



Study of cross-linked poly(methacrylic acid) and polyvinylimidazole as selective adsorbents for on-line preconcentration and redox speciation of chromium with flame atomic absorption spectrometry determination [☆]



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ABSTRACT

A redox speciation and preconcentration study of Cr(III) and Cr(VI) using a flow injection system with dual mini-columns prepared from cross-linked polymers-poly(methacrylic acid) and polyvinylimidazole was developed. Characterization of organic polymers was performed by using FTIR, SEM, TG, C:H:N and BET measurements. The equilibrium data obtained from Cr(III) adsorption on poly(methacrylic acid) and Cr(VI) on polyvinylimidazole were fitted very well to the dual site Langmuir–Freundlich model, suggesting the presence homogeneous and heterogeneous binding site and providing maximum adsorption capacities of 1.42 and 3.24 mg g⁻¹, respectively. The adsorption kinetics data were described by the pseudo-second-order model for both polymers, thus corroborating to isotherm data. The on-line preconcentration/speciation system was operated by loading 18.0 mL of a solution containing Cr(III) and Cr(VI) at pH 4.0 through the dual mini-columns at a flow rate of 3.0 mL min⁻¹, where Cr(III) was selectively retained on poly(methacrylic acid), while Cr(VI) was retained on polyvinylimidazole. The limits of detection were found to be 0.84 and 1.58 µg L⁻¹ for Cr(III) and Cr(VI), respectively. The preconcentration factor (PF), consumptive index (CI) and concentration efficiency (CE) were found to be 47.3/8.6, 0.38/2.1 mL and 7.88/1.43 min⁻¹ for Cr(III) and Cr(VI), respectively. The developed method was successfully applied to the speciation of chromium in different kinds of water samples. Satisfactory recovery values ranging from 89.9 to 108.3% were obtained.

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1. Introduction

The presence of chromium in waters has received much attention in recent years. Chromium contamination is generated from many engineering and chemical industries [1,2]. Cr(III) is found in natural waters as cationic and hydrolyzed form and it is considered a micronutrient having an important role in the metabolism of glucose and proteins in mammals [3]. On the other hand, Cr(VI) is highly toxic, whose presence of CrO₄²⁻, Cr₂O₇²⁻ and HCrO₄⁻ species in water samples is pH dependent [4,5]. Due to the toxic nature of Cr(VI) and the importance of low levels of Cr(III) for human health, analytical methodologies related to the determination and speciation of these species in environmental samples are of paramount importance to evaluate the real toxicity [6–8]. The

Brazilian National Council for the Environment (CONAMA) [9] establishes a maximum amount of 1.0 mg L⁻¹ of Cr(III) and 0.1 mg L⁻¹ of Cr(VI) for effluent discharges in aquatic bodies, while the U.S. EPA (U.S. Environmental Protection Agency) [10] establishes only a maximum amount of total Cr in drinking water of 0.1 mg L⁻¹. In similar way, the World Health Organization (WHO) [11] fixed a maximum amount of total Cr in drinking water of 0.05 mg L⁻¹. Hence, the development of sensitive and selective methods capable of differentiating the inorganic forms of Cr is very important, whereas the coupling of solid phase extraction (SPE) procedures with spectroanalytical techniques have been largely employed for this task [12,13]. Rajesh and co-workers [13] determined Cr(VI) ions by visible spectrophotometry after adsorption of its diphenylcarbazide complex on a mixture of acid activated montmorillonite (AAM) silica gel column and posterior elution with polyethylene glycol–sulphuric acid mixture. Bartyzel and Cukrowska [14], used silica gel modified with N,N-bis-(–methylsalicylidene)-2,2-dimethyl-1,3-propanediimine (SBTD) for selective retention of Cr(III) and posterior determination by GF AAS after elution with 1.0 mol L⁻¹ HNO₃. A mesoporous silica SBA-15 modified with –aminopropyltriethoxysilane

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(APTES) was employed for the retention of Cr(VI) in the presence of Cr(III). Cr(III) was determined after quantitative oxidation to Cr(VI) with hydrogen peroxide in NaOH medium [15]. These methods and other previously published [16–18], involve difficulties with regard to the shortening of analysis time, errors and risks of contamination, since one of the species is determined from the difference of the total chromium amount by exploiting oxidation or reduction chemical reactions [17, 19]. A survey of literature also shows some methods devoted to the redox speciation of chromium by using on-line dual mini-column system with the same adsorbent or by sequential elution using one mini-column. Chamjangali and co-workers used a mini-column packed with chloromethylated polystyrene functionalized with N,N bis(naphthylideneimino) diethylenetriamine (PS-NAPdien) for the simultaneous retention of Cr(III) and Cr(VI) at pH 6.7. The sequential elution of Cr(III) and Cr(VI) with FAAS determination was performed by using different eluents [20]. In the study performed by Sumida and co-workers [17], dual mini-columns packed with iminodiacetate chelating resin (Muromac A-1) were employed. The speciation was carried out by retention of Cr(III) in the first mini-column, while the Cr(VI) in the effluent was further reduced with hydroxyammonium chloride to Cr(III) than pre-concentrated in the second mini-column. Chromium species were sequentially eluted with $2.0 \text{ mol L}^{-1} \text{ HNO}_3$ and determined by ICP OES. This method was time-consuming (9.4 min) and required a chemical reduction step in the system to perform the pre-concentration/speciation.

According to aforementioned, there exists an actual need to develop pre-concentration/redox speciation methods of chromium avoiding chemical or oxidation reduction steps and without readjusting the sample pH. Such strategy has been recently achieved by using dual mini-columns with different adsorption properties. It can be cited that the use of chitosan cross-linked with 4-hydroxyphthalic acid modified ethyleneglycoldiglycidylether (CCTS-HPA resin) and ME-03 commercial resin able to retain selectivity Cr(VI) and Cr(III) at pH 3.5 [21] and biosorbent (*Chlorella vulgaris*) and 717 anion exchange resin to retain selectively Cr(III) and Cr(VI) at pH 6.0 [22]. More recently, our research group developed a pre-concentration/redox speciation method of chromium based on use of $\text{SiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2$ and chemically modified silica with 3-(2-aminoethylamino) propyltrimethoxysilane (AAPTMS) to adsorb Cr(III) and Cr(VI), respectively, at pH 5.0 [19].

As observed, the chemical nature of adsorbent plays an important role on efficiency and selectivity of separation process. Cross-linked organic polymers containing monomers with chelating properties seem to be an interesting solid phase for speciation studies due to their high stability in a wide pH range [23].

Therefore, the main aim of this work was to synthesize two cross-linked organic polymers-poly(methacrylic acid) and polyvinylimidazole by the bulk polymerization method and evaluate their selective adsorbent properties for the Cr(III) and Cr(VI) species. In the pre-concentration and redox speciation method for chromium using dual mini-column on-line coupled to FAAS, no readjustment of sample pH during pre-concentration and use of oxidizing/reducing agents was required.

2. Experimental

2.1. Apparatus

All measurements were carried out by using a flame atomic absorption spectrometer model AA-7000 (FAAS) (Shimadzu, Tokyo, Japan) equipped with a hollow cathode lamp for the determination of chromium and deuterium lamp for background correction. The hollow cathode lamp was operated at 10.0 mA and the wavelength was set at 357.9 nm. The flame was composed of acetylene at a flow rate of 2.8 L min^{-1} and air at a flow rate of 10.0 L min^{-1} . pH values of samples were measured on a Metrohm 826 digital pH meter (Herisau, Switzerland). The on-line pre-concentration and redox speciation were accomplished by using a peristaltic pump (ISMATEC, CPI-08, Switzerland) equipped with tygon

tubes to propel all solutions. The pre-concentration/elution steps were carried out by using a home-made injector commutator made of poly(tetrafluoroethylene). The mini-column made of polyethylene ($5.0 \times 1.0 \text{ cm}$) containing cotton fiber inlet and outlet of the mini-column to avoid removal of adsorbent was used to package the poly(methacrylic acid) and polyvinylimidazole. For characterization of polymers, an infrared spectrometer with Fourier transform (Shimadzu 8300, Tokyo) operating in the transmission mode between 4000 and 400 cm^{-1} was used to elucidate functional groups and the surface morphology of these materials was analyzed using a Philips FEI Quanta 200 scanning electron microscope (SEM) (Amsterdam, Netherlands). Analysis of surface area of the polymers was obtained according to the multipoint BET method, whereas the average pore size and pore volume were performed by the BJH method. Nitrogen adsorption experiments were performed on a Quantachrome Nova Model 1200E coupled to an automatic nitrogen gas adsorption instrument (Boynton Beach, FL, USA). Contents of carbon, nitrogen and hydrogen in the polymers were determined using an Elemental Analyzer (Perkin Elmer 2400) and the thermal stability of the materials was analyzed by thermogravimetry (TG) using a Perkin Elmer TGA 4000 in the temperature range of 30–700 °C at a scanning rate of 10 °C/min under flow nitrogen (20 mL min^{-1}).

2.2. Reagents and solutions

All reagents employed in the experiments were of analytical grade, as well as all the aqueous solutions were prepared with Milli-Q ultra-pure water (Millipore, Bedford, MA, USA). To avoid contamination, all glassware was kept in a solution of 10% (v/v) HNO_3 for 24 h and then washed with deionized water. The stock solution of 1000 mg L^{-1} of Cr(III) and Cr(VI) was prepared from the corresponding salts $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Vetec, Rio de Janeiro) and potassium dichromate — $\text{K}_2\text{Cr}_2\text{O}_7$ (Sigma-Aldrich, St. Louis, MO, USA) dissolved in 5% (v/v) HCl. Working solutions of $200.0 \text{ } \mu\text{g L}^{-1}$ were prepared from dilutions of the stock solution of Cr(III) and Cr(VI). 1-vinylimidazole was acquired from Sigma-Aldrich and methacrylic acid (purity 99.0%) from Acros Organics. Ethylene glycol dimethacrylate (EGDMA) as cross-linking reagent and 2,2'-isobutyronitrila-azobis (AIBN) as radical initiator were obtained from Sigma-Aldrich. Ethanol (J.T. Baker, Chicago, USA) and dimethylsulfoxide (DMSO) were obtained from Fmaia (Rio de Janeiro). Cationic solutions of Fe(II), Co(II), Cu(II), Zn(II), Cd(II), Ni(II), Pb(II), Ca(II) and Mg(II) used in the study of interfering were prepared from dilutions of the stock solutions of 1000 mg L^{-1} prepared from their nitrate salts (all analytical grade). For assessing the anionic interferences on the adsorption of Cr(VI), AsO_4^{3-} , SeO_4^{2-} , as well as NO_3^- , HCO_3^- , Br^- , CO_3^{2-} , Cl^- and SO_4^{2-} were used and prepared having as counter ion the sodium.

2.3. Synthesis of cross-linked poly(methacrylic acid) and polyvinylimidazole

The synthesis of cross-linked poly(methacrylic acid) was based on the bulk method according to described procedure with modification [24]. 42.66 mmol of methacrylic acid was mixed with 10.0 mL of ethanol and 15.0 mL of DMSO, followed by addition of 53.08 mmol of EGDMA and 1.83 mmol of AIBN. The solution was purged thoroughly with nitrogen gas for 5 min and the reaction flask was immediately sealed. Then, the mixture was subsequently polymerized in an oil bath at 65 °C for 24 h. After polymerization, the polymer was dried at 50 °C, ground in a mortar and sieved to obtain particle sizes between $106 \leq \mu\text{m} \leq 150$. To remove excess reagent incorporated into the polymeric matrix washings were performed with $2.0 \text{ mol L}^{-1} \text{ HNO}_3$ and water. The synthesis of cross-linked polyvinylimidazole was synthesized in similar way to the cross-linked poly(methacrylic acid), except by the initial part of synthesis, where 39.74 mmol of 1-vinylimidazole was dissolved in 25.0 mL of DMSO.

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