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Article

Determination of Metal Ions in Fuel Ethanol after Preconcentration on 5-Amino-1,3,4-Thiadiazole-2-Thiol Modified Silica Gel

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Este trabalho descreve a síntese e caracterização da sílica gel modificada com grupos 5-amino-1,3,4-tiadiazol-2-tiol (SiATT), e os resultados de um estudo de adsorção e pré-concentração (em batelada, e em fluxo utilizando-se técnica de coluna) de Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) e Zn(II) em meio etanólico. A capacidade máxima de adsorção da SiATT determinada para os íons metálicos estudados foram (mmol g^{-1}): Cd(II) = 0,11, Co(II) = 0,10, Cu(II) = 0,20, Fe(III) = 0,20, Ni(II) = 0,16, Pb(II) = 0,08 e Zn(II) = 0,12. Os resultados obtidos nos experimentos em fluxo, mostraram uma recuperação de praticamente 100% dos cátions metálicos adsorvidos na coluna empacotada com 2 g de SiATT, utilizando-se 5 mL de HCl 2,0 mol L^{-1} como eluente. A sorção-dessorção dos íons Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) e Zn(II), serviu como base para o desenvolvimento de um método de préconcentração e subsequente determinação por EAA de Chama do teor desses cátions em amostras de etanol combustível.

This work describes the synthesis and characterization of 5-amino-1,3,4-thiadiazole-2-thiol modified silica gel (SiATT), and the results of a study of the adsorption and preconcentration (in batch, and in flow using a column technique) of Cd(II), Co(II), Cu(II), Fe(III), Ni(II), Pb(II) and Zn(II) in ethanol medium. The adsorption capacities for each metal ion were (in mmol g^{-1}): Cd(II) = 0.11, Co(II) = 0.10, Cu(II) = 0.20, Fe(III) = 0.20, Ni(II) = 0.16, Pb(II) = 0.08 and Zn(II) = 0.12. The results obtained in the flow experiments, showed a recovery of *ca.* 100% of the metal ions adsorbed in a column packed with 2 g of SiATT, using 5 mL of 2.0 mol L^{-1} HCl solution as eluent. The sorption-desorption of the metal ions made possible the development of a preconcentration method and quantification by Flame AAS of metal ions at trace level in fuel ethanol.

Keywords: *preconcentration, 5-amino-1,3,4-thiadiazole-2-thiol modified silica gel, fuel ethanol*

Introduction

The direct determination of trace metals in fuel ethanol by conventional analytical chemical methods can be performed after a time-consuming liquid evaporation procedure prior to any measurements[1,2]. Methods using on line flow preconcentration system[3], liquid-liquid extraction[4], adsorption[5,6] and ion exchange[7,8] as separation procedures for metal ions have been successfully applied.

In recent years, the use of chemically modified silica gel with various chelating organofunctional groups aiming

to adsorb and preconcentrate metal ions from solutions, have been described[9-12]. In particular, a column packed with the material in line with a flow analysis system has been suggested as an effective and reliable process for preconcentration of the metal ions before analysing by atomic absorption spectrometry[13-15]. In this combined method the enrichment of the analyte and removal of some interferents which may be present in the solution, can considerably improve the method of analysis extending the limit of detection to lower concentrations.

This paper describes the preparation of silica gel chemically modified with 5-amino-1,3,4-thiadiazole-2-thiol aiming to find an efficient material for separation and determination of the metal ions present in ethanol, used as fuel for car engines. Primarily the material was tested with a synthetic ethanol solution containing some metal ions and further used in a real sample.

Experimental

Preparations

Silica gel (Merck) with specific surface area of 500 $m^2\ g^{-1}$ and average pore diameter of 0.6 nm, was activated at 420 K under vacuum (10^{-3} Torr). About 50 g of this silica was immersed in 200 mL of dry xylene and 15 mL of 3-chloropropyltrimethoxysilane was added. The mixture was refluxed under nitrogen atmosphere for 24 h, filtered, washed with xylene and heated under vacuum in order to eliminated all the solvent. The resulting solid was immersed in 150 mL of purified dimethylformamide and 17 g of 5-amino-1,3,4-thiadiazole-2-thiol was added. The mixture was stirred for 24 h at 380 K under nitrogen atmosphere. The resulting modified silica was filtered off, washed with dimethylformamide, ethanol and heated for 8 h at 348 K under vacuum (10^{-3} Torr).

The equations in Scheme 1 describe the preparation of the material.

The quantity of 5-amino-1,3,4-thiadiazole-2-thiol attached to the silica surface was determined by the nitrogen analysis using the Kjeldhal method. The specific surface area was determined by the BET[16] method on a Micromeritics Flow Sorb 300 equipment of Micromeritics Instrument Corporation.

Infrared spectra

The FT-IR spectra of SiATT of SiO_2 and SiATT were obtained in the region between 1800 and 1300 cm^{-1}, using the pressed disk technique and a Nicolet FT-IR Spectrophotometer, according to a previously described method[17].

Adsorption of the metal ions by SiATT

Adsorption of MX_n by SiATT from a solution can be described by the equilibrium equation[9]:

$$mSiATT_{(s)} + MX_{n(aq)} \rightleftharpoons (SiATT)_mMX_{n(s)} \quad (3)$$

The time required for this reaction to achieve the equilibrium condition was previously determined immersing 100 mg of SiATT in 50 mL of 5 x 10^{-3} mol L^{-1} of the metal solution and shaken. At different time intervals, an aliquot of the supernatant solution was separated and the metal ion analysed by complexometric titration using EDTA as the titrant[18].

The quantity of the adsorbed metal per unit mass of the adsorbent, N_f, was calculated applying the equation:

$$N_f = \frac{N_i - N_s}{m} \quad (4)$$

where N_i represents the initial mole number of the metal ion in the solution phase, N_s the mole number of the metal ion in equilibrium with the solid phase and m is the mass of the adsorbent.

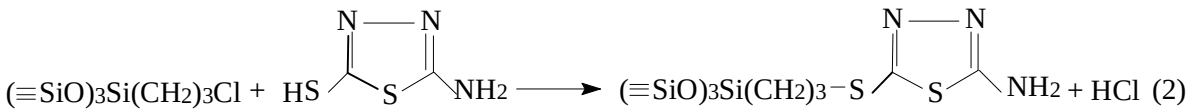
Isotherms of adsorption

The adsorption capacity of SiATT was determined at 298 K using the batch technique. In 50 mL of ethanol solutions of the metal ions (concentrations between 2.0 x 10^{-4} and 2.5 x 10^{-3} mol L^{-1}), about 100 mg of SiATT were added and the resulting mixture shaken for 30 min. The solid phase was separated by centrifugation and the metal ion determined in the supernatant solution by complexometric titration.

Anion influence

As can be seen in the equilibrium reaction (Eq. 3), the metal ion is followed by the counter ion in the adsorption process and thus, it occurs as an adsorption of a neutral species. Therefore, experiments in order to study the influ-

$$3{\equiv}SiOh + (CH_3O)_3Si(CH_2)_3Cl \longrightarrow (\equiv SiO)_3Si(CH_2)_3Cl + 3CH_3OH \quad (1)$$



Scheme 1. ≡SiOH stands for the silica surface silanol group. For the sake of brevity, (A) will here after be designated as SiATT.

ence of the anion in the adsorption process were also carried out. The isotherms of adsorption were determined in presence of 0.10 mol L^{-1} NaCl, $NaNO_3$, $NaClO_4$ and NaOAc solutions.

Preconcentration and recovery of the metal ions

This study was carried out using a 15 cm length and 0.6 cm inner diameter glass column packed with 2 g of SiATT. Initially, the column was washed with ethanol and then 100 mL of 0.50 mg L^{-1} $M(NO_3)_n$ [M = Cd(II), Co(II), Cu(II), Ni(II), Pb(II), Zn(II) and Fe(III)] ethanol solutions were percolated through the column with a flow rate of 2.0 mL min^{-1}. The column was washed with 50 mL of ethanol and then the metal was eluted with 5 mL 2.0 mol L^{-1} HCl solution. All fractions obtained during the elution stage were gathered separately and analysed by Flame AAS.

Determination of metal ions in ethanol fuel

About 250 mL of ethanol fuel samples were percolated through the column packed with 2 g of SiATT. The adsorbed metal ions were eluted with 5 mL of 2.0 mol L^{-1} HCl solution and the metal ions analysed by Flame AAS. The concentrations of the metal ions were also determined by Flame AAS after conventional preconcentration, in which the first step has been to evaporate the ethanol solution to dryness[19].

Determination by AAS

The concentrations of metal ions gathered from the SiATT column were determined by Flame AAS according to the standard guidelines of the manufacturers (Spectrometer: VARIAN-INTRALAB AA-1475), choosing resonance lines for the metals and deuterium-arc lamp background correction[20]. For the calibration, synthetic standard solutions containing on 1.0 mol L^{-1} HCl comparable to the samples, were used.

Results and Discussion

Characteristics of the material

Figure 1 shows the IR spectra of SiO_2 (Fig. 1a) and that of the chemically modified silica gel (Fig. 1b). In Fig. 1 b it is clearly observed that the band at 1660 cm^{-1} is due to the δNH_2 mode, indicating therefore that bonding to the silica matrix by the bridging propyl group is made by the sulphur atom as indicated in Eq. 2. The H_2O deformation mode is observed at *ca.* 1630 cm^{-1} as a shoulder. Other bands of interest are observed at 1500 and 1440 cm^{-1} and they can be assigned to the νCN and νCC coupled modes of the functional group.

The chemical analysis of SiATT yielded a 0.53 mmol g^{-1} of the functional groups attached to silica surface and 378 m^2 g^{-1} as the specific surface area. The attached functional groups were very stable under the various cycles of adsorption-elution of the metal ions by the adsorbent in the column.

Adsorption isotherms

An important aspect of this material is the time necessary for the adsorption process to achieve the equilibrium condition. Figure 2 shows the plot of N_f in function of time for Co(II) and Zn(II) as examples. The system achieves the equilibrium condition very rapidly, about 15 min for both metals, because in the present case, the functionalization occurs on the matrix surface having sufficiently large pores (0.6 nm).

The adsorption capacities for each metal ion, determined from saturation condition of the isotherms shown in Fig. 3, were (in mmol g^{-1}): Cd = 0.11, Co = 0.10, Cu = 0.20, Fe = 0.20, Ni = 0.16, Pb = 0.08 and Zn = 0.12.

In solvent with lower dielectric constant, the influence that an anion can have on the adsorption process due to the anion-cation interaction may be appreciable, since the anion follows the metal ion when it diffuses from the solution to the solid phase, and it is adsorbed as a neutral species[9] MX_n (see Eq. 3). Figure 4 shows the influence of various anions (Cl^-, NO_3-, ClO_4- and AcO^-), with a concentration

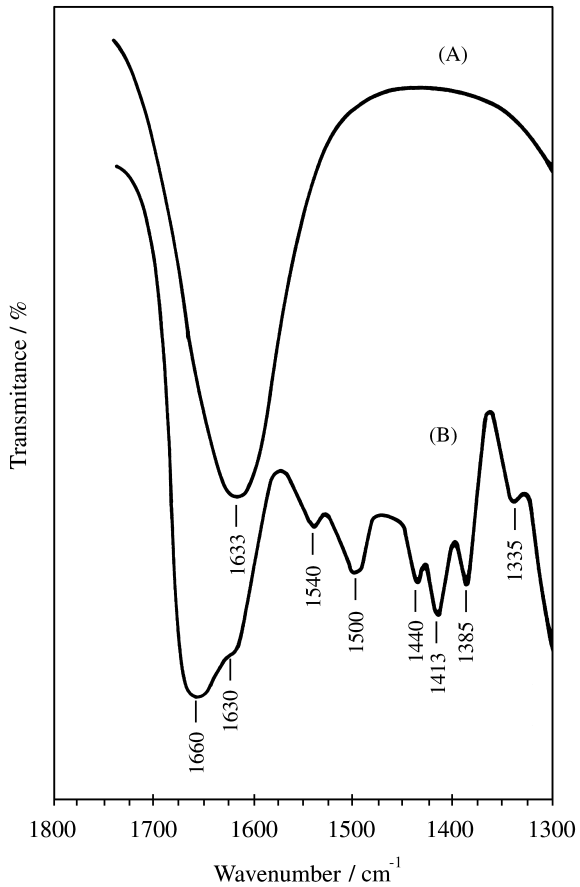


Figure 1. Infrared spectra of A, pure silica and B, silica modified with 5-amino-1,3,4- thiadiazole-2-thiol.

of 0.1 mol L^{-1}, on the copper adsorption. No significant decrease of the adsorption process for these anions is observed, indicating that the metal-to-ligand bond formation is the main fact that determines the amount of adsorbed metal.

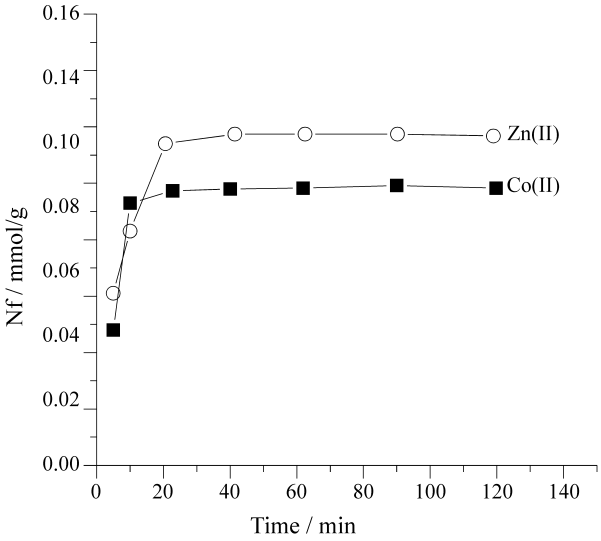


Figure 2. Plots of Nf *vs.* time (50 mL of 5 x 10^{-3} mol L^{-1} of the metal ions ethanol solution, 100 mg SiATT, 298 K).

Table 1. Recoveries of metal ions using the column method at 298 K, and 2.0 mol L^{-1} HCl solution as eluent (n = 3, 100 mL of 0.50 mg L^{-1} ethanol solution, Volume of eluent = 5 mL).

Ion	Recovery %
Cd(II)	98 ± 2
Co(II)	99 ± 2
Cu(II)	98 ± 2
Fe(III)	99 ± 1
Ni(II)	99 ± 2
Pb(II)	99 ± 2
Zn(II)	98 ± 2

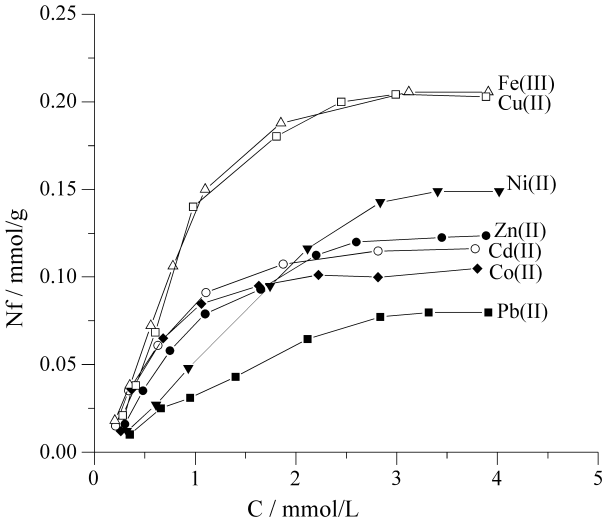


Figure 3. Adsorption of metal ions from ethanol solution (50 mL of 2.0 x 10^{-4} – 2.5 x 10^{-3} mol L^{-1} metal ions ethanol solution, 100 mg SiATT, 298 K).

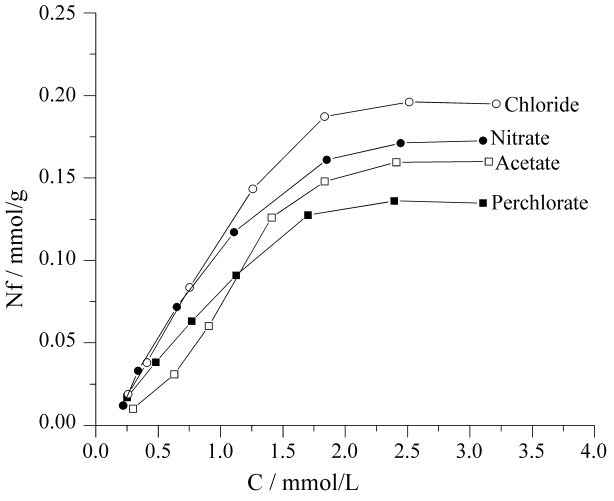


Figure 4. Influence of various anions on the adsorption of Cu(II) from ethanol solution (50 mL of 2.0 x 10^{-4} – 2.5 x 10^{-3} mol L^{-1} metal ions ethanol solution, 100 mg SiATT, 0.10 mol L^{-1} of Cl^-, NO_3^-, ClO_4^- and OAc^-, 298 K).

Table 2. Determination of metal ions in ethanol fuel after preconcentration by the proposed method (n = 3, 250 mL of sample, Volume of eluente = 5 mL) and by the conventional preconcentration method[19].

Samples	Concentration Found (μg L^{-1})							
	Cu		Fe		Ni		Zn	
	Proposed	Conventional	Proposed	Conventional	Proposed	Conventional	Proposed	Conventional
1	52 ± 6	49 ± 3	23 ± 5	21 ± 4	8 ± 1	10 ± 3	6 ± 2	8 ± 3
2	61 ± 9	57 ± 4	17 ± 4	14 ± 3	10 ± 1	11 ± 2	7 ± 2	10 ± 4
3	78 ± 9	76 ± 5	12 ± 3	11 ± 2	14 ± 1	13 ± 2	8 ± 2	11 ± 2

1. From Usina da Barra, 2. From Usina Barra Grande, 3. From Usina São Manuel.

Recovery and determination of the metal ions

Table 1 shows the recoveries of each ion from a column packed with SiATT using HCl as eluent. Passing 5 mL of 2.0 mol L^{-1} HCl solution, within the experimental error, 100% recovery was achieved for all metal ions.

The recovery experiment for each metal ion from a synthetic solution served as basis for a rapid method for preconcentration and determination of metal ions in a fuel ethanol.

Table 2 shows the concentrations of the metal ions in samples of fuel ethanol produced in three different plants. In general, Cd(II) does not occur in fuel ethanol or its content is lower than the contents of the other metals by a factor of 10-100. The metals, Co(II) and Pb(II) were not found in detectable amount. The content of Fe(III) depends on the degree of corrosion of the distillation equipment[21]. The concentrations of Cu(II) are the highest in the analysed samples, and correspond to the contents of this metal normally found in fuel ethanol[22]. These results are in accordance with results obtained using the conventional preconcentration method[19].

Conclusion

5-amino-1,3,4-thiadiazole-2-thiol groups attached to a silica gel surface can readily be used to adsorb metal ions from ethanol solution. Its relatively high chemical stability in ethanol, and the velocity with which the metal ions are adsorbed, turns this material potentially useful for analytical purposes.

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References

1. Bruning, I.M.R.A.; Malm, E.B. *Research and Development Center of Petrobras Company*, Rio de Janeiro, 1980, 15.
2. Bruning, I.M.R.A.; Malm, E.B. *Bol. Tec. Petrobras* **1982**, *25*, 217.
3. Carbonel, V.; Salvador, A.; de la Gardia, M. *Fresenius J. Anal. Chem.* **1992**, *355*, 529.
4. Sperling,M.; Yin, X.; Welz, B. *Spectrochim Acta*, **1992**, *46B*, 1789.
5. Fang, Z.; Guo, T.; Welz, B. *Talanta*, **1991**, *38*, 613
6. Zolotov, Y. A.; Spivakov, B.Y.; Baslsholov, T.A.; Paulenko, I.V. *Fresenius Z. Anal. Chem.* **1989**, *355*, 938.
7. Caroli, S.; Alimont, A.; Petrucci, F.; Horvarth, Z. *Anal. Chim. Acta.* **1991**, *248*, 716.
8. Porta, V.; Sarzanini, C.; Abolino, O.; Mentasti, E.; Cartini, E. *J. Anal. Spectrom* **1992**, *7*, 19.
9. Filho, N.L.D.; Gushikem, Y.; Rodrigues, E.; Moreira, J.C.; Polito, W.L. *J. Chem. Soc. Dalton Trans.* **1994**, *9*, 1493.
10. Filho, N.L.D.; Gushikem, Y.; Polito, W. L. *Anal. Chim. A.cta* **1995**, *306*, 167.
11. Filho, N.L.D.; Gushikem, Y. *J. Mol. Struct. (Theochem.)* **1995**, *335*, 175.
12. Lessi, P.; Filho, N.L.D.; Moreira, J.C.; Campos, J.T.S. *Anal. Chim. Acta* **1996,** *327*, 183.
13. Moreira, J.C.; Gushikem, Y. *Anal. Chim. Acta* **1985**, *176*, 263.
14. Filho, N.L.D.; Gushikem, Y.; Polito, W.L.; Moreira, J.C.; Rodrigues, E. *J. Braz. Chem. Soc*. **1994**, *5(1)*, 53.
15. Filho, N.L.D; Gushikem, Y; Polito, W.L.; Moreira, J.C.; Ehirim, E.O. *Talanta* **1995**, *42*, 1625.
16. Brunaur, S.; Emmet, P.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
17. Gushikem, Y.; Moreira, J.C. *J. Colloid Interface Sci.* **1985**, *13*, 70.
18. Kubota, L.T.; Ionashiro, M.; Moreira, J.C. *Ecl. Quim.* **1988**, *13*, 19.
19. Bruning, I.M.R.A . and Malm, E.B. *Bol. Tec. Petrobras* **1982**, *25*, 217.
20. Operation Manual – Atomic Absorption Spectrophotometer AA-1475, VARIAN -INTRALAB, **1980**.
21. Tanaka, N.L.D.K.; Wolynec, S.; Fairbanks, S.; Pinto, F.B.P. *VIIIth National Seminar on Corrosion*, Rio de Janeiro, Brazil, **1981**, 59.
22. Tanaka, D.K.; Wolynec, S. *Proc. of IXth National Seminar on Corrosion*, Rio de Janeiro, Brazil, 1982, 166.

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