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Adsorption studies of Cd(II) onto Al_2O_3/Nb_2O_5 mixed oxide dispersed on silica matrix and its on-line preconcentration and determination by flame atomic absorption spectrometry

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ABSTRACT

The present study describes the adsorption characteristic of Cd(II) onto Nb_2O_5/Al_2O_3 mixed oxide dispersed on silica matrix. The characterization of the adsorbent has been carried out by infrared spectroscopy (IR), scanning electronic microscopy (SEM), energy dispersive spectroscopy (EDS), energy dispersive X-ray fluorescence analysis (EDXRF) and specific surface area (S_{BET}). From batch experiments, adsorption kinetic of Cd(II) was described by a pseudo-second-order kinetic model. The Langmuir linear isotherm fitted to the experimental adsorption isotherm very well, and the maximum adsorption capacity was found to be 17.88 mg g^{-1}. Using the effective material, a method for Cd(II) preconcentration at trace level was developed. The method was based on on-line adsorption of Cd(II) onto $SiO_2/Al_2O_3/Nb_2O_5$ at pH 8.64, in which the quantitative desorption occurs with 1.0 mol L^{-1} hydrochloric acid towards FAAS detector. The experimental parameters related to the system were studied by means of multivariate analysis, using 2^4 full factorial design and Doehlert matrix. The effect of SO_4^{2-}, Cu^{2+}, Zn^{2+} and Ni^{2+} foreign ions showed no interference at 1:100 analyte:interferent proportion. Under the most favorable experimental conditions, the preconcentration system provided a preconcentration factor of 18.4 times, consumption index of 1.08 mL, sample throughput of 14 h^{-1}, concentration efficiency of 4.35 min^{-1}, linear range from 5.0 up to 35.0 μg L^{-1} and limits of detection and quantification of 0.19 and 0.65 μg L^{-1} respectively. The feasibility of the proposed method for Cd(II) determination was assessed by analysis of water samples, cigarette sample and certified reference materials TORT-2 (Lobster hepatopancreas) and DOLT-4 (Dogfish liver).

1. Introduction

Pollution of aquatic environments by heavy metals, particularly as a result of industrialization, is increasingly being associated with public health in an urban setting, since heavy metals not only lead to contamination of aquatic life, but also cause harm to people's health, even at low concentrations [1]. Among heavy metals, Cd(II) is seriously considered to be toxic for animals and humans alike, and it is classified by the International Agency for Research on Cancer as a human carcinogen [2]. The National Council for the Environment in Brazil (CONAMA) [3] established the maximum level of 0.2 mg L^{-1} for cadmium present in effluent discharge that flows to aquatic bodies, while 5.0 μg L^{-1} is the maximum level of contaminant in drinking water allowed by EPA [4]. In this perspective, the search for improved methods focusing the determination of heavy metals in water samples is necessary because it provides a meaningful surveillance and an early warning for quality control of waters. Nevertheless, low concentrations of Cd(II) ions in environmental water samples associated with high matrices effects, make the direct determination of the element a very difficult task. This way, separation and preconcentration procedures must be performed prior to the analysis [5]. Methods based on solid-phase extraction (SPE) have been increasingly used to the detriment of liquid–liquid extraction, due to their advantages including cost-effectiveness, easiness of automation with flow injection analysis, environmentally friendly, faster, simpler, higher preconcentration factors and improved sensitivity [6]. Apart from available adsorbents, such as ion-imprinted polymers [7], carbon nanotubes [8], natural adsorbents [9], activated carbon [10] and polymeric resins [11], the development of new synthetic materials with relevant properties through variation of their chemical compositions and/or physical dimensions has currently attracted the attention of researchers around the world. An efficient solid-phase adsorbent should present a stable and insoluble porous matrix containing suitable active groups that

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interact with heavy metal ions, large surface area, high wettability, absence of swelling effect and high adsorption capacity [12]. In this sense, inorganic adsorbents such as the Al_2O_3, ZrO_2 and Nb_2O_5 oxides show these characteristics slightly and, depending on adsorption pH, they have amphoteric properties. However, it is very well documented that these solid inorganic adsorbents, when dispersed or anchored on solid support present different chemical and physical properties in relation to those observed for bulk metal oxide [13]. The control of the local structure of oxides, revealing better orientation degree of active groups, stronger ion-exchanger and high mechanical resistance when the material is submitted to high sample flow rates, are also described [14]. Some studies have reported the dispersion of inorganic adsorbents on silica matrix, such as silica–niobia (SiO_2/Nb_2O_5) [15], silica–titania (SiO_2/TiO_2) [16], and silica–zirconia (SiO_2/ZrO_2) [17] for metal preconcentration. In other studies, carbon nanotubes (CNTs) have been used as supports to deposit Al_2O_3 or CeO_2 with application to adsorption of nickel, fluoride, arsenate and chromium from water samples [18–21].

In this study, our objective is to investigate the feasibility of Nb_2O_5/Al_2O_3 double oxides dispersed on solid substrate of silica matrix, prepared by sol–gel process, as a promising adsorbent for Cd(II) ions. Adsorption kinetic and isotherms were investigated and an on-line preconcentration procedure for Cd(II) determination by FAAS in water samples, cigarette sample and certified reference material, was also developed. Up to now, the use of double oxides dispersed on silica matrix, *i.e.*, $SiO_2/M_xO_y/N_zO_w$, has only been reported by our research group, whose adsorbent was applied to Zn(II) ions preconcentration in a flow system coupled to UV/Vis spectrophotometry [12]. The experimental parameters of the preconcentration method were optimized by means of factorial design and Doehlert matrix [22].

2. Experimental

2.1. Apparatus

A Shimadzu AA-6800 flame atomic absorption spectrometer (Shimadzu, Tokyo, Japan), equipped with a hollow cathode lamp for cadmium and with a deuterium lamp for background correction, was used. The hollow cathode lamp was operated at 8.0 mA and the wavelength was set at 228.8 nm. The flame composition was operated with an acetylene flow rate of 1.8 L min^{-1} and air flow rate of 10.0 L min^{-1}. The flow preconcentration system was constructed by using a peristaltic pump from Ismatec, Model IPC (Ismatec IPC-08, Glattzbrugg, Switzerland) furnished with Tygon® tubes to propel all samples and reagent solutions. A home-made injector commutator made of Teflon® (PTFE, polytetrafluoroethylene) was used for switching between the preconcentration and elution stages. Polyethylene tubes of 0.8 mm in diameter were used to transport the sample and reagents. The scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analyses were performed in a JEOL model JSM 6360-LV scanning electron microscope. Prior to the analyses, the samples were coated with a thin layer of gold/palladium alloy, in a Bal-Tec MED 020 equipment, in order to minimize charging under the incident electron beam. The specific surface area was obtained from nitrogen adsorption experiments by means of the physical adsorption method, using an automatic nitrogen gas adsorption instrument (Micromeritics Flow Sorb 2300). The specific surface area value was determined from adsorption isotherms by using the Brunauer, Emmett and Teller (BET) multipoint method and by submitting the sample to previous activation at 150 °C in a vacuum for 2 h. The Al_2O_3 and Nb_2O_5 contents in the sample were determined by energy dispersive X-ray fluorescence analysis (EDXRF) on a Shimadzu model EDX 800 HS. The infrared spectra were obtained by using the conventional KBr pellet technique in a Nicolet Magna-IR 760 spectrometer, operating in the transmission mode between 4000 and 400 cm^{-1}. The sample pH was measured by a Schott Handylab 1 pHmeter (Stafford, UK). The digestion of certified reference materials and cigarette sample was carried out by microwave radiation using a microwave oven (Milestone, Sorisole, Italy) ETHOS PLUS that reaches an output of 1000 W. For data acquisition related to analysis of variance, the STATISTICA program (version 6.0) was used.

2.2. Reagents and solutions

All solutions were prepared from analytical grade chemical reagents and the water used in the process was obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). Before using, all laboratory glassware were kept overnight in a 10% (v/v) HNO_3 solution, in order to avoid any metal contamination. After that, they were rinsed with deionized water and submitted to a drying step.

A standard stock solution of Cadmium 1000.0 mg L^{-1} was used to prepare standard solutions of concentration 30.0 μg L^{-1}. The latter was properly diluted from an intermediate solution of 10.0 mg L^{-1} Cd(II). Concentrated HNO_3 (Merck) and 30% (v/v) H_2O_2 (Merck) were used for the decomposition of the certified reference material in a microwave oven. Concentrated HNO_3 was previously purified from a sub-boiling system (Milestone, Sorisole, Italy).

2.3. Preparation of Nb_2O_5/Al_2O_3 mixed oxide dispersed on silica matrix

The preparation of $SiO_2/Al_2O_3/Nb_2O_5$ mixed oxide by sol–gel process was carried out according to previously described procedure, but with some modifications [12]. First of all, 5.2 mL of 3.5 mol L^{-1} HCl were added to 92.0 mL of a 50% (v/v) solution of ethanol/TEOS (TEOS = tetraethylorthosilicate, 98%, Sigma-Aldrich, St. Loius, MO, USA). The mixture was stirred for 3 h at 60 °C. After the pre-hydrolysis step, 8.2 g of aluminum isopropoxide (98%, Sigma-Aldrich) dissolved in small amounts of trifluoroacetic acid and 4.11 g of $NbCl_5$ (99%, Sigma-Aldrich), previously solubilized in ethanol under a nitrogen atmosphere, were added and the resulting mixture was stirred for 2 h at 60 °C. Next, the mixture was stirred for a period of 12 h at room temperature. The solvent was slowly evaporated at 60 °C until gel formation. The gel obtained was ground (≤250 μm) and the remaining solvent and acids were evaporated for 4 h at 60 °C under vacuum (about 10^{-3} mmHg), resulting in a xerogel completely dried. The resulting particles were washed with ethanol in a soxhlet extractor for 4 h. Finally, the material was washed with 100 mL of 0.1 mol L^{-1} HNO_3, deionized water and ethanol, and dried under vacuum (1.3×10^{-2} Pa) for 2 h at room temperature and then stored.

2.4. Adsorption isotherm

Amounts of 80.0 mg of adsorbent were mixed with 25.0 mL of Cd(II) with concentrations ranging from 25.0 to 55.0 mg L^{-1} in polyethylene flasks, during 15 min at room temperature. The pH of Cd(II) solution was adjusted at 8.64 in 0.09 mol L^{-1} Tris–HCl buffer. After shaking time, suspensions were separated by centrifugation at 3000 rpm for 10 min. The amounts of Cd(II) in the initial solution and in the supernatant were quantified by FAAS. The experimental isotherm was built by plotting the amount of adsorbed metal per gram of adsorbent q_{eq} (mg g^{-1}) as a function of equilibrium concentration, C_{eq} (mg L^{-1}). In order to determine the maximum adsorption capacity (MAC), Langmuir and Freundlich linear isotherm models were applied to the experimental isotherm [23].

2.5. Adsorption kinetic

In order to better understand the dynamics of adsorption as dependent on contact time, pseudo-first-order and pseudo-second order kinetic models were applied. Pseudo-first-order kinetic model is expressed by Eq. (1) [24],

$$\log\left(q_{eq}-q_t\right) = \log q_{eq} - (k_1/2.303)t \quad (1)$$