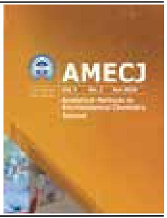
AMECJ

Research Article, Issue 2
Analytical Methods in Environmental Chemistry Journal
Journal home page: www.amecj.com/ir



Aluminum separation from drinking water and serum samples based on djenkolic acid immobilized on the multi walled carbon nanotubes by ultrasound-assisted dispersive micro solid phase extraction

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ARTICLE INFO:

Received 2 Mar 2020
Revised form 30 Apr 2020
Accepted 21 May 2020
Available online 29 Jun 2020

Keywords:
Aluminum,
Poly methyl ether thiol sorbent,
Dispersive micro solid phase extraction,
Waters,
Human serum,
Electrothermal atomic absorption spectrometry

ABSTRACT

A new method for aluminum extraction from drinking water and human serum samples was used by djenkolic acid (DJKA) immobilized on multi walled carbon nanotubes (MWCNTs-DJKA). By procedure, the mixture of 25 mg of MWCNTs-DJKA sorbent and hydrophobic ionic liquid ([OMIM][PF6]) were dispersed with ultrasonic bath in 10 mL of drinking water and serum samples for 10 min at pH=5. The aluminum ions were extracted based on MWCNTs-DJKA sorbent in liquid phase by ultrasound-assisted dispersive micro solid phase extraction (USA-D-μ-SPE). After centrifuging, the Al (III) was separated from liquid phase by ionic liquid phase in bottom of centrifuge PVC tube. Finally, the Al (III) were back-extracted from sorbent/IL in acidic pH and measured by electrothermal atomic absorption spectrometry (ET-AAS). In optimized study, LOD, LOQ, the linear range, the working range and the enrichment factor were obtained 0.1 μg L^{-1}, 0.3 μg L^{-1}, 0.3-12.8 μg L^{-1}, 0.3-30.7 μg L^{-1} and 9.92, respectively (RSD< 5%). The adsorption capacity of the MWCNTs-DJKA sorbent was obtained in batch system. Based on proposed procedure, the mean concentrations of aluminum in drinking waters and serum samples were lower than world health organization (WHO) and American conference of governmental industrial hygienists (ACGIH) references. The method was validated by spiking samples and standard reference materials (SRM) in water and human biological samples.

1. Introduction

Aluminum used in different products such as pharmaceuticals (Al-Mg/S), cover or additives for foods, plates, cars and airplanes. The aluminium compounds have solid forms with high melting points and solubility in water in low pH. The aluminium cation (Al^{3+}) has a strong affinity to hydroxide form [$Al\,(OH)_3$] as precipitation. Aluminium production" has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC). Aluminium in the diet has ranges between 0.1 to 0.3% based on aluminium intake and urinary elimination. Over dose of aluminum caused to Alzheimer's disease (AD). Aluminium is the most

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https://doi.org/10.24200/amecj.v3.i02.105

abundant metal and the third most abundant element in the Earth's crust. This metal separated from its ores by industrial scale and caused to change from decorative metal to the most widely used metal in different industries [1]. WHO reported that aluminum salts can be absorbed by the gut and concentrated in various human tissues including bone, parathyroid, and brain. Aluminum concentrations in brain tissue should be lower than 2 µg g^{-1}. The daily dietary intake of aluminum (510 mg) is completely eliminated. On the other hand, the pervious works showed that the high aluminum intake may be harmful to some patients with bone or renal diseases [2]. Also, the aluminum can be detected in brain tissues of patients with Alzheimer's disease [3] and the pulmonary fibrosis have been evident under high-dose aluminum exposure [4]. The neurotoxicity of aluminium has been demonstrated in humans, animal models and in tissue and cell culture. The neurotoxicity of aluminum is indisputable and it is difficult to understand the mechanism of neurotoxin in human body [5].Aluminium toxicity created from the interaction between aluminum and plasma membrane and in humans Mg^{2+} and Fe^{3+} are replaced by Al^{3+}, which causes many disturbances associated with intercellular interaction [6]. Workers are exposed to various occupational hazardous factors such as fumes and gases, mineral dusts, and VOCs. Workers in aluminum factory were shown the respiratory symptoms, phlegm, dyspnea, wheezing and chest tightness [7].Also, it has been shown that Bauxite mining causes respiratory and skin problems, in addition to other injuries consistent with mining and heavy industries. Workers in alumina refineries have symptoms include osteosclerosis, sinus trouble, chest pains, coughs, thyroid disorders, anemia, dizziness, weakness and nausea. As hazards of aluminium in environment and humans, determination and separation aluminum in human body and waters is very necessary. Many analytical techniques was used for determination of aluminum in different matrix such as flame atomic absorption spectrometry (F-AAS) [9], stripping Voltammetry (SV) [10], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [11], High performance liquid chromatography/ inductively coupled plasma mass spectrometry (HPLC/ICPMS) [12,13], electrothermal atomic absorption spectrometry (ETAAS) [14] and inductively coupled plasma mass spectrometry (ICP-MS) [15]. Also, sample preparation was needed for separating of contaminations from water and biological samples. For this purpose, the vary preconcentration/separation techniques such as liquid–liquid extraction (LLE), dispersive liquid–liquid microextraction (DLLME) [16, 17], and solid phase extraction (SPE) [18] was applied. Recently, the SPE methods were used as a suitable technique for extraction aluminum as compared to others. The SPE have some advantages including simplicity, lower cost, higher enrichment factor, less lower LOD, and the ability to combine with different detection techniques such as ICP-MS [19, 20]. The aim of this study is to develop a novel technique based on MWCNTs-DJKA sorbent for separation and determination of aluminum from drinking water and human serum samples by USA-D-µ-SPE procedure coupled to ET-AAS.

2. Experimental

2.1. Instrumental

The spectra GBC atomic absorption spectrometer (AAS, Plus 932, Australia) using a electrothermal module (ET-AAS) was used for determination aluminum in different samples. The parameters of alminum of were adjusted by recommended of the manufacturer. A multi cathode lamp for Al (MCL) with the current lamp (6 mA), the wavelength (396.2 nm) and spectral bandwidth (0.5 nm) was applied. All results were performed by auto injection of samples (1-100µL) and ANANTA software. The pH in water and serum samples were determined and adjusted by a pH-meter of Metrohm (744, Switzerland) which was with a glassy electrode. The samples were separated using a centrifuge accessory (Eppendorf, 5702 Series Centrifuge, 022629905, 4,400rpm) with rotor (A-4-38) and round bucket(4 × 85 mL), rotary knobs. An ultrasonic bath (100DE, China) with temperature control was used in this study.

Table 1. Comparind of the structure of MWCNTs and MWCNTs-DJKA

Carbon Nano Structure	Diameter (nm)	Length (um)	Surface Area (m^2/gr)
MWCNT	14-30	11-24	375
MWCNTs-DJKA	15-38	13-30	345

2.2. Material and Reagents

The reagents such as acids, bases and organic and inorganic solvents were purchased from Merck Company (Germany, ultra-trace grade). MWCNTs (particle size <100 µm) was prepared from RIPI, Iran. DL-djenkolic acid ($C_7H_{14}N_2O_4S_2$, DJKA, CAS N.: 28052-93-9) was purchased fron sigma Aldrich, Germany. 1-methyl-3-octylimidazolium hexafluorophosphate ([OMIM] PF6]), CAS N: 304680-36-2, Purity > 99.0). Standard stock solutions (1000 ppm) of Al (III) purchased from Merck, Darmstadt, Germany. Deionized water (DW) prepared from Milli-Q plus water purification system (Millipore, Bedford, MA, USA). The all solutions of procedure were daily prepared by diluting of standard solutions with DW. The eight point of calibration curve for aluminum were prepared daily by diluting the stock solutions of alminum ions with DW prior to analysis. The pH adjustments were made using appropriate buffer solutions including ammonium acetate (CH_3COOH/$CHCOONH_4$, 0.2 Mol) for pH 4-6 in this study.

2.3. Sampling

All glasses and PVC tubes were cleaned with a mixture of 0.1 M of HNO_3/H_2SO_4 solution for 12 h and washed for 10 times with DW before using. As trace concentrations of Al in serum and drinking water, even low contamination at any step of sample storage, preparation, and analysis can be effected on the accuracy of the results. Human serum samples collected into 2 mL of Eppendorf tube tubes and kept at -20^{O}C. Serum and wastewater samples were collected from aluminum factories, Iran. The water prepared and stored by standard method for sampling from water by adding HNO_3 (2%) to waters. In this study, the world medical association declaration of Helsinki (WMADH) based on guiding physicians in human body research was considered.

2.4. Characterization

The Brunauer-Emmett-Teller (BET) method was used for studying the microstructure (surface area and pore size) of nanostructure. The surface area and porosity of the MWCNTs and MWCNTs-DJKA, before and after heat treatment in 350^{O}C were almost similar. The structure of MWCNTs and MWCNTs-DJKA including length, diameter and surface area were provided in **Table 1**. In this study, the surface area of MWCNTs was found 375 m^2 g^{-1}, which was similar to previous literature for MWCNT. The low specific surface area in CNTs depended on the large diameters and many walls**.** The surface area of MWCNTs-DJKA (345 m^2 g^{-1}) is little lower than simple MWCNT (375 m^2 g^{-1}) because of MWCNTs functionalized with DJKA.

2.5. Procedure of aluminum extraction

By procedure, the aluminum ions were extracted from drinking water and human serum samples by MWCNTs-DJKA. In this work, the mixture of 25 mg of MWCNTs-DJKA adsorbent and [OMIM][PF6] were added to 10 mL of samples and dispersed with ultrasonic bath for 10 min at pH=5. The aluminum ions were extracted based on MWCNTs-DJKA sorbent by ultrasound-assisted dispersive micro solid phase extraction (USA-D-µ-SPE). After centrifuging at 4000 rpm, the Al (III) ions were separated from liquid phase by hydrophobic ionic liquid phase in bottom of centrifuge PVC tube. Finally, the Al (III) were back-extracted from sorbent/IL with 0.5 mL of HNO3 (0.1 M) and measured by ET-AAS after dilution up to 1 mL with DW **(Fig.1)**.

3. Results and Discussions

3.1. Synthesis of MWCNT

High-purity MWCNTs were synthesized by use of camphor, an environment-friendly hydrocarbon as a carbon source using chemical vapor deposition

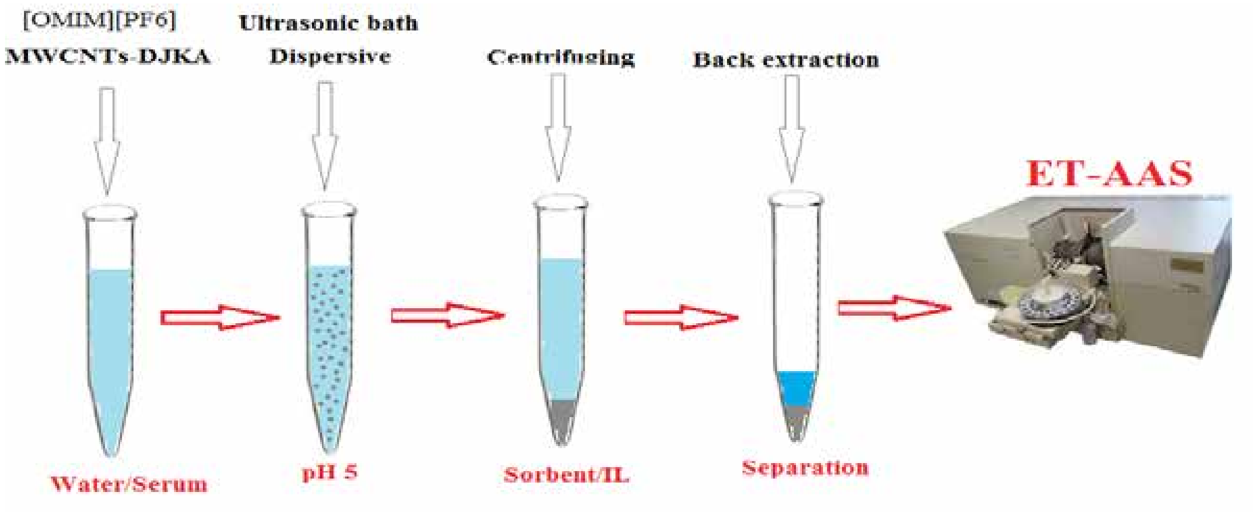

Fig. 1. Procedure of aluminum extraction based on MWCNTs-DJKA by USA-D-μ-SPE

(CVD) method on Co-Mo/MgO Nano-catalysts. The Nano-catalyst synthesized by sol-gel method. MWCNTs growth at temperatures of about 900-1000 °C in 45-60 minutes was conducted. Concentration of active metals was 5-10%. The Nano-catalyst (Co-Mo/MgO) was prepared by our special sol-gel method (Sayes et al., 2006, Rashidi et al., 2007). The composition of Co: Mo: Mgo for MWCNTs was 2.5:2.5:95 molar ratio. In chemical vapor deposition method, generally a precursor gas as a carbon source enters the furnace. In this study, the used experimental setup for CNTs production consisted of a quartz tube reactor with a length of 150 and 7 cm in diameter. It was heated in a resistive furnace in the temperature range from 900 to 1000 °C and at ambient pressure. The camphor was used as the carbon precursor and placed in the early part of the reactor and copper Nano-catalyst was placed in the middle of the reactor. The reactor was then put in a three thermal zone furnace, the first part for the evaporation of camphor, Part II for the reaction zone and Part III for cooling of the exhaust vapors. Before using MWCNT as adsorbent, purification process and meshing were performed.

3.2. Synthesis of Djenkolic on MWCNTs

The immobilization of 3,3′-(Methylenedithio) dialanine (djenkolic acid, DJKA) on multi-wall carbon nanotubes was obtained. The pure MWCNTs (0.5 g) were mixed with H_2SO_4 and HNO_3 solutions and chaked with 300 rms for 2 h. The MWCNTs were oxidized based on carboxyl groups (MWCNTs-COOH). Then, the MWCNTs-COOH were washed with DW many times before it filtered with Watman filter (0.2 nm) based on vacuum accessory. Them, the carboxyl groups on MWCNTs (COOH) convert to hydroxil group (OH) by reducing agent and washed and dried before using. The 0.5 g of MWCNTs-OH were dispersed in 10 mL of toluene and 1 mL of 3-(trimethoxysilyl)propyl chloride added drop by drop very quickly. The chloro silica on MWCNTs prepared by refluxing, washing and driing at 70 °C. Finally, the cholor functionized on MWCNTs was used by djenkolic acid in ethanolic solution which was shaked with 20 micro liter of N,N-diethylethanamine for 20 min before refluxed at 70 °C for 2 h. Finally the product of MWCNTs-DJKA was synteszed. The sulfur groups of this molecule act as chelation sites to which divalent metal ions coordinate. In addition to these groups, the formation of a stable ring with metal ions is a factor of increasing efficiency on the trapping process in the variable conditions (**Fig. 2**).

3.3. FTIR Analysis

The appearance of a broad peak in the range 2500–3600 cm^{-1} in the FTIR spectra of these compounds is due to the characteristic O–H and NH stretching vibration of enolic, carboxylic, and

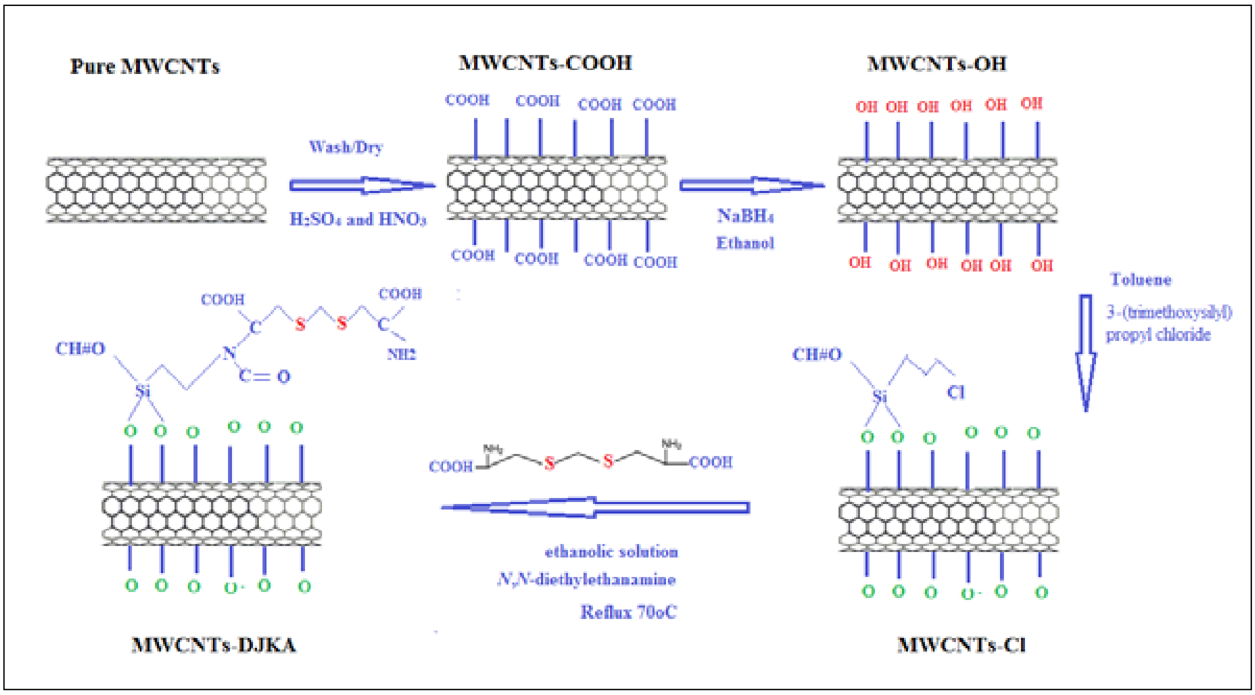

Fig. 2. Synthesis of Djenkolic on MWCNTs

Amine functionalities. As **Figure 3**, The absorption bands at 3420, 1718, 1623, and 1060 cm^{-1} shown in the spectra of MWCNT and MWCNTs-DJKA are ascribed to the stretching bands ν(O–H), ν(C=O), ν(C=C), and ν(C–O) respectively. Moreover, the peak at 1410 cm^{-1} may be attributed to tertiary OH groups [53,54]. Also, the characteristic bands observed at around 1062 and 1169–1218 cm^{-1} in the spectra of the MWCNTs-DJKA and GO correspond to the vibration bands of ν(S=O) derived from SO3H groups. The presence of SO3 group is also confirmed by the presence of the peak at 1221 cm^{-1}.

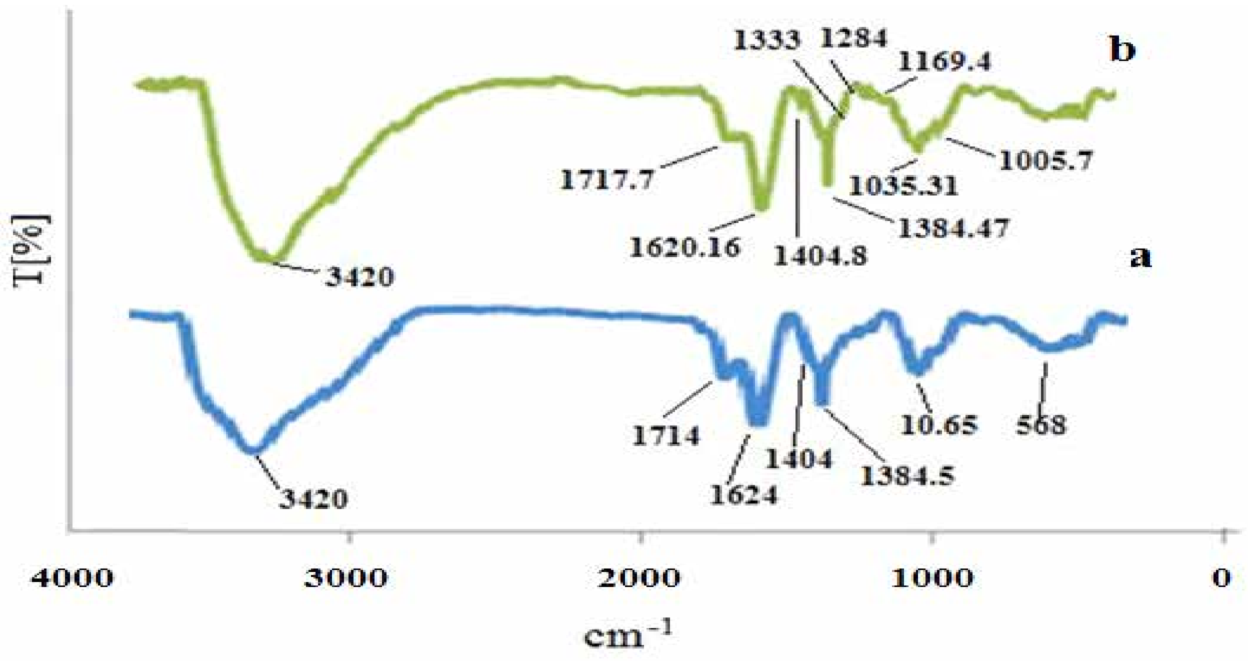

Fig. 3. FTIR spectra of a) MWCNT and b) MWCNTs-DJKA

3.4. SEM and XRD Analysis

After synthesis, the SEM images of MWCNTs and MWCNTs-DJKA were obtained which was shown in **Figure 4a and 4b**. Nitrogen adsorption The X-ray diffraction (XRD) spectrum of MWCNTs and MWCNTs-DJKA was shown in **Figure 5**. The XRD of MWCNTs-DJKA is similar to MWCNTs and the crystallinity /morphology of MWCNTs were preserved during synthesis of MWCNTs-DJKA. The MWCNTs-DJKA showed typical peak of (002), (110), and (400) at 2θ = 26.5, 42.4, and 52.7°, respectively.

3.5. Optimization of pH

The main factor for extraction aluminum from serum and water samples is pH. So, the effect of different pH from 2 to 10 was investigated by USA-D-μ-SPE procedure. The results showed that the MWCNTs-DJKA could be simply extracted alminum in a pH of 4-6. Therefore, the efficient extraction for Al(III) were achieved more than 97% at optimized pH and the recoveries were decreased at pH more than 6 and less than 4. So, pH=5 was used for further works in this study **(Fig. 6)**. The results showed that, aluminum can

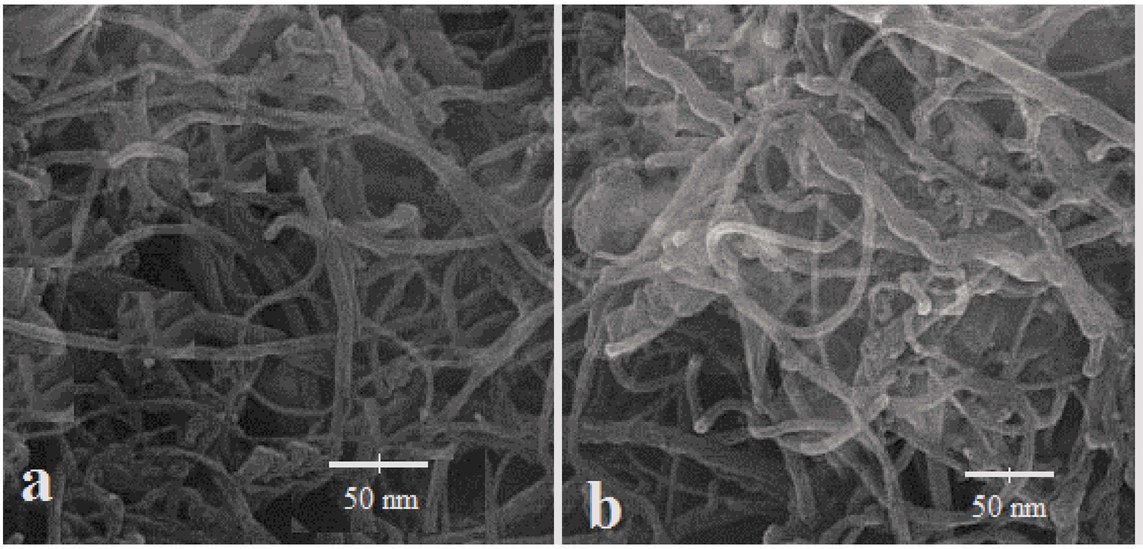

Fig. 4. SEM of images of a) MWCNTs and b) MWCNTs-DJKA

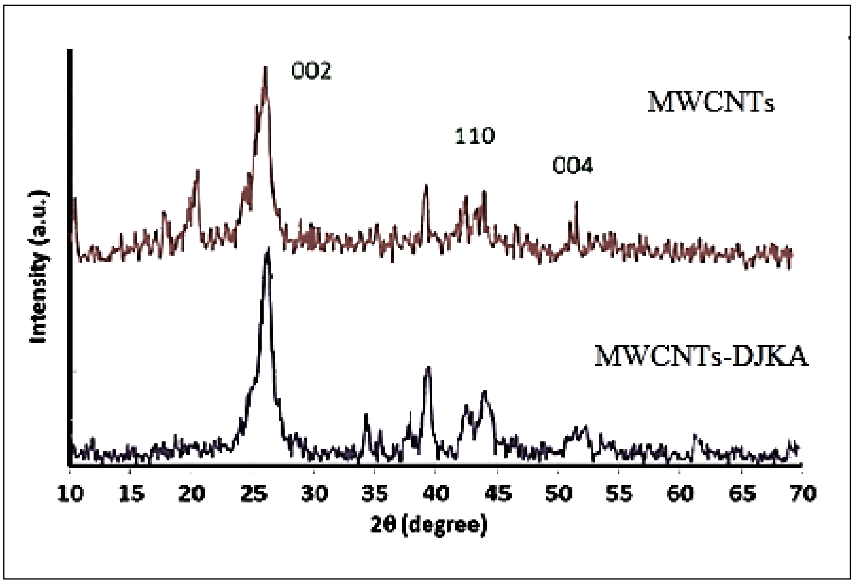

Fig. 5. The X-ray diffraction (XRD) of MWCNTs and MWCNTs-DJKA

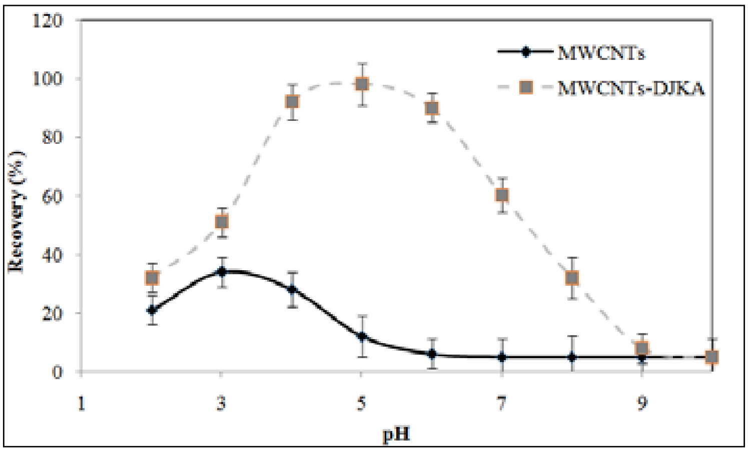

Fig. 6. The effect of pH on aluminum extraction by MWCNTs and MWCNTs-DJKA

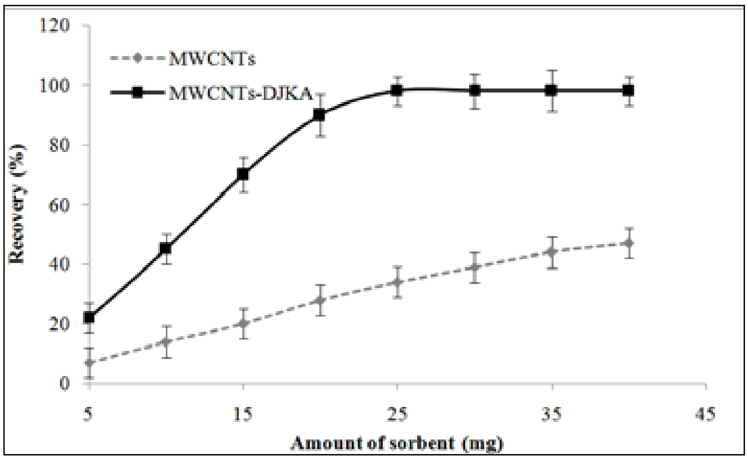

Fig. 7. The effect of amount of MWCNTs and MWCNTs-DJKA for aluminum extraction in serum and water samples

be physically extracted by MWCNTs at pH=3 up to 34%. The mechanism of extraction was carried out based on the coordination of covalent bond between positively charged of Al^{3+} and sulfur of DJKA which is highly dependent on pH.

3.6. The effect of Ionic liquids and sonication time

The different hydrophobic ionic liquids such as [OMIM][PF6], [HMIM][PF_6] and [BMIM][PF_6] were used for separation of MWCNTs and MWCNTs-DJKA from samples. The amounts of ILs on the separation of MWCNTs and MWCNTs-DJKA sorbents were tested between 0.01-0.2 g in Al concentration from 0.3 μg L^{-1} as LLOQ and 12.8 μg L^{-1} as ULOQ. The results showed the the best recovery was obtained by 0.1 g of [OMIM][PF_6]. Therefore, 0.12 g of [OMIM][PF_6] was used as optimum IL for separation of aluminum in water and serum samples.

3.7. Optimazation of amount of MWCNTs-DJKA sorbent

For optimization of extraction, the amount of MWCNTs and MWCNTs-DJKA was studied at pH=5. For this purpose, the amounts of MWCNTs and MWCNTs-DJKA between 1—40 mg were evaluated for Al(III) extraction by the USA-D-μ-SPE procedure. By results, the high recoveries in water and serum samples were achieved from 22 mg of MWCNTs-DJKA by proposed procedure. So, 25 mg of MWCNTs-DJKA was selected as optimum amount of sorbent (Fig. 7). The higher amount of MWCNTs-DJKA had no effect on the extraction recovery for Al(III) in water samples.

3.8. The effect of elution and sample volume

The volume/ concentration of elution for back extraction Al ions from MWCNTs-DJKA were studied at pH of 5. So, the different solutions such as HCl, HNO_3, H_2SO_4 and NaOH with different volume (0.2-1.0 mL) and concentration (0.1-0.5 M) was used for back extraction Al(III) from sorbents by USA-D-μ-SPE procedure. The results showed that 0.2 mol L^{-1} HNO_3(0.5 mL) was quantitatively back-extracted aluminum from MWCNTs-DJKA.The sample volume based on MWCNTs-DJKA was evaluated for aluminum extraction between 1-20 mL serum and water samples in ranges (0.3-12.8 μg L^{-1}). The results showed us the efficient extraction were obtained for 10 mL of samples. By

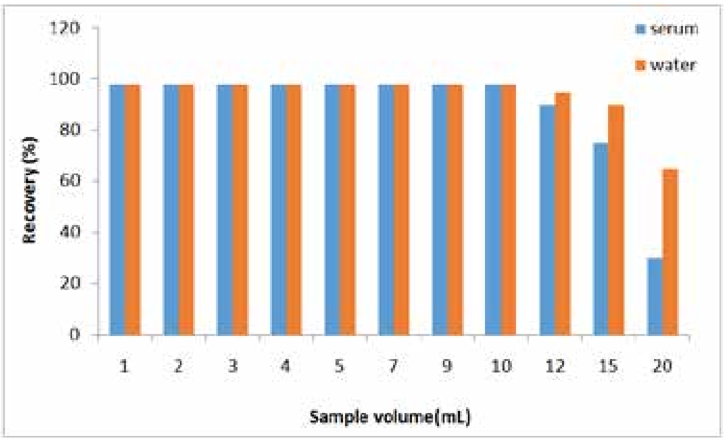

Fig. 8. The effect of sample volume on aluminum extraction by USA-D-μ-SPE procedure

increasing sample volume, the extraction recovery was decreased **(Fig. 8)**.

3.9. The effect of interfernce ions in extraction

The effect of interference of coexisting ions for aluminum extraction in water and serum samples was investigated by USA-D-μ-SPE procedure. So, the different concentrations of the interfering cations and anions added to 10 mL of aluminum standard solution based on MWCNTs-DJKA at in ranges of 0.3-12.8 μg L^{-1} at pH=5. The results showed us that the most of the concomitant ions have no effect on the extraction recovery of Al (III) ions by USA-D-μ-SPE procedure **(Table 2)**.

Table 2. The effect of interferences ions on extraction of Al(III) based on MWCNTs-DJKA in water/serum samples by USA-D-μ-SPE procedure

Interfering Ions (I)	Mean ratio ($C_I/C_{Al(III)}$)	Recovery (%)
	Pb(II)	Pb(II)
Ni^{2+}, Co^{2+}, Cd^{2+}	600	97.4
Zn^{2+}, Cu^{2+}	900	98.2
Mo^{2+}, V^{3+}, Cr^{3+}	700	96.7
Hg^{2+}, Ag^{+}	100, 200	98.3
Br^{-}, F^{-}, Cl^{-}, I^{-}	900	99.2
Na^{+}, K^{+}	1000	99.4
CO_3^{2-}, PO_4^{3-}, NO_3^{-}	1100	98.0
Ca^{2+}, Mg^{2+}	550	97.1
Pb^{2+}, Se^{2+}	750	96.9
S^{2-}, SO_3^{2-}	850	98.6

3.10. Validation of methodology

The ultra-trace aluminum in human serum and water samples were evaluated by the USA-D-μ-SPE procedure. As results in **Table 3**, the Al (III) ions in human serum and water samples was efficiently extracted based on MWCNTs-DJKA with high recovery. The results showed us that the proposed procedure was well validated by spiking of standard solution between 0.3 μg L^{-1} to 12.8 μg L^{-1} with the high accuracy. The obtained recoveries of spiked samples demonstrated that MWCNTs-DJKA adsorbent can be used as applied and simple procedure for aluminum separation in different samples in short time. Moreover, the validating of methodology was obtained based on the standard reference materials (SRM) and ICP-MS analysis for aluminum determination in water and serum samples by USA-D-μ-SPE

Table 3. Method validation for aluminum extraction/determination in water and serum samples by spiking samples

Sample	**Added (μg L^{-1})**	***Found (μg L^{-1})**	**Recovery (%)**
Water 1	---	0.524 ± 0.023	---
	0.5	1.012 ± 0.053	97.6
Water 2	---	5.536 ± 0.247	---
	5.0	10.602 ± 0.503	101.3
Water 3	---	6.464 ± 0.288	---
	6.0	12.231 ± 0.573	96.1
Serum 1	---	0.398 ± 0.021	---
	0.5	0.901 ± 0.043	100.6
Serum 2	---	3.241 ± 0.152	---
	3.0	6.132 ± 0.332	96.4
Serum 3	---	7.207 ± 0.346	---
	5.0	12.155 ± 0.574	98.9

*Mean of three determinations of samples ± confidence interval (P = 0.95, n =10)

Table 4. Validation of methodology for aluminum extraction in water and serum samples by the standard reference materials (SRM) and ICP-MS

Sample	Added(µg L^{-1})	*Found(µg L^{-1})	Recovery (%)
SRM 1643	--------	7.52 ± 0. 34	97.7
	5.0	12.36 ± 0. 58	96.8
SRM 1643d	--------	2.61± 0. 12	102.7
	2.0	4.54± 0. 19	96.5
[a] Serum SRM	--------	4.96 ± 0.22	95.4
	5.0	9.88 ± 0.48	98.4

*Mean of three determinations of samples ± confidence interval (P = 0.95, n =10)

SRM 1643, aluminum in water, 77± 1 µg g^{-1}, 1 g of sample diluted in 100 mL of DW with HNO_3 (2%) after dilution 10 mL of stock solution was used as 7.7± 0. 1 µg L^{-1}

SRM 1643d, aluminum in water: 127.6 ± 3.5 µg L^{-1}, after dilution with DW (1:50) was used as 2.54± 0. 08 µg L^{-1}

[a]ICP-MS: Serum aluminum concentration was obtained 5.2 ± 0.11 µg L^{-1}

procedure (**Table 4**). Analytical results in serum and water samples were confirmed by SRM and ICP-MS.

4. Conclusions

In this study, a novel MWCNTs-DJKA adsorbent was used for aluminum extraction/separation and preconcentration from water and human serum samples in pH=5 by USA-D-µ-SPE procedure. The ionic liquid of [OMIM][PF6] was dispersed in samples for separating of MWCNTs-DJKA from liquid phase. The adsorption capacity of the MWCNTs-DJKA and MWCNTs sorbent was achieved 122.6 mg g^{-1} and 33.7 mg g^{-1} for 20 min, respectively. The mean aluminum in drinking water and serum samples was obtained 48.56 ± 2.92 and 11.64 ± 0.73 µg L^{-1} which was lower than reference value in drinking water and human biological samples. The methodology was validated with SRM and ICP-MS analyzer.

5. Acknowledgment

The authors are thank to the Iranian Petroleum Industry Health Research Institute and IAUPS for preparation human serum samples based on the world medical association declaration of Helsinki (R.IAU.SN.1396.944000978)

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