



Solid-phase extraction of metal ions from fuel ethanol with a nanostructured adsorbent



Isaac V. Soares, Eduardo G. Vieira, Devaney R. do Carmo, Newton L. Dias Filho *

Departamento de Física e Química, Unesp-Univ Estadual Paulista, Av. Brasil, 56-Centro, Caixa Postal 31, 15385-000 Ilha Solteira-SP, Brazil

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ABSTRACT

This work describes the synthesis and characterization of a new octakis[3-(2,2'-dipyridylamine)propyl] octasilsesquioxane (T_8 -Pr-DPA), and a study of the metal ion preconcentration in fuel ethanol. Batch and column experiments were conducted to investigate the removal of heavy metal ions from fuel ethanol. The results showed that the Langmuir allowed to describe the sorption equilibrium data of the metal ions on T_8 -Pr-DPA in a satisfactory way. The following maximum adsorption capacities (in mmol g^{-1}) were determined: 3.62 for Fe (III), 3.32 for Cr (III), 2.15 for Cu (II), 1.80 for Co (II), 1.62 for Pb (II), 1.32 for Ni (II) and 0.88 for Zn (II). The thermodynamic parameters for the adsorption process such as free energy of adsorption (ΔG), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated. Thermodynamic parameters showed that the system has favorable enthalpic, Gibbs free energy, and entropic values. The sorption-desorption of the metal ions has made possible the development of a preconcentration and determination method of metal ions at trace level in fuel ethanol. The method of quantitative analysis for Fe, Cu, Ni and Zn in fuel ethanol by Flame AAS was validated. Several parameters have been taken into account and evaluated for the validation of method, namely: linearity, limit of detection, limit of quantification, and the relative standard deviation and accuracy. The accuracy of the method was assessed by testing analyte recovery in the fuel ethanol samples.

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1. Introduction

The depletion of petroleum fuels and ecological problems have generated permanent concern for scientist in many countries in developing a clean and renewable alternative fuel for gasoline and diesel fuels. Ethanol is considered to be a good candidate as alternative automotive engine fuel, due to it is biodegradable and renewable and can be produced from biomass [1–3].

Brazil is the most successful country in promotion of ethanol and gasoline–ethanol mixtures (up to 20% ethanol by volume) as fuel in vehicles, followed by the United States, China and other European countries [4]. Fuel ethanol in Brazil normally designates a mixture of ethanol with a low percentage of water, and it is used as an automotive engine fuel. Ethanol has some advantages over gasoline, as better car engine anti-knock characteristics and a reduction of gas emissions [2].

Lately, much attention has been given to the investigation and development of methods to determine traces of metals in fuel ethanol. Studies indicated that fuel ethanol can induce corrosion in the vehicle components in contact with the liquid due to metal ions, such as Cu (II), Fe (III), Zn (II) and Ni (II) metal ions [5–7]. The presence of metals in fuel ethanol has a significant impact on the fuel performance and quality, because some metals can catalyze oxidative reactions in

hydrocarbon mixtures and also reduce the efficiency of catalytic reactors used in vehicle exhaust systems. Some metal ions can be naturally present in ethanol as a result of the soil composition where the sugar cane has grown. Alternatively, these elements can be introduced during the sugar cane production, fermentation process, or transport and storage of final product [8,9].

Therefore, the removal of the metal ions in fuel ethanol has raised the interest to explore novel adsorbents with low cost and high adsorption capabilities for metal ions in ethanol. Organic–inorganic hybrid silsesquioxane cores with eight pendant organic molecular “arms”, which are known as polyhedral oligomer silsesquioxanes (POSS), are of particular interest in this respect. In the POSS, the cubic silica cores are “hard particles” rigid with 0.53 nm diameter and a spherical radius of 1–3 nm including peripheral organic units [10,11]. The nanocage cores of the POSS are surrounded by eight organic groups, which may serve as ligands of metal ions from non-aqueous solution system such as ethanol [12–14].

Our interest in hybrid silsesquioxanes is in the development of materials that would be used as sorbents of metal ions from ethanol medium. As far as we know, there have been few reports about the applications of modified silsesquioxane adsorbents in removal of metals in fuel ethanol.

The main objective of this research is the preparation and application of the nanostructured adsorbent octakis[3-(2,2'-dipyridylamine)propyl]octasilsesquioxane (T_8 -Pr-DPA) in the preconcentration and determination of metal ions from commercial ethanol.

* Corresponding author. Tel.: +55 18 37431078; fax: +55 18 37424868.
E-mail address: nldias@dfq.feis.unesp.br (N.L. Dias Filho).

2. Experimental

2.1. General procedures

All reagents were obtained from Aldrich and used as received. Commercial grade solvents were dried and deoxygenated by standard procedures (toluene over Na/benzophenone ketyl), distilled under nitrogen, and kept over 4 Å molecular sieves.

All the solutions were prepared with high purity chemicals and high purity water (18.3 MΩ cm).

Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded on a Nicolet 670 FT-IR spectrometer (Nicolet Instruments, Madison, WI). About 600 mg of KBr was ground in a mortar and pestle, and a sufficient quantity of the solid sample was ground with KBr to produce a 1 wt.% mixture resulting in pellets. A minimum of 32 scans was collected at a resolution of 4 cm^{-1} .

A Perkin-Elmer Analyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study.

^{13}C NMR and ^{29}Si NMR solid-state spectra were recorded on a BRUKER DRX 400 spectrometer and obtained at 100.6 MHz and 79.48 MHz, respectively.

2.2. Preparations

2.2.1. Synthesis of octakis[3-(2,2'-dipyridylamine)propyl]octasilsesquioxane (T_8 -Pr-DPA)

3-Chloropropyltriethoxysilane (225 mL) was added to a stirred mixture of methanol (4 L) and concentrated hydrochloric acid (135 mL) under a slow continuous nitrogen purge. The reaction

mixture was allowed to stir for six weeks. The resultant solution was then filtered and dried to give a white solid in 39% yield, named octakis(3-chloropropyl)octasilsesquioxane (T_8 -PrCl).

A solution of 2,2'-dipyridylamine (65.5 g, 385 mmol) in anhydrous dimethylformamide (200 mL) was added via an addition funnel, over a period of 30 min, to a stirred suspension of sodium hydride (60% dispersion in mineral oil) (15.4 g, 385 mmol) in anhydrous dimethylformamide (100 mL), at 0 °C under nitrogen. The mixture was stirred continuously for 2 h at that temperature. T_8 -PrCl (50 g, 48 mmol) and (200 mL) of anhydrous dimethylformamide were then added to the reaction mixture. The temperature was allowed to rise to room temperature and stirring was continued for 22 h to afford a pale yellow solution. Distilled water was then added and the desired product was extracted with chloroform. The resulting solution was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness under vacuum to give the modified silsesquioxane T_8 -Pr-DPA in 74% yield.

2.3. Isotherms of adsorption

The loading capacity of the collector octakis[3-(2,2'-dipyridylamine)propyl]octasilsesquioxane (T_8 -Pr-DPA) from ethanol solutions was determined at 298 K by the batch adsorption technique (isotherms of adsorption). In the ethanol solutions of metal ions (FeCl_3 , CrCl_3 , CuCl_2 , CoCl_2 , PbCl_2 , NiCl_2 and ZnCl_2), concentrations between 0.5×10^{-3} and 5.0×10^{-3} M, about 0.01 g of the adsorbent was added. An ethanolic T_8 -Pr-DPA salt solution suspension was kept under constant agitation at 600 rpm. As the preliminary tests showed that the system achieves the equilibrium condition very rapidly, about 10 min for all metals, the mixture was shaken for 15 min, and then the solids were

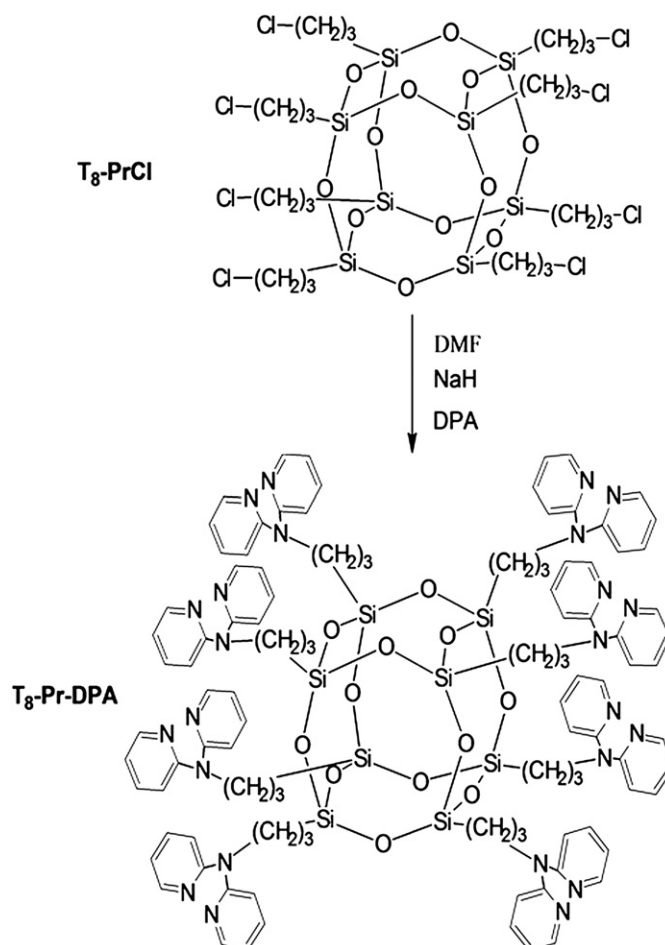


Fig. 1. Schematic representation of the synthesis of T_8 -Pr-DPA.

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