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Original Research Article

Development of a new method for determination of aluminum (Al) in Jordanian foods and drinks: Solid phase extraction and adsorption of Al^{3+}-D-mannitol on carbon nanotubes

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ABSTRACT

In this work, a new method was developed for determination of aluminum (Al) in traditional Jordanian foods (Mansaf, Kofta, Tabboola, Hummous, bread), tea, Arabian coffee and water samples. The method involved solid phase extraction (SPE) of Al^{3+} from the digested samples after complexation with D-mannitol using carbon nanotubes (CNT) as the extractive sorbent. Formation of the Al^{3+}-D-mannitol complex was confirmed by infrared spectroscopy. Optimization of the SPE method involved sample pH, D-mannitol-to-Al mole ratio, sample loading and elution flow rates, adsorbent mass, eluent concentration and volume. Based on spiked water samples, the characteristics of the method were as follows: the limit of quantification: 23 $\mu g\,l^{-1}$; sensitivity: 0.0036 $(mg\,l^{-1})^{-1}$; %RSD range: 0.4–1.9%; recovery range: 76.0–93.0%. The equilibrium, thermodynamic and kinetic adsorption studies of Al^{3+}-D-mannitol on CNT revealed that adsorption was spontaneous, exothermic, preferred, of physical nature; followed second-order rate kinetics; pore diffusion was not the only rate-controlling step; both Langmuir and Freundlich isotherms represented the data satisfactorily.

1. Introduction

Aluminum (Al) is a non-essential toxic metal. Humans are frequently exposed to Al by the use of Al-containing medicines, drinking waters and foods. This element may cause several clinical and neuropathological diseases, particularly in patients with chronic renal failure (Sombra et al., 2003). On average, 20–50 mg of Al is ingested daily, but the total burden in normal persons is about 30 mg, so that it is impossible for humans to avoid exposure to Al compounds. Al ion is a possible cause of renal osteodystropy, Parkinson's disease and Alzheimer's disease (Sombra et al., 2003). Al may present in some products manufactured for human use as a result of intentional addition due to manufacturing protocol or through unintentional contamination occurring during the manufacturing process. Some guidelines were established for maximum permissible content of Al in some products. This necessitates continuous development of new methods for monitoring very low levels of Al in foods and drinks.

Aluminum compounds are applied in the processing, packaging, and preservation of foods (Rajwanshi et al., 1997). They have also been used in cosmetics, in antiperspirant preparations and in clarifying water; as anti-caking agents, and as antacids (Rajwanshi et al., 1997). One of the most widely used potential sources of additional dietary Al is aluminum-cookware. The use of Al skillets, pressure cookers, roasting pans, pots, saucepans, frozen dinner trays, foils and wrappers can increase the amount of Al in foods (Rajwanshi et al., 1997). The use of Al in packaging and cooking of foodstuffs is gaining popularity and acceptance, because of the low cost of Al utensils compared to other pots. Al may be leached into food from Al cookware in the presence of organic acids. Gramiccioni et al. (1998) and Rajwanshi et al. (1997) reported that tomato juice leached moderate Al concentrations from Al-cookware.

Flame atomic absorption spectrometry (FAAS) is a fast, sensitive, selective and economical technique that can be successfully employed for the determination of Al at low concentrations if it is combined with a suitable preconcentration step. Due to matrix effects and because of being at trace levels of Al,

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separation and pre-concentration steps are still necessary. Solid phase extraction (SPE) is a modern simple technique that is usually used for preconcentration and separation of metal ions from complex matrices (Tuzen and Soylak, 2008; Sari and Tuzen, 2009; Barbosa et al., 2007). Carbon nanotubes (CNT) have been widely used as adsorbents for preconcentration of trace heavy metals and organics. This subject was reviewed by Rao et al. (2007), Lemos et al. (2008), Pyrzynska (2007), Valcarcel et al. (2008), Cserháti (2009) and Pyrzynska (2008). For example, Liang and coworkers reported preconcentration of rare earth elements, cadmium and copper ions using CNTs (Liang et al., 2005; Liang and Han, 2006). Tarley et al. (2006) reported determination of cadmium using a simple flow injection mini-column preconcentration system using CNTs. Munoz et al. (2005) reported the use of CNT for speciation of organomettalic compounds of lead, mercury and tin in environmental samples. They found that the preconcentration performance of CNT was better than those of carbon black and RP-C18. Profumo et al. (2006) reported the use of CNT-chemically modified gold electrode for determination of As^{3+} and Bi^{3+} in saline water. A CNT/nafion composite film-modified glassy carbon electrode was prepared by Yuan et al. (2006) for electrochemical determination of Eu^{3+}.

The main objective of the present work was to develop new method for SPE of Al^{3+} after complexation with D-mannitol using CNT as adsorbent for the determination of Al in real water samples and in popular Jordanian drinks and meals. Adsorption properties (equilibrium, thermodynamic and kinetic properties) were also studied. D-Mannitol was chosen in this work because of its availability, high solubility in water, low toxicity, and good complexing property with Al^{3+} (Zajc et al., 2005). D-Mannitol solution is mildly acidic.

2. Materials and methods

2.1. Chemicals, reagents and materials

The following aqueous standard solutions (each of $1000 \pm 2\ \text{mg l}^{-1}$) were purchased from Panreac Química S.L.U. (Barcelona, Spain): Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Fe^{3+}, Zn^{2+}, Ca^{2+}, K^{+}. Stock and standard solutions of Al^{3+} were prepared using aluminum potassium sulfate 12-hydrate (98.0–102%) (VWR BDH Prolabo, Leicestershire, England) in 1.0 M nitric acid. D-Mannitol and nitric acid (69%) were purchased from VWR BDH Prolabo (Leicestershire, England). Triethyl amine (99%) was purchased from ACROS (Geel, Belgium). Ammonium chloride and sodium sulfate anhydrous were purchased from Scharlau (Barcelona, Spain). Sodium hydroxide was purchased from Poch (Gliwici, Poland). Hydrochloric acid (36%) and acetic acid glacial were purchased from (VWR BDH Prolabo, Leicestershire, England). Sodium acetate trihydrate was purchased from Frutarom Ltd (Teesside, UK). Magnesium metal powder was purchased from s.d. Fine-Chem Ltd (Mumbai, India). All chemicals were of Analar grade except D-mannitol was of technical grade. Certified reference material (INCT-PVTL-6 Polish Virginia Tobacco Leaves) was purchased from Institute of Nuclear Chemistry and Technology (Warsaw, Poland). Multi-walled carbon nanotube (length 5–15 μm, external diameter 60–100 nm) was purchased from Shenzhen Nanotechport Co. Ltd., Shenzhen, China. Other characteristics provided by the manufacturer are as follows: purity ≥95%; ash ≤0.2 wt%; amorphous carbon <3%; and specific surface area 40–300 m^2/g.

2.1.1. Synthesis of Al^{3+}-D-mannitol complex

The Al^{3+}-D-mannitol complex was prepared by dissolving 0.5 g (2.7 mmol) of D-mannitol in 10 ml distilled water. 0.7 g (2.7 mmol) of aluminum potassium sulfate 12-hydrate was dissolved in 10 ml distilled water. The two solutions were added to each other and then stirred at ca. 25 °C for 12 h and then dried in vacuum. The produced compound (the complex) was characterized by FT-IR spectrometry.

2.2. Instruments and equipments

A Varian SpectrAA 250plus flame atomic absorption spectrometer (Varian, Palo Alto, CA, USA), was used for the quantitative determination of Al under the following operational conditions: wavelength: 309.3 nm, slit width: 0.5 nm, signal type: non continuous, lamp current: 10 mA, flame type: nitrous oxide-acetylene, fuel flow: $8.6\ \text{l min}^{-1}$, nebulizer uptake: 6–8 s, burner height: 3.4 cm. The instrument was equipped with a deuterium lamp background corrector and a fully computerized data handling system. SPE was performed using a Supelco-visiprep-12-port vacuum manifold (Sigma–Aldrich, St. Louis, MO, USA). Based on the required solution loading flow rate control method, the outlet tip of the manifold was either connected to a Rotavac vacuum pump (Heidolph Instruments, Schwabach, Germany) or to suction tap or not connected to any of them. The adsorbent was packed in cartridge by placing a specific mass of the adsorbent in an empty 6 ml polypropylene Supelco-SPE-tube "filtration tube" (Sigma–Aldrich, St. Louis, MO, USA). Polyethylene frits (Sigma–Aldrich, St. Louis, MO, USA) were used to hold the adsorbent packing in the cartridge. All pH measurements of water samples were made using a digital pH meter (pH level 1 model D-82362) (InoLab, Weilheim, Germany). A 47900-Thermolyne muffle furnace (Barnstead International, Dubuque, IA, USA) with temperature range of 25.0–1200.0 °C was used for dry-ashing food samples. A Moulinex (type code 278) domestic blender (SEB group, Ecully Cedex, France) was used for fine pureeing food samples. WTC binder drying oven model ED115 (Tuttlingen, Germany) was used for drying the samples. Infrared (IR) spectra of D-mannitol and Al^{3+}-D-mannitol complex were recorded as KBr discs on Nicolet-Magna-IR-560 spectrometer (Nicolet Instrument Inc., Madison, WI, USA).

2.3. Equilibrium, kinetic and thermodynamic adsorption studies

Stock solution of Al^{3+}-D-mannitol was prepared by mixing stock Al^{3+} and D-mannitol (mole ratio 1:20) to get Al^{3+} concentration of $50\ \text{mg l}^{-1}$. Lower concentrations Al^{3+}-D-mannitol were prepared by proper dilution of the stock solution. Batch equilibrium adsorption experiments of Al^{3+}-D-mannitol on CNT were performed to determine equilibrium adsorption and thermodynamic constants. These experiments were performed in 100 ml conical flasks, in which 50 mg-masses of CNT were mixed with 50 ml solutions of Al^{3+}-D-mannitol at pH 7.0, within the concentration range of $0–15\ \text{mg l}^{-1}$. Mixtures were agitated for 6 h using thermostated shaker at 303, 323 or 343 K to reach equilibrium. The remaining concentrations of Al^{3+}-D-mannitol in the equilibrated solutions were estimated by FAAS. q_e, which is the amount of Al^{3+}-D-mannitol removed per unit mass of sorbent at equilibrium (mg g^{-1}), was calculated using the following mass balance equation:

$$q_e = \frac{(C_o - C_e)V}{m}$$

where C_o is the initial Al^{3+}-D-mannitol concentration (mg l^{-1}), C_e is the Al^{3+}-D-mannitol concentration at equilibrium (mg l^{-1}), V is the total volume of mixture (l) and m is the mass of the adsorbent (g). Kinetic adsorption experiments were performed by adding 0.500 g of CNT into a 500 ml solution of Al^{3+}-D-mannitol containing $15\ \text{mg l}^{-1}$ of Al^{3+} at pH 7.5 ml samples from the equilibrated mixture were withdrawn, centrifuged and analyzed for the