami, A.K. Singh, 1,8-Dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic absorption spectrometry, *Talanta* 58 (2002) 669–678.
- [7] Y. Cui, X. Chang, X. Zhu, H. Luo, Z. Hu, X. Zou, Q. He, Chemically modified silica gel with p-dimethylaminobenzaldehyde for selective solid-phase extraction and preconcentration of Cr(III), Cu(II), Ni(II), Pb(II) and Zn(II) by ICP-OES, *Microchem. J.* 87 (2007) 20–26.
- [8] M. Tuzen, M. Soylak, D. Citak, H.S. Ferreira, M.G.A. Korn, M.A. Bezerra, A preconcentration system for determination of copper and nickel in water and food samples employing flame atomic absorption spectrometry, *J. Hazard. Mater.* 162 (2009) 1041–1045.
- [9] M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A. Pourfarokhi, N. Khanjari, A.S. Mirsadeghi, M. Soylak, Preconcentration and separation of trace amount of heavy metals ions on bis(2-hydroxy acetophenone) ethylenediimine loaded on activated carbon, *J. Hazard. Mater.* 162 (2009) 1408–1414.
- [10] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, Chemically modified silica gel with aminothioamidoanthraquinone for solid phase extraction and preconcentration of Pb(II), Cu(II), Ni(II), Co(II) and Cd(II), *Talanta* 71 (2007) 1075–1082.
- [11] R.K. Iler, *The Chemistry of Silica*, John Wiley & Sons, New York, USA, 1979, p. 865.
- [12] F.A. Pavan, I.S. Lima, E.V. Benvenuti, Y. Gushikem, C. Airoidi, Hybrid aniline/silica xerogel cation adsorption and thermodynamics of interaction, *J. Colloid Interface Sci.* 275 (2004) 386–391.
- [13] I.L. Alcântara, P.S. Roldan, G.R. Castro, F.V. Moraes, F.A. Silva, C.C.F. Padilha, J.D. Oliveira, P.M. Padilha, Determination of cadmium river water samples by flame AAS after on-line preconcentration in mini-column packed with 2-aminothiazole-modified silica gel, *Anal. Sci.* 20 (2004) 1029–1032.
- [14] I. Hatay, R. Gup, M. Ersoz, Silica gel functionalized with 4-phenylacetophenone 4-aminobenzoylhydrazone: synthesis of a new chelating matrix and its application as metal ion collector, *J. Hazard. Mater.* 150 (2008) 546–553.
- [15] B. Gao, F. An, K. Liu, Studies on chelating adsorption properties of novel composite material polyethyleneimine/silica gel for heavy-metal ions, *Appl. Surf. Sci.* 253 (2006) 1946–1952.
- [16] G.R. Castro, V.M. Cristante, C.C.F. Padilha, S.M.A. Jorge, A.O. Florentino, A.G.S. Prado, P.M. Padilha, Determination of Cd(II), Cu(II) and Ni(II) in aqueous samples by ICP-OES after on-line preconcentration in column packed with silica modified with 2-aminothiazole, *Microchim. Acta* 160 (2008) 203–209.
- [17] N. Tokman, S. Akman, M. Ozcan, U. Koklu, Preconcentration and separation of copper(II), cadmium(II) and chromium(III) in a syringe filled with 3-aminopropyltriethoxysilane supported on silica gel, *Anal. Bioanal. Chem.* 374 (2002) 977–980.
- [18] I.H. Gubbuk, R. Gup, M. Ersoz, Synthesis, characterization, and sorption properties of silica gel-immobilized Schiff base derivative, *J. Colloid Interface Sci.* 320 (2008) 376–382.
- [19] G.R. Pearson, Hard and soft acids and bases, *J. Am. Chem. Soc.* 85 (1963) 3533–3539.
- [20] M.C. Minello, A.L. Paço, M.A.U. Martines, L. Caetano, A. Santos, P.M. Padilha, G.R. Castro, Sediment grain size distribution and heavy metals determination in a dam on the Paraná River at Ilha Solteira, Brazil, *J. Environ. Sci. Health. Part A Toxic./Hazard. Subst. Environ. Eng.* 44 (2009) 861–865.
- [21] L.P.C. Romão, G.R. Castro, A.H. Rosa, J.C. Rocha, P.M. Padilha, H.C. Silva, Tangential-flow ultrafiltration: a versatile methodology for determination of complexation parameters in refractory organic matter from Brazilian water and soil samples, *Anal. Bioanal. Chem.* 375 (2003) 1097–1100.
- [22] A.G.S. Prado, J.A.A. Sales, R.M. Carvalho, J.C. Rubim, C. Airoidi, Immobilization of 5-amino-1,3,4-thiadiazole-thiol onto silica gel surface by heterogeneous and homogeneous routes, *J. Non-Cryst. Solids* 333 (2004) 61–67.
- [23] S.M. Evangelista, E. Oliveira, G.R. Castro, L.F. Zara, A.G.S. Prado, Hexagonal mesoporous silica modified with 2-mercaptothiazoline for removing mercury from water solution, *Surf. Sci.* 601 (2007) 2194–2202.
- [24] J. Aguado, J.M. Arsuaga, A. Arencibia, M. Lindo, V. Gascón, Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica, *J. Hazard. Mater.* 163 (2009) 213–221.
- [25] M.R.M.C. Santos, C. Airoidi, Urea derivatives anchored on silica gel, *J. Colloid Interface Sci.* 183 (1993) 416–423.
- [26] R.S.A. Machado, J.M.G. Fonseca, L.N.H. Arakaki, J.G.P. Espinola, S.F. Oliveira, Silica gel containing sulfur, nitrogen and oxygen as adsorbent centers on surface for removing copper from aqueous/ethanolic solutions, *Talanta* 63 (2004) 317–322.
- [27] W. Ngeontae, W. Aeungmaitrepirom, T. Tuntulani, A. Imyim, Highly selective preconcentration of Cu(II) from seawater and water samples using amidoxime silica, *Talanta* 78 (2009) 1004–1010.
- [28] A.P. Jadid, H. Eskandari, Preconcentration of copper with solid phase extraction and its determination by flame atomic absorption spectrometry, *Eur. J. Chem.* 5 (2008) 878–883.
- [29] G.R. Castro, I.L. Alcântara, P.S. Roldan, D.F. Bozano, P.M. Padilha, A.O. Florentino, J.C. Rocha, Synthesis, characterization and determination of the metal ions adsorption capacity of cellulose modified with p-aminobenzoic groups, *Mater. Res.* 7 (2004) 329–334.
- [30] E.A. Takara, S.D. Pasini-Cabello, S. Cerutti, J.A. Gásquez, L.D. Martines, On-line preconcentration/determination of copper in parenteral solutions using activated carbon by inductively coupled plasma optical emission spectrometry, *J. Pharm. Biomed. Anal.* 39 (2005) 735–739.
- [31] Analytical Methods Committee, Recommendations for the definition, estimation and use of the detection limit, *The Analyst* 112 (1987) 199–204.