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Development of a new method for determination of aluminum (Al) in Jordanian foods and drinks: Solid phase extraction and adsorption of Al³⁺-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, Taboola, Hummous, bread), tea, Arabian coffee and water samples. The method involved solid phase extraction (SPE) of Al³⁺ from the digested samples after complexation with D-mannitol using carbon nanotubes (CNT) as the extractive sorbent. Formation of the Al³⁺-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 µg 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 Al³⁺-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.

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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 osteodystrophy, 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 organometallic 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/naion 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 $\geq 95\%$; ash $\leq 0.2 \text{ wt}\%$; 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 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 Rotovac 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 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 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:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where C_0 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 mg l^{-1} of Al^{3+} at pH 7.5 ml samples from the equilibrated mixture were withdrawn, centrifuged and analyzed for the

remaining Al^{3+} -D-mannitol complex concentration in the solution (q_t) at different time (t) intervals.

2.4. Sample collection and preparation

2.4.1. Waters and drinks

“Drinking water” sample was taken from commercial water purification system at different times. “Tap water” sample was taken after flowing for 1 min from four different water taps. “Sweetened tea infusion” was prepared by using 300 ml boiled drinking water, a porcelain cup, 3 small spoonfuls of sugar (5.8 g), and a tea bag (2.0 g) “Tea infusion” was prepared similarly but without adding sugar. “Arabian coffee” was prepared by boiling one liter of drinking water, 22.9 g of Arabian coffee and 2.1 g of crushed cardamom in a stainless steel teapot for 70 min at 70 °C. Next, the water phase was transferred to a glass vacuum bottle leaving most of the solid coffee and cardamom in the pot.

2.4.2. Jordanian foods

All food samples were purchased from local restaurants at Zarqa city (Jordan). Blending process was conducted using a domestic blender. “Mansaf” meal (a mixture of goat meat and fried rice in aged yoghurt) was treated by initially removing the bones. The sample was then weighed and then blended with 800 ml distilled water for 8 min. “Kofta” meal (ground beef and goat meat cooked in tomato sauce) was weighed, and then blended for 2 min with 200 ml distilled water. “Tabboula” (mainly parsley salad with some crushed wheat) sample was weighed and then blended with 100 ml distilled water for 1 min. “Hummous” (mashed chickpeas dip, blended with tahini “milled sesame”, olive oil, lemon juice, salt and garlic) was weighed and then blended with 150 ml distilled water for 1 min. “Bread” flat loaves were weighed, cut with a knife to small pieces, dried in an oven at 110 °C overnight, and then ground for 1 min. All food samples were stored after treatment in a freezer (at –18 °C).

2.5. Sample digestion

2.5.1. Wet digestion of drink samples

40 ml of tea infusion, 40 ml of sweetened tea infusion and 50 ml of Arabian coffee infusion were transferred individually into 250-ml pyrex beakers on a hot plate set at 200 °C and boiled for 20 min (evaporation to near dryness). Then 30 ml of concentrated nitric acid was added to each sample and then boiled at about 100 °C for 20 min. After that 10 ml concentrated nitric acid was added to tea infusion and sweetened tea infusion; and 20 ml concentrated nitric acid for coffee infusion, and boiled for 20 min. Next, 15 ml distilled water was added to each beaker and boiled for 5 minutes. Solution was then cooled by adding ~90 ml distilled water. D-mannitol was added to the mixture in 20:1 mole ratio (D-mannitol: Al^{3+}). The solution was then adjusted to pH 7, transferred quantitatively into a 100-ml volumetric flask and the volume was completed to the mark with distilled water. SPE was then performed as described in Section 2.6.

2.5.2. Dry-ashing of food samples and tobacco leaves

25.0 g of Mansaf, Kofta, Tabboula, and Hummous; 5.5 g of dried bread; 2.0 g of Tobacco leaves CRM were each taken into separate 50 ml-pyrex beakers, placed in a muffle furnace and covered with porcelain crucible cover and ignited at 550 °C for 8 h to oxidize the organic matter completely. The ash was dissolved in 15 ml of 1.0 M nitric acid and heated for 34 min on a hot plate to near dryness. Next, 10 ml of distilled water was added to each beaker and heated for 5 min. Solution was then cooled by adding ~90 ml distilled water. D-mannitol was added to the mixture in 20:1 mole ratio (D-mannitol-to- Al^{3+}). The solution was then adjusted to pH 7,

transferred quantitatively into a 100-ml volumetric flask and the volume was completed to the mark with distilled water. SPE was performed as described in Section 2.6.

2.6. General SPE/separation procedure of Al

The general SPE procedure consisted of three steps: cartridge preparation and conditioning, loading sample that contains the analyte, and finally elution of the retained analyte.

Cartridge was prepared by placing 200 mg CNT in an empty 6-ml polypropylene SPE-tube “filtration tube” (Supelco). Polyethylene frits of 20 μm porosity (Supelco) were used to hold the adsorbent packing in the cartridge. Cartridge was preconditioned by washing with 10 ml of 1.0 M nitric acid, then with 50 ml of distilled water, then with 10 ml of buffer solution (pH 7). The Al containing solution was then passed through the cartridge under the force of vacuum pump. This was followed by passing 10 ml of distilled water to remove any un-adsorbed ions. Subsequently, metal species retained on the cartridge were eluted with 10 ml of 1.0 M nitric acid solution under the force of vacuum pump.

2.6.1. Optimization and recovery studies

Optimization of various SPE parameters was conducted following the general SPE procedure described above and by using 0.200 g CNT; 100 ml of 1.0 mg l^{-1} of Al^{3+} solution at pH 7; 1:20 Al^{3+} -to-D-mannitol mole ratio; 10 ml of 1.0 M HNO_3 ; fast flow rate. Three methods (of different flow rates) of sample pumping and nitric acid elution through the CNT bed were tested: slow flow rate “under the force of gravity” (1.67 ml min^{-1}), medium flow rate “using water suction” (0.15 ml s^{-1}), and fast flow rate “using vacuum pump” (0.23 ml s^{-1}). The recovery of Al was estimated by comparing the found Al concentration with the spiked Al concentration.

2.6.2. Figures of merit of the SPE procedure

Characteristics and figures of merit of the proposed SPE procedure were evaluated by spiking 100 ml water samples with 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0 mg l^{-1} of Al^{3+} . The solutions were treated similarly as in Section 2.6.1.

3. Results and discussion

3.1. Formation of the Al^{3+} -D-mannitol complex

The FTIR spectroscopy data of D-mannitol and Al^{3+} -D-mannitol are shown in Fig. 1. The assigned absorption bands confirmed that the D-mannitol and Al^{3+} -D-mannitol showed differences in almost all the IR wave-number range (Barashkov et al., 2004; Bruni et al., 2009; Williams et al., 2006). For example the band due to the –OH stretching was broader in the D-mannitol than in the Al-D-mannitol. Furthermore this band was centered at two different frequencies (3490 cm^{-1} in D-mannitol and 3289 cm^{-1} in the Al-D-mannitol). Moreover the stretching of the –CH₂– and of –CH– residues showed significant changes too. Again pronounced differences were present as regards the bands due to –OH deformation. These vibrations were shifted to lower frequencies or disappeared upon complex formation and/or deprotonation. This is true either for the in plane –OH deformation (see the broad band centered at 1280 cm^{-1} in the D-mannitol and the quite narrow peak at 1248 cm^{-1} in the Al-D-mannitol), and for the out of plane deformation (see the bands 882–864 cm^{-1} in the D-mannitol with relative maxima at 889–874 cm^{-1} in the case of the Al-D-mannitol). Another interesting spectral feature is that of the 2494 cm^{-1} bands which were assigned to Al–O–Al unsymmetrical stretching, and 970 cm^{-1} and 504 cm^{-1} bands which were assigned to Al–O–H and Al–O bending vibrations, respectively.

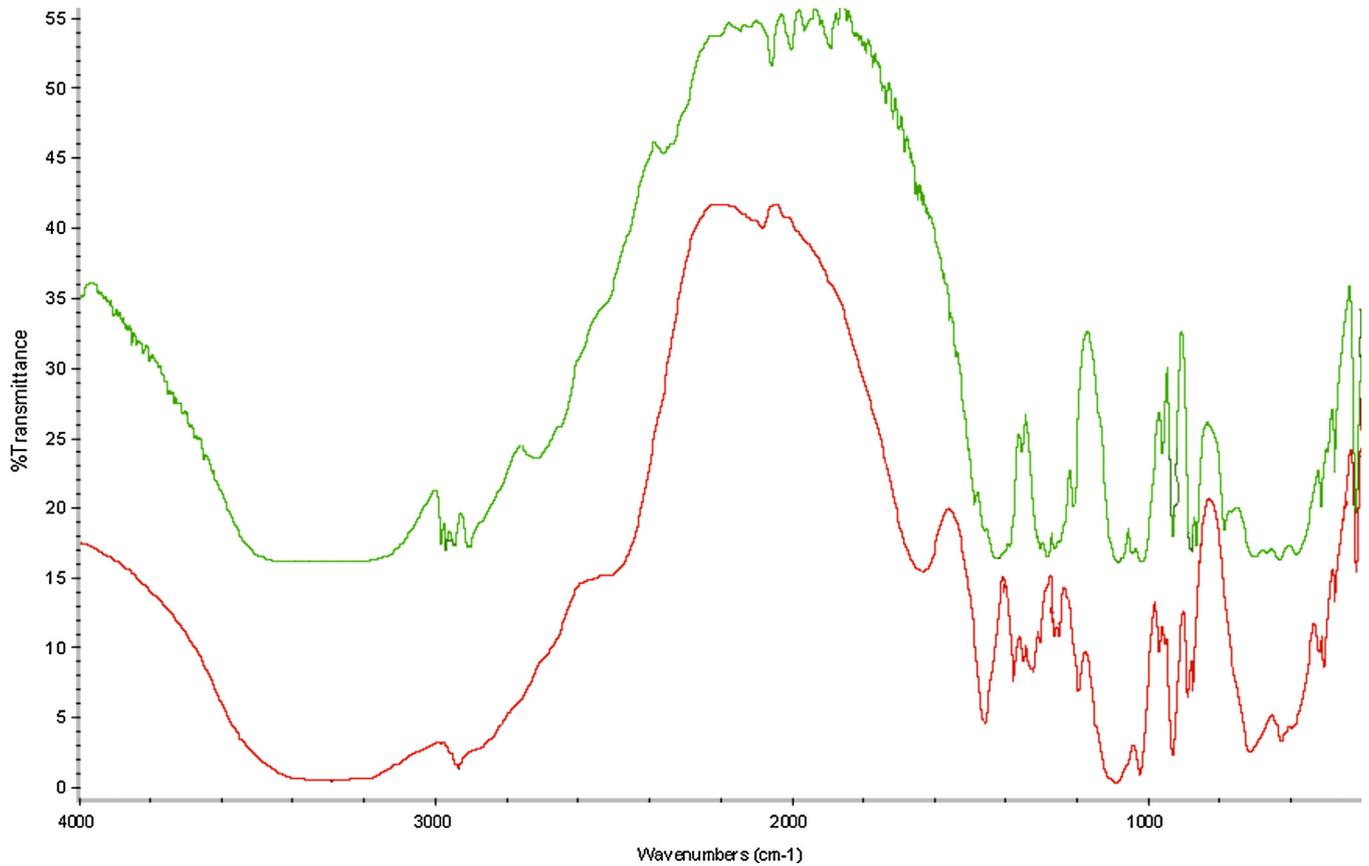


Fig. 1. Infra-red spectrum of D-mannitol (upper spectrum) and Al^{3+} -D-mannitol (lower spectrum).

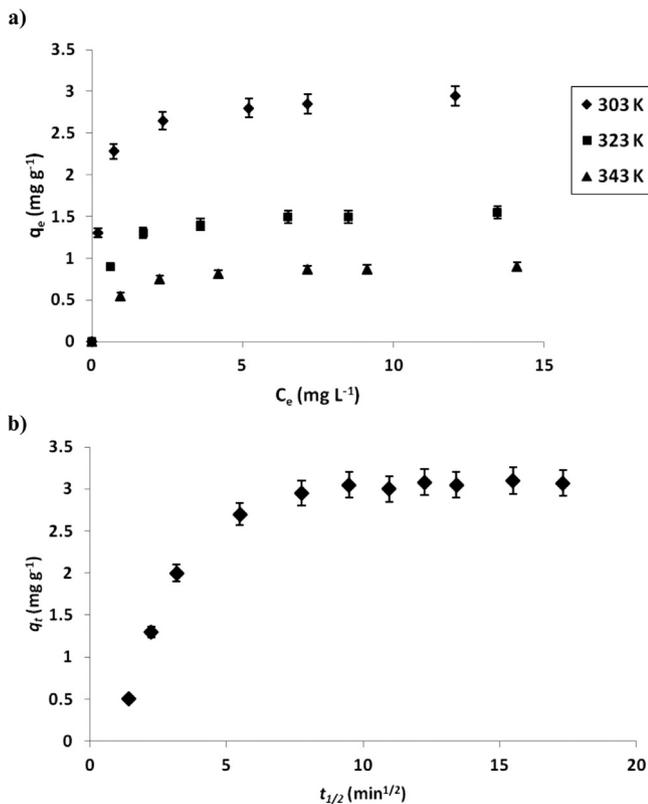


Fig. 2. Adsorption of Al^{3+} -D-mannitol on CNT. (a) Equilibrium adsorption isotherms at various temperatures; (b) application of the intra-particle diffusion model on the kinetic adsorption data ($n = 3$).

3.2. Equilibrium, thermodynamic and kinetic adsorption properties of Al^{3+} -D-mannitol on CNT

Adsorption isotherms of Al^{3+} -D-mannitol complex on CNT (q_e vs. C_e) at various temperatures (303, 323 and 343 K) are shown in Fig. 2a. It was clear that adsorption isotherms followed the L2-shape according to the classification of Giles et al. (1974). The initial curvature in L2 isotherm revealed that the adsorbed solute molecules in the monolayer were so oriented that they had low attraction for solute molecules remaining in the solution Giles et al. (1974).

Equilibrium adsorption data were modeled by applying the Langmuir isotherm model, which has the following linear form (Langmuir, 1918):

$$\frac{C_e}{q_e} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}$$

where C_e is the equilibrium concentration of the remaining solute in solution in mg l⁻¹; q_e is the amount of solute adsorbed per unit mass of sorbent at equilibrium (mg g⁻¹); Q_{\max} is the amount of adsorbate at complete monolayer coverage (mg g⁻¹), and b represents the equilibrium adsorption constant (l mg⁻¹) (adsorption/desorption rate constants). Equilibrium adsorption data were also tested by Freundlich isotherm model, which has the following linear form (Freundlich, 1906):

$$\log q_e = \log K_F + n \log C_e$$

where K_F (mg¹⁻ⁿ g⁻¹ Lⁿ) represents the adsorption capacity; n represents the adsorption intensity (Frimmel and Huber, 1996).

Table 1
Adsorption isotherm parameters for adsorption of Al³⁺-D-mannitol on carbon nanotubes.

Temperature (K)	Dubinin–Raduchkevich			Langmuir			Freundlich		
	q_m (mg g ⁻¹)	r^2	E (kJ mol ⁻¹)	b (L mg ⁻¹)	Q_{max} (mg g ⁻¹)	r^2	K_F (mg ¹⁻ⁿ g ⁻¹ L ⁿ)	n	r^2
303	2.85	0.9351	3.16	3.20	3.01	0.9997	7.43	0.09	0.9688
323	1.53	0.9780	2.24	2.21	1.60	0.9688	1.67	0.08	0.9715
343	0.75	0.9171	1.12	1.60	0.97	0.9351	0.44	0.10	0.9820

q_m : sorption capacity; E : energy of adsorption; b : Langmuir constant; Q_{max} : monolayer capacity; K_F and n : Freundlich constants.

The Dubinin–Radushkevich (D–R) isotherm was also applied to estimate the mean free energy of adsorption (E). D–R model is represented by the following linear equation (Memon et al., 2005):

$$\ln q_e = \ln q_m - B \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2$$

where, B (J² mol⁻²) is a constant that is related to free energy change (E) and q_m (mg g⁻¹) represents the adsorption capacity. E (J mol⁻¹) was calculated (Bansode et al., 2004) from B using the equation: $E = 1/(-2B)^{1/2}$.

Adsorption parameters are presented in Table 1. The adsorption capacity parameters (Q_{max} and X_m) indicated that the adsorption capacity of Al³⁺-D-mannitol complex decreased with increasing temperature. This of course revealed that the adsorption process was exothermic. Similarly the favorability of adsorption decreased by increasing temperature as indicated by b and K_F values. The adsorption process was preferred over the entire concentration range as indicated by the value of $n < 1$. The energy of adsorption (E) was less than 8 kJ mol⁻¹, which revealed that the adsorption of Al³⁺-D-mannitol on CNT was of physical nature and thus may be easily eluted from the adsorbent (Bansode et al., 2004). E decreased with increasing temperature which indicated that adsorption became weaker with increasing temperature.

The temperature dependence (thermodynamics) of the adsorption of Al-D-mannitol on CNT was studied using the equations:

$$\ln K_c = \left(\frac{-\Delta H^\circ}{RT} \right) + \left(\frac{-\Delta S^\circ}{R} \right) \quad \text{and} \quad \Delta G^\circ = -RT \ln K_c$$

where ΔH° (kJ mol⁻¹), ΔS° (kJ mol⁻¹ K⁻¹), ΔG° (kJ mol⁻¹), T (K) and K_c are enthalpy, entropy, Gibbs free energy, absolute temperature and equilibrium constant, respectively; R is the gas constant (8.314 J mol⁻¹ K⁻¹). K_c is the thermodynamic equilibrium constant, which was determined by plotting $\ln(q_e/C_e)$ against q_e and extrapolating to $q_e = 0$. van't Hoff plots of $\ln K_c$ as a function of $(1/T)$ yielded straight line ($y = 7343x - 22.2$, $r^2 = 0.9998$), from which ΔH° and ΔS° were calculated from the slope and intercept of the plots, respectively. The following results were obtained: ΔG° (at 303 K) = -5.1 kJ mol⁻¹, ΔG° (at 323 K) = -1.4 kJ mol⁻¹, ΔG° (at 343 K) = 2.3 kJ mol⁻¹, ΔH° = -61 kJ mol⁻¹, ΔS° = -183 J K⁻¹ mol⁻¹. The value of ΔG° revealed that the spontaneity of the adsorption process decreased with increasing temperature. Since the value of ΔG° lied between -20 and 0 kJ mol⁻¹, then physisorption took place. The negative value of ΔH° reflected that the adsorption was exothermic, while the negative value of ΔS° (-183 J K⁻¹ mol⁻¹) reflected that the randomness in the adsorption system decreased.

Kinetics of the adsorption process was studied to estimate the rate constant of adsorption of Al³⁺-D-mannitol on CNT. Kinetic data did not obey the pseudo first-order kinetic equation but obeyed the pseudo second-order kinetic equation (Ho and McKay, 2000):

$$\frac{t}{q_t} = \left(\frac{1}{k \cdot q_e^2} \right) + \left(\frac{1}{q_e} \right) t$$

where q_t is the amount of Al³⁺-D-mannitol adsorbed at time t (min), k is the 2nd order rate constant (mg g⁻¹ min⁻¹). Plotting (t/q_t) vs.

time (t) yielded a straight line ($y = 0.3179x + 1.6079$, $r^2 = 0.9993$), where k_2 was estimated to be 0.105 mg g⁻¹ min⁻¹. The kinetic data were used to test the mechanism of adsorption (Memon et al., 2005) by applying the Weber–Morris equation: $q_t = k_{id} (t)^{1/2}$ (Weber and Morris, 1963), where k_{id} is the rate constant of intra-particle transport (mg g⁻¹ min^{-1/2}) of Al³⁺-D-mannitol into the interior of the adsorbent. A plot of q_t against $t^{0.5}$ is shown in Fig. 2b. This plot shape indicated that intra-particle diffusion mechanism was involved, but it was not the only rate-controlling step.

3.3. Optimization of the SPE procedure

3.3.1. Effect of pH value of water sample

Browne et al. (1990) studied the species distribution of Al³⁺ in aqueous medium. Below pH 4, Al³⁺ predominates. The mole fraction of free Al³⁺ and [Al(OH)]²⁺ predicted to occur at pH 5 was about 0.3 for each. At increasing values above pH 5, Al hydroxo species predominate e.g., [Al(OH)]²⁺, [Al(OH)₂]⁺, Al(OH)₃, [Al(OH)₄]⁻. At alkaline pH values, the predominant species appear to be [Al(OH)₄]⁻ Browne et al. (1990). The effect of pH of water sample on Al recovery was studied in this work. Results are shown in Fig. 3a. It was clear that the best condition for preconcentration of Al³⁺ was achieved at pH 7. Slightly lower recoveries were obtained in solutions adjusted to pH 8, while much lower recoveries were obtained for other tested pH values. Therefore, pH 7 was selected in the optimum SPE procedure. The low recovery in acidic solutions (below pH 5) may be attributed to the competition of higher levels of hydronium ion which tend to compete with Al³⁺ for active sites on the CNT sorbent and protonation of D-mannitol which prevented complexation with Al³⁺. At high pH values, the lower recovery might be due to the lower Al³⁺ species concentration by formation of Al hydroxo species [Al(OH)]²⁺, [Al(OH)₂]⁺, Al(OH)₃ and [Al(OH)₄]⁻, which were less adsorbed on the CNT and lowered the fraction of Al available as the Al-D-mannitol complex.

3.3.2. Effect of flow rate of loading water sample and nitric acid eluent

It was found that there was only a marginal change in Al % recovery irrespective of the method of sample or nitric acid eluent pumping through the CNT bed. This meant that adsorption and desorption kinetics of Al-D-mannitol complex on CNT was fast and it was not affected by aspiration method. So that fast loading flow rate of aqueous solution and fast nitric acid elution was considered in the optimum SPE procedure.

3.3.3. Effect of concentration and volume of nitric acid eluent

Various concentrations and volumes of nitric acid eluent were tested. Fig. 3b shows that using 0.5 M nitric acid was enough to attain the highest recovery of Al, but there was no big difference in recovery between 0.5 M nitric acid and 1.0 M nitric acid. Higher acid concentrations yielded the same or slightly lower percent recovery. For this reason 1.0 M nitric acid was selected as the optimum nitric acid eluent to be used for further optimization tests. Fig. 3c showed that there was a sharp rise in % recovery of Al as the eluent volume was increased. Above 10 ml eluent volume,

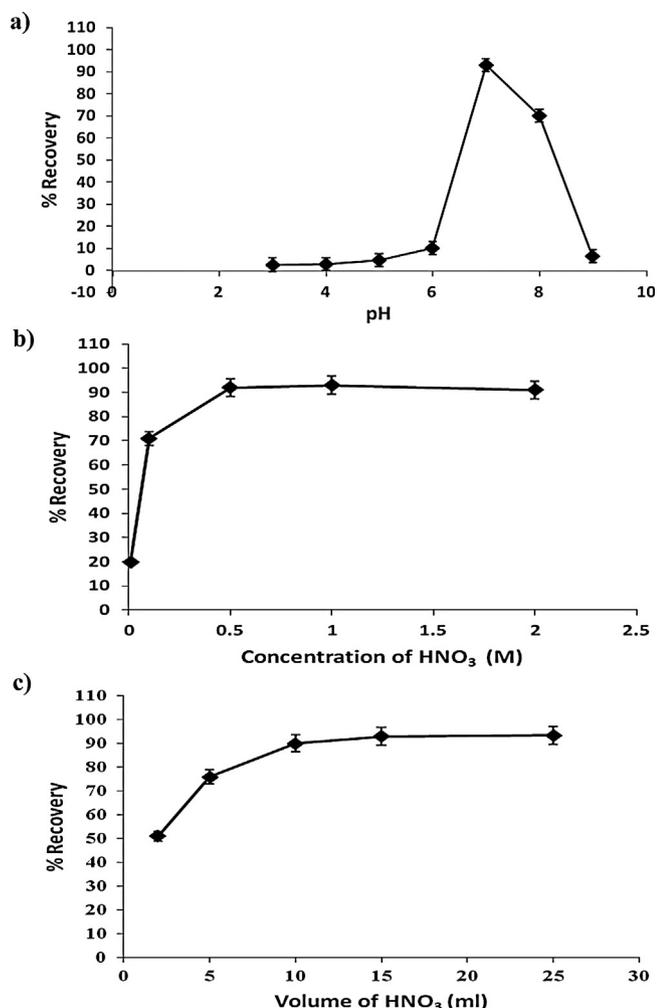


Fig. 3. Effect of (a) solution pH; (b) concentration of HNO₃ eluent; (c) volume of HNO₃ on SPE of Al³⁺ (*n* = 3).

the increase in Al recovery was modest. 15 and 25 ml acid eluent volumes gave slightly higher Al recoveries; however, this increase was not worth the sacrifice of obtaining lower enrichment factors with those larger volumes. Therefore, 10 ml was used as an optimum nitric acid eluent volume in the SPE procedure because of full Al recovery, high enrichment factor and because this volume was adequate for multiple determination by FAAS.

3.3.4. Effect of mass of CNT adsorbent

The effect of changing the mass of CNT on the % recovery of Al is shown in Fig. 4a. It was clear that 50, 100 or 200 mg of CNT was sufficient to retain all Al-D-mannitol from 100 ml of 1.0 mg l⁻¹ and gave the highest recovery. Larger masses yielded essentially the same recovery. 200 mg of CNT was selected because it could retain more Al-D-mannitol as did 100 mg of CNT. Furthermore, the 200 mg mass of CNT would fill a suitable volume of about one third of the SPE tube and leave enough void to add the liquid solutions.

3.3.5. Effect of D-mannitol-to-Al³⁺ mole ratio

Various D-mannitol-to-Al³⁺ mole ratios were tested. Results are shown in Fig. 4b. It was noted that the presence of D-mannitol in 1:1 mole ratio raised the %recovery of Al by 30%. Higher mole ratios increased the recovery of Al³⁺. The highest recovery was recorded for 20:1 mole ratio, which was selected as the optimum mole ratio of D-mannitol-to-Al³⁺ during the SPE process.

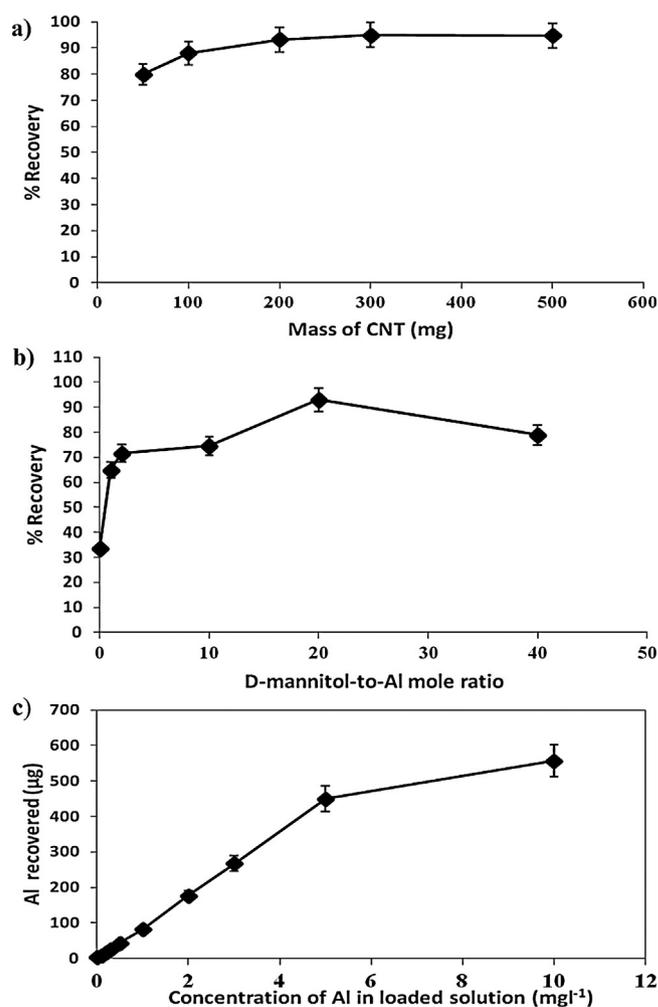


Fig. 4. Effect of (a) mass of CNT; (b) D-mannitol-to-Al³⁺ mole ratio; (c) concentration of Al³⁺ in the solution on SPE of Al³⁺ (*n* = 3).

3.4. Figures of merit of the optimum SPE procedure

It is evident from Fig. 4c that there was a linear relationship between the spiked Al³⁺ concentration in the loaded water sample and the recovered Al in the eluate up to 5 mg l⁻¹ spiked Al. Plotting absorbance of the eluate versus spiked Al concentration (mg l⁻¹) gave a regression coefficient (*r*²) of 0.9995 within the concentration range 0.1–5.0 mg l⁻¹. The lower recovery for concentrations >5 mg l⁻¹ was probably due to the limited mass of CNT used in the SPE. This determined the upper limit of linearity (LOL) of the method to be 5 mg l⁻¹. In case of samples with Al concentration >5 mg l⁻¹, smaller volumes should be used. The limit of detection (LOD) of Al³⁺ was estimated as three times the standard deviation of the blank (*n* = 10) and found to be 6.8 µg l⁻¹, while the limit of quantification was estimated as ten times the standard deviation of the blank signal (*n* = 10) and found to be 23.0 µg l⁻¹. So that the dynamic range of the method was estimated to be 0.023–5.000 mg l⁻¹. The method sensitivity (slope of the calibration curve) was found to be 0.0036 AU l mg⁻¹, where AU stands for absorbance unit. The %RSD range was 0.4–1.9%. The spike recovery range of Al was between 76.0 and 93.0%.

3.4.1. Selectivity test: effect of common ions on SPE of Al³⁺

The effect of the presence of ions commonly found in foods and drinks on SPE of Al using CNT should be studied to determine the potential interference effects of such ions on SPE and recovery of Al.

Table 2

Al³⁺ concentration in drink samples (wet digestion then solid phase extraction using carbon nanotubes).

Type of drink	Al concentration in infusion solution (mg l ⁻¹) (mean ± sd, n = 3)	Al concentration in the original solid sample, (μg g ⁻¹) (mean ± sd, n = 3)
Sweetened tea infusion	2.2 ± 0.1	321 ± 15
Tea infusion	2.1 ± 0.1	312 ± 18
Arabian coffee	0.63 ± 0.03	27.5 ± 1.3

n: number of replicates.

Tolerance limit was defined as the concentration of coexisting ion needed to reduce the recovery of Al into 90%. The values of tolerance limits of the coexisting ions were as follows: 400 mg l⁻¹ Na⁺, 400 mg l⁻¹ K⁺, 120 mg l⁻¹ Ca²⁺, 120 mg l⁻¹ Mg²⁺, 40 mg l⁻¹ Mn²⁺, 15 mg l⁻¹ Fe³⁺, 15 mg l⁻¹ Zn²⁺, 12 mg l⁻¹ Cu²⁺, 15 mg l⁻¹ Cd²⁺, 12 mg l⁻¹ Ni²⁺, 12 mg l⁻¹ Pb²⁺, 75 mg l⁻¹ Cl⁻, 100 mg l⁻¹ SO₄²⁻.

3.4.2. Method validation: determination of Al in tobacco leaves CRM

A tobacco certified reference material, Polish Virginia Tobacco Leaves (INCT-PVTL-6), was included to check the method's recovery for Al (Certified value for Al is 252 ± 49 μg g⁻¹). Dry ashing of tobacco leaves followed by SPE then determination by FAAS yielded an Al content of 226 ± 45 μg g⁻¹ (n = 3), which represents ~90% recovery of the certified concentration.

3.5. Determination of Al in real water samples

To evaluate the applicability and reliability of the proposed method for real water sample analysis, two types of waters were used: tap water and drinking water. 100 ml volume of water was taken for each trial. The optimum SPE preconcentration procedure was performed for the two water samples to investigate whether these water samples contain Al or not. It was found that tap water sample contained 26.0 ± 0.6 μg l⁻¹, while drinking water sample contained 16.0 ± 0.4 μg l⁻¹. These results agreed with that of [Ulusoy et al. \(2011\)](#), in which they determined the concentration of Al³⁺ in mineral water and found that it ranged between 15.3 ± 0.1 and 39.8 ± 0.7 μg l⁻¹. Their results for Al in drinking water ranged from 22.5 ± 0.1 to 23.5 ± 0.1. On the other hand, [Khan et al. \(2011\)](#) determined the concentration of Al³⁺ in river water which ranged from 10 to 150 μg l⁻¹.

3.6. Determination of Al in Jordanian drinks and foods

3.6.1. Drinks

The Al contents in tea and coffee drinks were analyzed after wet digestion then SPE by CNT. The results are shown in [Table 2](#). The concentration of Al in tea infusion and sweetened tea infusion were 2.1 ± 0.1 and 2.2 ± 0.1 mg l⁻¹, respectively (i.e. 311.8 ± 18.0 and 320.8 ± 15.0 μg g⁻¹, respectively), on dry sample basis. Al was not detected in sugar solution. [Matsushima et al. \(1993\)](#) found that Al ranged between 0.64 and 4.35 mg l⁻¹ in tea infusion. [López et al., 2000](#) reported somehow lower values for Al in black tea (between 43.4 and 58.0 μg g⁻¹). [Matsushima et al. \(1993\)](#) and [Muller et al. \(1997\)](#) determined Al content in dry sample of black tea and they found that it was 576 μg g⁻¹ and 899 μg g⁻¹, respectively. This variation may be attributed to different origins of the tea samples. [Muller et al. \(1997\)](#) indicated that about 30% of the Al stored in black tea's dry matter was transferred into the infusion. Our results are reasonable if we assume that the content of Al in black tea is 899 μg g⁻¹ and that about 35% of the Al stored in black tea was transferred into the infusion. The concentration of Al³⁺ in Arabian coffee infusion was 0.63 mg l⁻¹, which represent 27.5 μg g⁻¹ in dry

Table 3

Al³⁺ concentration in Jordanian foods (dry-ashing then solid phase extraction using carbon nanotubes).

Food	Al concentration (μg g ⁻¹) (mean ± sd, n = 3)
Kofta	5.0 ± 0.3
Mansaf	2.9 ± 0.2
Tabboula	10.3 ± 0.7
Bread	5.4 ± 0.4
Hummous	4.2 ± 0.2

n: number of replicates.

sample. These values agree with those published by [López et al. \(2000\)](#); they reported 25.6–29.1 μg g⁻¹ for Al content in coffee.

3.6.2. Food samples

The content of Al in food samples was determined by dry ashing followed by SPE with CNT. The results are shown in [Table 3](#). Sample digestion by dry ashing is simpler, easier to get rid of the fat, didn't need much amount of acid consumption and the number of steps are less than wet digestion. Dry-ashing then SPE provided a simple matrix by removing potential interfering species in Al determination. From [Table 3](#), it is noted that the concentration of Al in the analyzed foods in this work (expressed based on dry mass) ranged from 2.9 to 10.3 μg g⁻¹. It is important here to mention some Al concentrations in previous studies. For example, It was reported by [Gramiccioni et al. \(1998\)](#), [Müller et al. \(1998\)](#), and [López et al. \(2000\)](#) that Al concentrations in foodstuffs ranged in meat: 0.5–30 mg kg⁻¹; in flour, bread and rice: 2–22 mg kg⁻¹; in milk: 2–6 mg kg⁻¹; in infant formulas: 0.03–0.2 mg l⁻¹; in beverages: 25.6–58.0 μg g⁻¹; in tea infusion: 43.4–58.0 μg g⁻¹; in coffee infusions: 25.6–29.1 μg g⁻¹. Higher concentrations of Al may be found in vegetables (up to 80 mg kg⁻¹); in lettuce (up to 1000 mg kg⁻¹); in herbs (300 mg kg⁻¹); in spices 1000 mg kg⁻¹); in black tea leaves (600–1200 mg kg⁻¹).

4. Conclusion

This research improved preconcentration/SPE performance of Al³⁺ and developed a new efficient, reliable, accurate and precise method for preconcentration and separation of Al after complexation with D-mannitol using CNT as preconcentrating adsorbent prior to FAAS determination of Al. This procedure could be applied for determination of Al in real water samples, many food and drink samples, and tobacco leaves. From this work, we can conclude that CNT could be used as an efficient adsorbent for preconcentration of Al species in presence of D-mannitol as a complexing agent, where adsorption of Al³⁺-D-mannitol on CNT was spontaneous, preferred, exothermic, of physical nature, followed second-order rate kinetics and pore diffusion was not the only rate-limiting step. This research shows that CNT was a good adsorbent for preconcentration and separation of Al from food samples. This method can be farther expanded by using other kinds of complexing agents for preconcentration of Al³⁺; or it may be applied for other metals or for other kinds of food and drinks; or it may be applied for other matrices; or different methods of digestion may be applied.

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