



Separation and determination of cadmium in water samples based on functionalized carbon nanotube by syringe filter membrane-micro solid-phase extraction

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ABSTRACT

A simple and fast separation of cadmium (Cd) based on functionalized carbon nanotubes with 2,3-dimercapto-1-propanol (CNTs@DHSP) was achieved in water samples before a determination by atom trap flame atomic absorption spectrometry (AT-FAAS). In this study, Cd(II) ions were extracted by syringe filter membrane-micro solid phase extraction procedure (SFM- μ -SPE). Firstly, 20 mg of the CNTs@DHSP as solid-phase added to 20 mL of water sample in a syringe, then dispersed for 3 min after adjusting pH up to 7 and pass through SFM very slowly. After extraction, the Cd(II) ions were back-extracted from SFM/CNTs@DHSP by 1.0 mL of eluent in acidic pH. Finally, the cadmium concentration was measured by AT-FAAS. Under the optimal conditions, the linear range (2–90 $\mu\text{g L}^{-1}$), LOD (0.75 $\mu\text{g L}^{-1}$) and enrichment factor (19.6) were obtained (RSD < 1.5%). The adsorption capacity of Cd(II) with the CNTs@DHSP was obtained about 152.6 mg g⁻¹. The method was validated by certified reference materials (SRM, NIST) and ET-AAS in water samples.

1. Introduction

Cadmium (Cd) as a toxic non-essential metal release from industrial activity to water, soil, food, agricultural product and air, then, cadmium ions cause to environmental and human health hazards. Cadmium is naturally creating in the environment matrixes from agricultural and chemical industrial sources. The sources of cadmium have various applications in different industry such as PVC products in petrochemical industries, pigments in color factories, and Ni-Cd batteries [1,2]. The cadmium enters to the human body through

gastrointestinal and respiratory tract system from food, water, air pollution and smoking. The cadmium exposure causes to hepatic dysfunction, the pulmonary edema, the testicular damage, the osteoporosis and cancer in different organs such as, breast, renal, lung and pancreas [3,4]. The Cd ions absorb through the respiratory tract or the gastrointestinal tract and enters into the bloodstream via erythrocytes and accumulated in the kidneys liver [5]. Cadmium ions excrete from the human body through urine. The liver and kidneys are able to synthesize metallothioneins (MT) which protect the cells from cadmium toxicity through bonding to cadmium (Cd-MT) [6]. Mitochondria play a crucial role in the formation of ROS (reactive oxygen species) for cadmium [7]. Moreover, the different methodologies

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such as microbial fermentation based on TiO_2 nanoparticles have been used to remove cadmium from waters efficiently [8,9]. The cytotoxic effects of cadmium cause to apoptotic effect in human which was reported by international Agency for research on cancer (IARC) [10]. *Itai itai* disease or osteomalacia is chronic cadmium poisoning was reported in Japan. The cadmium intake to the human body is about $7 \mu\text{g Cd}$ per week. This value cause to create the cadmium concentration in renal and urine between $100\text{-}200 \mu\text{g g}^{-1}$ and less than $0.5 \mu\text{g g}^{-1}$ creatinine, respectively. Blood and urinary cadmium at $0.38 \mu\text{g L}^{-1}$ and $0.67 \mu\text{g g}^{-1}$ creatinine were associated with tubular impairment. Urinary cadmium at $0.8 \mu\text{g g}^{-1}$ creatinine was associated with glomerular impairment [11]. So, the extraction and determination of Cd(II) in waters is very important, due to the environment and human health safety. Recently, various analytical techniques can be used for cadmium extraction in different water, foods and environmental samples. The various methods such as flame atomic absorption spectrometry (AAS) [12], the optical microscopy based on laser-induced photoluminescence (UV-VIS-NIR) [13], the $\text{SrFe}_{12}\text{O}_{19}$ @CTAB magnetic nanoparticles with electrothermal atomic absorption spectrometry (ET-AAS) [14-17], the colorimetric sensor [18], the electrothermal vaporization coupled with optical emission spectrometry with inductively coupled plasma (ETV-ICP-OES) [19] and laser-induced breakdown spectroscopy (LIBS) [20] were used for cadmium determination in various environmental samples. Due to the low concentration of cadmium in water samples and difficulty matrixes in wastewater samples, the pretreatment is required before the determination of cadmium by instrumental analysis. The different extraction methods such as, the ultrasound-assisted liquid-liquid spray extraction (USA-LLSE) [21], the solvent extraction [22], the liquid-liquid extraction [23], the cloud point assisted dispersive ionic liquid-liquid microextraction [24] the dispersive solid-phase extraction (DSPE) combined with ultrasound-assisted emulsification microextraction [25], solid-phase extraction (SPE) [26, 27], the coagulating homogenous dispersive micro solid-phase extraction exploiting

graphene oxide nanosheets (CHD- μSPE) [28] and graphene oxide-packed micro-column solid-phase extraction [29] were used before cadmium analysis in water samples. Recently, the membrane micro solid-phase extraction procedure (M- μSPE) was reported as micro SPE (μSPE) for separation/determination of cadmium in water samples. This method showed several advantages, such as easy and fast extraction of cadmium in water samples. The properties of adsorbents have a main role for cadmium extraction by the syringe filter membrane micro solid-phase extraction procedure (SFM- μSPE). In this study, a novel sorbent based on CNTs@DHSP was used for extraction of Cd(II) in water and wastewater samples by SFM- μSPE at pH of 7. The proposed method was validated with CRM and spike samples in waters and high recovery was obtained by AT-FAAS.

2. Experimental

2.1. Material and Methods

Atom trap flame atomic absorption spectrophotometer (GBC 932, AT-FAAS, Aus) was used for cadmium determination in water and wastewater samples. The atom trap accessory /air-acetylene controlled by *AVANTA* software which was placed on the air-acetylene burner. The cadmium determines in water and wastewater samples with 1.0 mL of the sample with LOD of 0.025 mg L^{-1} , the wavelength of 283.3 nm and 5 mA. The lower limit of quantitation (LLOQ), ULOQ and linear range for AT-FAAS was obtained $100 \mu\text{g L}^{-1}$, $1800 \mu\text{g L}^{-1}$ and $100\text{-}1800 \mu\text{g L}^{-1}$, respectively. All water samples were injected by an auto-sampler to the injector of AT-FAAS for 1-1.5 min. The electrothermal atomic absorption spectrophotometer (ET-AAS) was used for the validation of water samples in ultra-trace analysis of Cd(II). The Metrohm pH meter was used for measuring pH in water samples (E-744, Switzerland). The shaking of water samples was used based on 250 rpm speeds by vortex mixer (Thermo, USA). The standard solution of cadmium (Cd^{2+}) was purchased from Sigma Aldrich. (Germany) with a concentration of 1000 mg L^{-1} in 1 % HNO_3 . The various concentration of cadmium was daily prepared by dilution of the standard Cd

solution with DW. Ultrapure water was purchased from Millipore Company (USA) for the dilution of water samples. 2,3-Dimercapto-1-propanol (CASN:59-52-9, HOCH₂CH(SH)CH₂SH) was prepared from Sigma Aldrich, Germany. The pH was adjusted pH by 0.2 mol L⁻¹ of sodium phosphate buffer solution (Merck, Germany) for a pH of 7.0 (Na₂HPO₄/NaH₂PO₄). The analytical grade of reagents such as HNO₃, HCl, acetone, and ethanol were prepared from Merck, Germany. The syringe Whatman filter membrane (SFM) with glass microfiber pre-filter (100 nm, Anotop filters, SN: WHA68091112, D:10 mm, polypropylene housing polypropylene membrane) was purchased from Sigma Aldrich, Germany. Anotop syringe filters contain the proprietary alumina and use for difficult separation samples.

2.2. Human sample preparation

The glass analysis was washed with a HNO₃ solution (1 M) for at least 12 h and rinsed 10 times with DW. The cadmium concentrations in water and wastewater have a low concentrations less than 50 µg L⁻¹ and low contamination for sampling and determination caused to low accuracy of results. By procedure, 20 mL of the water samples were prepared from well water, drinking water and wastewater factories from Iran. Clean syringes were prepared for sample treatment. The water is prepared and stored by standard method for sampling from water by adding nitric acid to waters.

2.3. Synthesis of CNTs@DHSP adsorbent

First, the CNTs@COOH was prepared according to the acid oxidation method reported in the literature [30]. In the final step, 1 g of CNTs@COOH was added in 50 mL of methanol and maintained under ultrasonic conditions for 15 min. Sodium borohydride was also simultaneously added to the solution. Then, the mixture was stirred at room temperature for 3 h. Then, the product was washed with methanol three times and dried under vacuum. Typically, CNTs@OH (0.5 g) and dry xylene (40 mL) were sonicated for 15 minutes in a 100 mL round-bottomed flask. 3 mL of (3-chloropropyl) trimethoxysilane (CPTMS) was added to the above

mixture, drop by drop, at room temperature. After sonicating for 15 min, the resulting mixture was refluxed at 60 °C under N₂ atmosphere to remove the produced HCl. In order to obtain the CNTs@Cl, it was dried at 100 °C under vacuum. Then, 1 g of CNTs@Cl and 1 mL of DMP were mixed in 60 mL ethanol using an ultrasonic bath for 30 min. Then, a few drops of triethylamine were added to the above slurry, and the mixture was refluxed at 60 °C for three extra hours. The product was separated from the reaction mixture by a PTFE membrane filter and washed with ethanol three times and finally dried under vacuum at 100 °C.

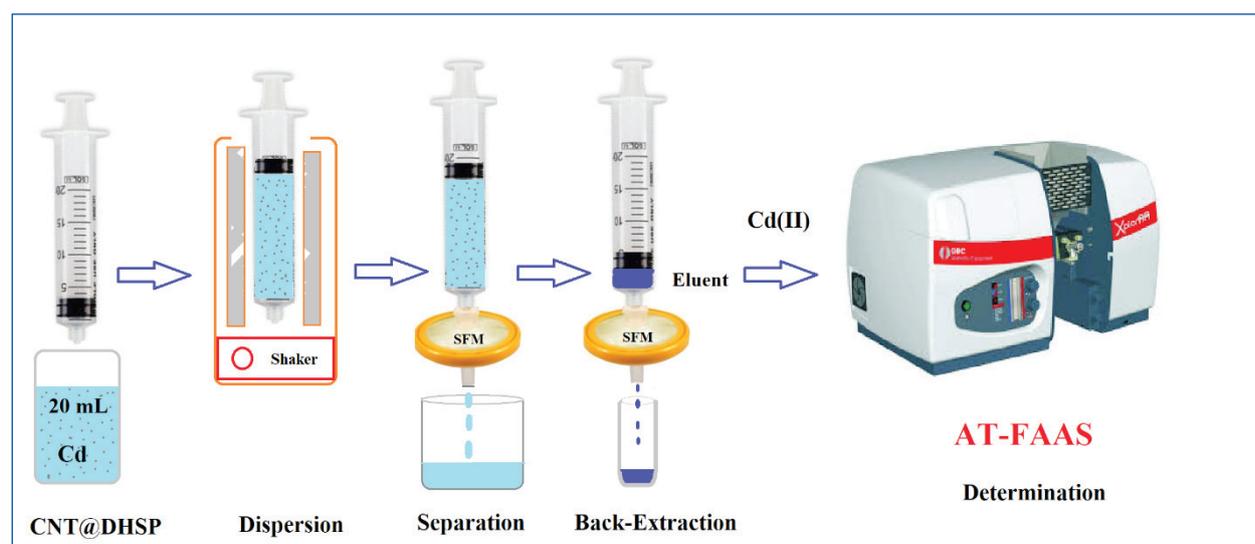
2.4. Extraction Procedure

By SFM-µ-SPE procedure, 20 mL of water and standard samples (3 µg L⁻¹ and 90 µg L⁻¹) were used for the separation and determination of cadmium ions at pH 7. Firstly, the CNTs@DHSP added to water or cadmium standard solution and shaken for 3 min at pH=7. Then, the water sample was slowly passed through SFM with glass microfiber pre-filter and the solid-phase was separated by filtering (100 nm, polypropylene housing polypropylene membrane). After shaking, the Cd(II) ions were extracted by sulfur group of CNTs@DHSP as coordination bond or dative bond at pH from 6-8 (Cd²⁺ →: SH @CNTs) and then the Cd (II) ions on SFM/CNTs@DHSP back-extracted by 0.5 mL of eluent (1.5 M, HNO₃) at pH 2. Finally, the cadmium concentration in remained solution was determined by AT-FAAS after dilution with DW up to 1 mL (Fig.1). The procedure was used for a blank solution without cadmium ten times. The calibration curve for Cd in standards solutions was prepared (3- 90 µg L⁻¹) and enrichment factor (EF) was calculated. The analytical parameters showed in Table 1. Validation of methodology was achieved by CRM for cadmium samples and ETAAS analysis. The recovery was obtained for cadmium by equation 1. The C_p and C_f is the primary and final concentration of Cd(II), which was determined by SFM-µ-SPE procedure coupled to AT-FAAS (n=10, Eq. 1).

$$\text{Re (\%)} = (C_p - C_f) / C_p \times 100 \quad (\text{Eq.1})$$

Table 1. The analytical features for determination cadmium by SFM- μ -SPE procedure

Features	value
Working pH	6-8
Amount of CNTs@DHSP (mg)	20.0
Sample volume of water (mL)	20.0
Volume of sample injection (mL)	1.0
Linear range for water ($\mu\text{g L}^{-1}$)	3.0-90
working range for water ($\mu\text{g L}^{-1}$)	3.0-170
Mean RSD %, n=10	1.5
LOD ($\mu\text{g L}^{-1}$)	0.75
Enrichment factor for water	19.6
Volume and concentration of HNO_3	1 mL, 1.5 M
Shaking time	3.0 min
Correlation coefficient	$R^2 = 0.9998$

**Fig. 1.** Cadmium extraction in water sample based on CNTs@DHSP by SFM- μ -SPE procedure

3. Results and discussion

3.1. Extraction Mechanism

The carboxylic acid-functionalized CNTs were synthesized by using the acid oxidation method. Then, for the generation of OH groups on surface CNT, these materials were treated with sodium borohydride in methanol. Afterward, hydroxyl-

functionalized CNTs were functionalized by (3-chloropropyl) trimethoxysilane (CPTMS) to provide chloroalkylsilane. Finally, thiol derivative as a DHSP was covalently immobilized on CNTs. Finally, SH group of DHSP on the surface of CNTs can be complexed with cadmium ions in a water solution (Fig.2).

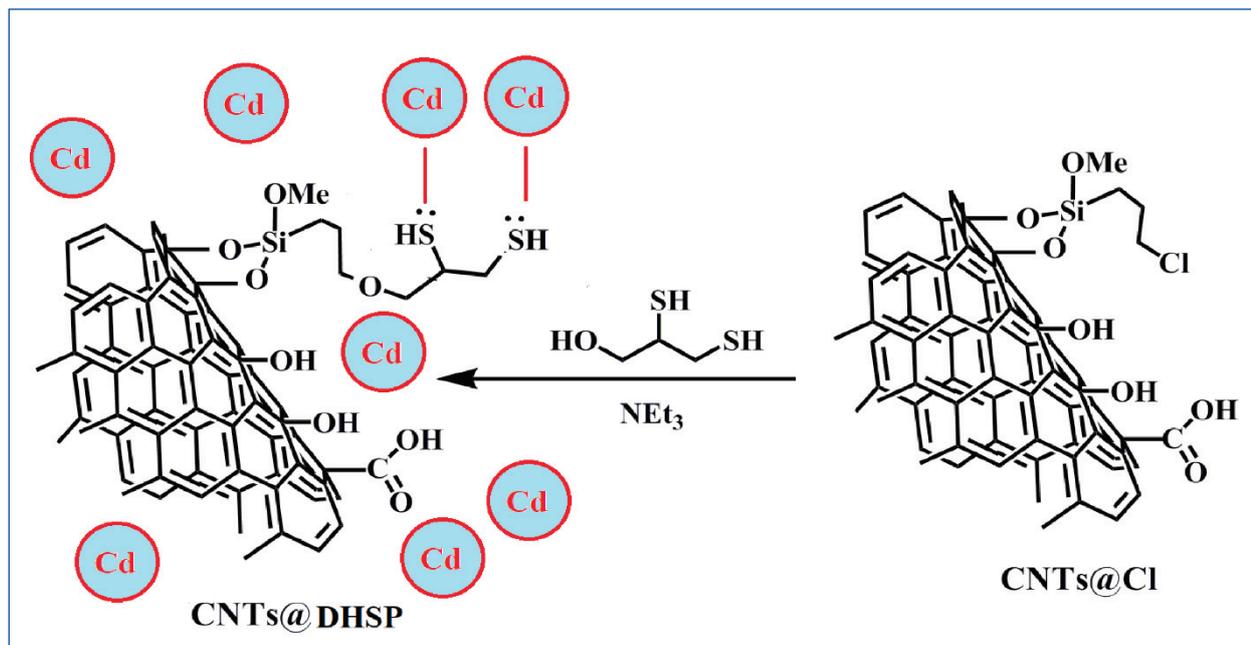


Fig. 2. The extraction mechanism of cadmium by CNTs@DHSP

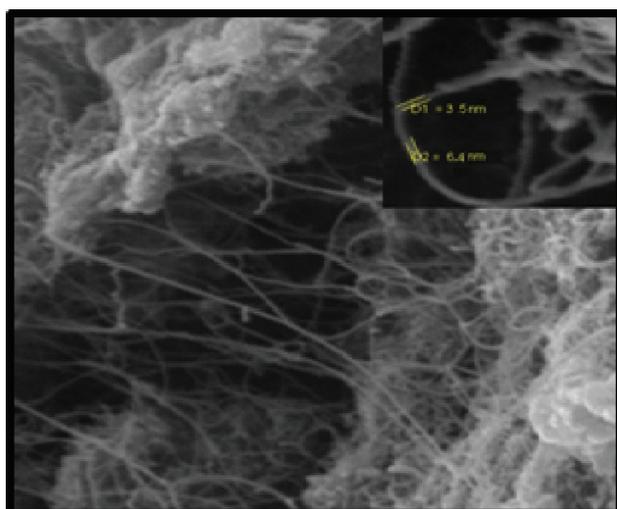


Fig.3a. SEM image of CNTs@DHSP

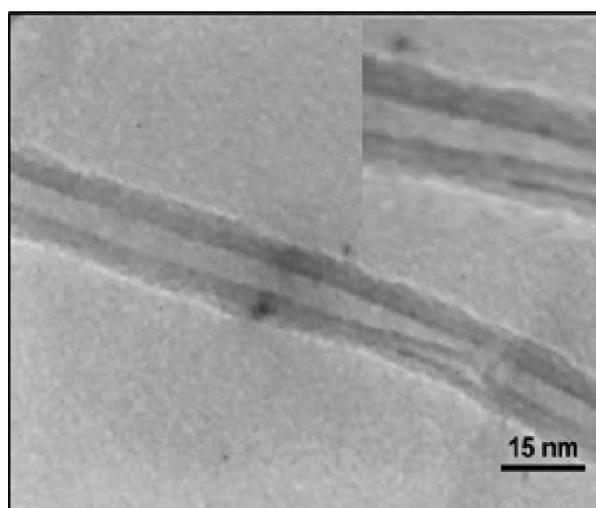


Fig.3b. TEM image of CNTs@DHSP

3.2. SEM and TEM analysis

The nanotubes of CNTs syntheses in University of Tabriz (Iran) and used for the synthesis of 2,3-dimercapto-1-propanol immobilized on CNTs (CNTs@DHSP). The Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) of CNTs@DHSP showed low nanoparticles size between 40-100 nm which was shown in Figures 3a and 3b.

3.3. Optimization of cadmium extraction SFM- μ -SPE procedure

The SFM- μ -SPE procedure based on novel CNTs@DHSP was optimized for cadmium extraction in water samples. So, different parameters such as pH, CNTs@DHSP Mass, eluent, sample volume and sonication time were studied.

3.3.1. The effect of pH

The effect of various pH was studied from 2 to 10 for Cd(II) extraction in water samples. The results showed the CNTs@DHSP can be removed cadmium ions from water samples at pH between 6 to 8. Moreover, the efficient extraction was achieved for cadmium ions at pH=7 (> 95%) and the recoveries reduced at $6 < \text{pH}$ and $\text{pH} > 8.5$. So, the pH of 7.0 was used as optimum pH for cadmium extraction in waters for further works (Fig. 4). The mechanism of cadmium extraction depended on the coordination bond or dative covalent bond of the thiol group in CNTs@DHSP adsorbent ($\text{Cd} \rightarrow \text{:SH}$). The positively charge of Cd^{2+} adsorbed on the surface of adsorbent with negative charge at optimized pH. At low pH ($\text{pH} < \text{pH}_{\text{pzc}}$), the surface of CNTs@DHSP has a positive charge. Therefore, low recovery is related to the electrostatic repulsion between Cd^{2+} and positive charge of CNTs@DHSP. In addition, at a pH of 7, the surface of CNTs@DHSP have negatively charged and absorbed Cd^{2+} . Also, in the $\text{pH} > 8.5$, the Cd ions participated as OH group and the recovery was decreased.

3.3.2. Effect of CNTs@DHSP mass

The efficient extraction was obtained by optimizing of CNTs@DHSP mass in $\text{pH}=7$. Therefore, the various of CNTs@DHSP mass was studied between 5-50 mg for Cd(II) extraction by SFM- μ -SPE procedure. The results showed us, a high recovery of more than 95% was achieved for 18 mg of CNTs@DHSP in water samples. So, 20 mg of CNTs@DHSP as optimum adsorbent mass was used for the experimental run. (Fig. 5). Based on Figure 6, The higher amount of CNTs@DHSP had no effect on cadmium recovery.

3.3.3. Effect of eluent and sample volume on cadmium extraction

The volume and concentration of eluent for back extraction cadmium ions from SFM/CNTs@DHSP adsorbent were optimized at $\text{pH}=7$. Acidic pH dissociated thiol binding to cadmium and caused to release of free cadmium ions into the eluent phase. The different acid solution such as HCl, HNO_3 , NaOH and H_2SO_4 , was selected for back-extraction of cadmium from SFM/CNTs@

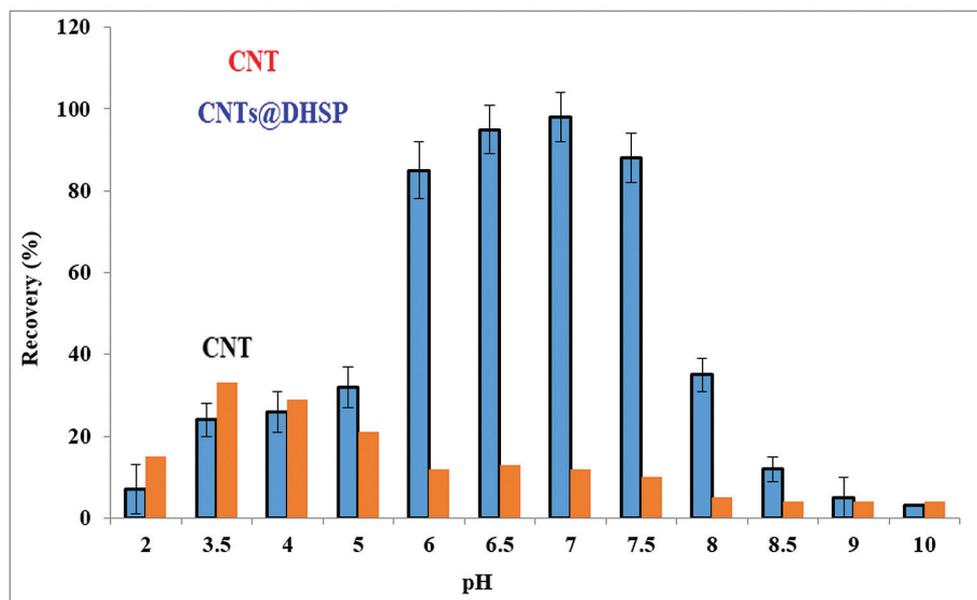


Fig. 4. The effect of pH on cadmium extraction based on CNTs@DHSP by SFM- μ -SPE procedure

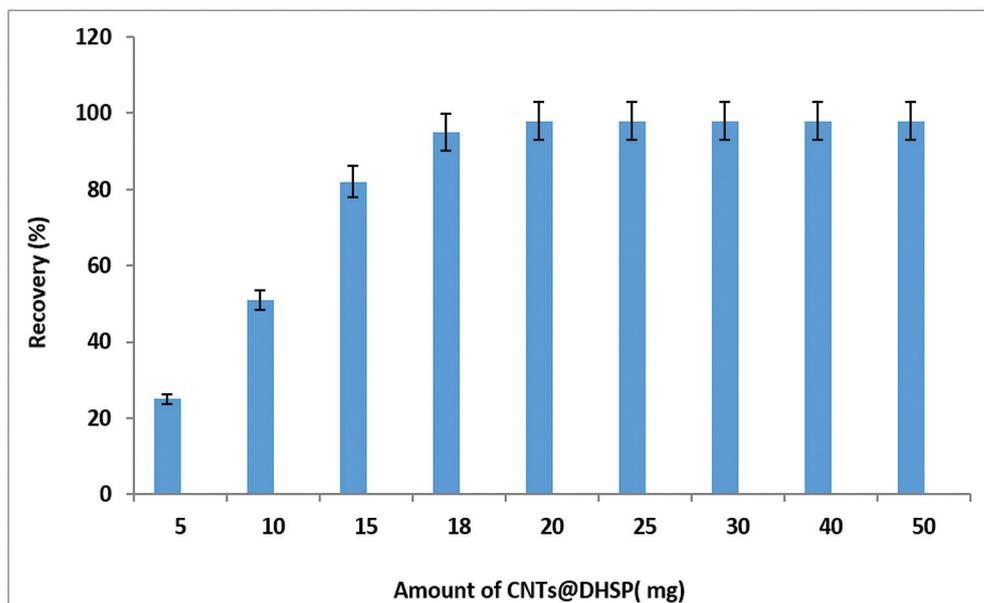


Fig. 5. The effect of CNTs@DHSP amount on cadmium extraction by SFM- μ -SPE procedure

DHSP adsorbent. The results showed that 1.5 mol L⁻¹ HNO₃ was quantitatively back-extracted the cadmium from SFM/CNTs@DHSP adsorbent. The sample volume between 1-100 mL for cadmium extraction was studied in water samples by SFM- μ -SPE procedure. For optimization, the cadmium concentration ranges (3-90 μ g L⁻¹) based on 20 mg of CNTs@DHSP adsorbent were examined by the proposed procedure. The results showed us the high recoveries were achieved 25 mL of water samples at pH=7. Therefore, 20 mL of water was used as the optimal value for further study.

3.3.4. Effect of sonication time and adsorption capacity

The extraction time depended on the dispersion of nanoparticles CNTs@DHSP adsorbent in the water samples and caused to increase interaction between HS with Cd(II) at pH=7. The effect of sonication time was studied from 0.5 to 5 min. It was observed that the sonication of 3.0 min had favorite extraction for cadmium in water samples.

The absorption capacities of cadmium for CNTs@DHSP and CNTs adsorbents were evaluated in optimized conditions. First, 20 mg of CNTs@DHSP or CNTs adsorbents added to 20 mL of water sample (standards cadmium solution: 200 mg L⁻¹) at pH 7. After sonication for 20 min, the cadmium extracted on the CNTs@DHSP or CNTs adsorbents at optimizing pH. The cadmium concentration in the liquid phase is directly determined as the final cadmium concentration after adsorption processes. The results showed the adsorption capacity for the CNTs@DHSP or CNTs adsorbents was obtained 152.6 mg g⁻¹ and 19.7 mg g⁻¹, respectively.

3.3.5. Interference of coexisting ions

The effect of interference ions on cadmium extraction based on CNTs@DHSP adsorbent in water samples was studied by SFM- μ -SPE procedure. The various interfering ions were added to 20 mL of cadmium solution (ULOQ: 90 μ g L⁻¹) at pH 7. Based on results the most of the probable concomitant ions have no effect on the extraction recovery of Cd(II) ions in optimized conditions (Table 2).

Table 2. The effect of interferences ions on cadmium extraction in water samples by SFM- μ -SPE procedure

Interfering Ions (I)	Mean ratio ($C_1/C_{Cd(II)}$)	Recovery (%)
	Cd(II)	Cd(II)
Al ³⁺ , V ³⁺	600	96.8
Zn ²⁺ , Cu ²⁺	900	08.0
I ⁻ , Br ⁻ , F ⁻ , Cl ⁻	1200	99.2
Na ⁺ , K ⁺	1000	98.4
Ca ²⁺ , Mg ²⁺	900	97.7
CO ₃ ²⁻ , PO ₄ ³⁻	1000	97.2
Co ²⁺ , Mn ²⁺ , Sn ²⁺	350	98.3
Ni ²⁺	150	96.7
NH ₄ ⁺ , NO ₃ ⁻	800	98.5
Hg ²⁺	100	97.4

3.3.6. Real samples analysis

The separation and determination of cadmium in water samples was done based on CNTs@DHSP adsorbent by the SFM- μ -SPE procedure. The results showed us, the cadmium was efficiently extracted by the thiol group of CNTs@DHSP adsorbent in water samples at pH=7. By spiking water samples, the accuracy of the results was satisfactorily validated at optimized pH and confirmed that the SFM- μ -SPE

procedure could be efficiently extracted/determined cadmium in water samples (Table 3). Due to results, the high recovery for extraction cadmium in water and wastewater samples was achieved by nanoparticles of CNTs@DHSP. Moreover, the certified reference materials (NIST; CRM) were used for validating results by the SFM- μ -SPE procedure (Table 4). Also, the results were validated by ET-AAS analysis which was compared to SFM- μ -SPE/AT-FAAS (Table 5).

Table 3. Validation of SFM- μ -SPE/AT-AAS procedure for Cd(II) determination in waters by spiking of real samples

Sample*	Added ($\mu\text{g L}^{-1}$)	*Found ($\mu\text{g L}^{-1}$)	Recovery (%)
Water A	---	4.23 \pm 0.18	---
	4.0	8.14 \pm 0.31	97.8
Water B	---	2.03 \pm 0.09	---
	2.0	3.98 \pm 0.21	97.5
Water C	---	ND	---
	2.0	1.93 \pm 0.08	96.5
Wastewater A	---	50.75 \pm 1.23	---
	40	88.83 \pm 2.64	95.2
Wastewater B	---	48.32 \pm 1.87	---
	40	89.56 \pm 3.45	103.1
Wastewater C	---	29.56 \pm 1.34	---
	30	57.95 \pm 2.08	94.6

*Mean of three determinations of samples \pm confidence interval (P = 0.95, n=5)

Water A: Varamin River; Water B: Karaj River; Water C: drinking water Tehran; Wastewater A: Paint Factory of Karaj; Wastewater B: Petrochemical waste; Wastewater C: Chemical Factory in Industrial Varamin Co.

Table 4. Validation of SFM- μ -SPE procedure for cadmium determination by certified reference materials in waters (CRM, NIST)

Sample	conc. ($\mu\text{g L}^{-1}$)	Added	Found* ($\mu\text{g L}^{-1}$)	Recovery (%)
SRM 1643f	5.89 \pm 0.13	-----	5.82 \pm 0.16	-----
		5.0	10.79 \pm 0.25	99.4
SRM 3108	50.10 \pm 1.1	-----	48.77 \pm 1.42	-----
		40	87.64 \pm 2.61	97.2

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

SRM 3108: Certified Cadmium Mass Fraction: 10.007 mg g⁻¹ \pm 0.027 mg g⁻¹ dissolved in 1 L DW (C=10 mg L⁻¹), make by dilution DW up to 0.05 mg L⁻¹.

Table 5. Comparing of SFM- μ -SPE procedure with ET-AAS for cadmium determination in water samples

Sample	Added ($\mu\text{g L}^{-1}$)	ET-AAS* ($\mu\text{g L}^{-1}$)	AT-FAAS* ($\mu\text{g L}^{-1}$)	Recovery (%)
Water A	-----	4.18 \pm 0.17	4.06 \pm 0.13	-----
	4.0	-----	7.98 \pm 0.24	98.0
Water B	-----	2.12 \pm 0.11	2.18 \pm 0.08	-----
	2.0	-----	4.09 \pm 0.16	95.5
Water C	-----	0.25 \pm 0.02	^a ND	-----
	2.0	-----	1.97 \pm 0.09	98.5
Well water	-----	6.12 \pm 0.28	5.94 \pm 0.18	-----
	5.0	-----	11.03 \pm 0.34	101.8

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

^aND: Not Detected

4. Conclusions

A novel CNTs@DHSP nanostructure was used for cadmium extraction/separation/determination in water samples by the SFM- μ -SPE method coupled with AT-FAAS. By the proposed procedure, the efficient/easy/fast extraction for cadmium was obtained in a short time at pH=7. The CNTs@DHSP nanostructure has excellent recovery for Cd(II) extraction without any chelating ligands. The procedure had many advantages such as reusability of adsorbent, fast/easy pretreatment and a wide linear range for determination cadmium in waters. Therefore, the CNTs@DHSP nanostructure can be used as the favorite methodology for the determination and separation of cadmium in water samples by AT-FAAS.

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