

Disposable single-use electrochemical sensor: A novel hollow fiber based tool for environmental monitoring of cadmium

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Received: 12 Feb 2018 , Accepted: 24 July 2018 , Published: 25 July 2018

Abstract

The objective of this study is to design a simple, fast, sensitive and single-use electrode with the simultaneous capability of preconcentration and measuring for application in a three-electrode voltammetry system to identify and measure the heavy metal cadmium. The design process of this sensor consists of several stages. The polyurethane foam and multi-walled carbon nanotube nanoparticles were functionalized and the new nanocomposite was synthesized. Besides, with the help of an organic solvent, established on the pencil graphite electrode, it was covered with hollow fiber. In this work, for the first time, the organic solvent was employed instead of ionic liquid. The designed sensor was used to detect and measure heavy metal cadmium through differential pulse voltammetry technique, whose appearance of a sharp peak at -0.82 V indicates the presence of cadmium. It was found that the presence of air molecules as the analyte carrier (between hollow fiber cavities and in fixed nanocomposite on the graphite) instead of organic solvents or ionic liquids was desirable. All the synthesis stages of nanocomposite were analyzed by infrared spectroscopy. Finally, the nanocomposite morphology was obtained with a Scanning Electron Microscope. A calibration curve was drawn and a linear response with a range of 2.39 to 47.6 μM was plotted. The LOD of the designed sensor was 0.399 μM for cadmium. The mentioned sensor was used to recognize the measurement of analyte in real biological samples of urine, nail, and wastewater of the laboratory.

Keywords: Cadmium; DPV; polyurethane foam; hollow fiber; one-use electrode.

Introduction

Heavy metals such as lead, cadmium, and mercury are rapidly increasing to an alarming level. Cadmium has seventh-ranked in 'Top hazardous substances priority list' published by the Environmental Protection Agency. Cadmium can be easily dissolved and transported by water [1]. Therefore, the development of simple analytical instruments, methods, and procedures with low detection limits are needed

[2]. Different analytical methods such as coprecipitation, liquid-liquid extraction, synthesized nanoparticles, solid phase extraction and also electroanalysis of different electrode surfaces, including solid electrodes, Nafion-modified electrodes, and microelectrodes were described for the separation and determination of cadmium [3-12].

Among them, stripping voltammetry determination of cadmium

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using mercury-based electrodes are of the very sensitive analytical methods available. But it is strongly recommended to replace mercury with other materials. Nowadays, modified carbon electrodes with features such as sensitivity, rapid renewal of the electrode surface and simplicity of preparation are the viable alternatives of mercury-based electrodes [13,14].

Because of mercury toxicity, the development of voltammetry methods for measuring cadmium with no mercury is desirable [15]. In this research, we designed a novel electrode with high detection limit to replace mercury electrode in cadmium detection. The adsorption is the most common method for trace element concentrations, therefore, the research focus is on natural organic or mineral adsorbents [16,17].

Many types of adsorbents and recently polyurethane foam has been developed for the recovery of metal ions from aqueous media [18-20]. The importance of polyurethane foam (PUF) has been increased as a sorbent due to its efficiency, low cost, handling and storage [21]. The application of polyurethane foam for separation and preconcentration of various metal ions has attracted considerable attention [22].

The aim of this work is to design a sensor out of new nanocomposite via simultaneous approaches of preconcentration and determination of trace concentration of cadmium in real aqueous and biological samples with supporting of hollow fiber as phase divider and organic solvent instead of ionic liquid for the first time in three electrodes system with differential pulse voltammetry technique. The interference of some common heavy metal ions, such as Cu (II), Zn (II) and Fe (II) and other ions was investigated.

Experimental

Apparatus

All differential pulse voltammetry (DPV) measurements were done by Metrohm Model 797 Computrace (Switzerland) using a three electrode system. The working electrode was a newly designed sensor based on Pencil Graphite Electrode (PGE). A Metrohm pH meter 827 (Switzerland) was applied to solutions pH measurements. Dispersing nanocomposite in an organic solvent and their fixing on the graphite pencil electrode were carried out by an Ultrasonic Processor, model UP 400S (Germany). The FTIR spectra were recorded *via* application of a Shimadzu FTIR-8400 Fourier Transform Infrared spectrophotometer (Japan). All experiments were carried out at room temperature.

Chemical and reagents

Organic solvents and all reagents in analytical grade were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich. The Cd (II) stock solution was prepared by dissolving the calculated amount of cadmium nitrate in deionized water. Phosphate buffers in various pH were prepared by mixing disodium hydrogen phosphate and sodium dihydrogen phosphate salts in suitable ratios. The polypropylene hollow fiber membrane was obtained from Membrana (Wuppertal, Germany, wall thickness 200 μm , the inner diameter 600 μm , and the pore size 0.2 μm). The multi-walled carbon nanotube (MWCNTs) with 10–40 nm diameters, 1–25 μm length, 5–10 nm core diameter, 40–600 m^2/g BET surface area (SBET), V total 0.9 cm^3/g , bulk density of 0.1 g/cm^3 , true density of 2.1 g/cm^3 and 98% < purity, were purchased from Research Institute of the Petroleum Industry, Tehran, Iran.

Synthesis of nanocomposite

Functionalization of MWCNT and PUF

At first, 1g of multi-walled carbon nanotube was functionalized by sonication in the mixture of nitric acid and sulfuric acid (30:70) for 6 h with 60% amplitude and 0.5 Sec cycles. FTIR spectrum of the initial and functionalized MWCNT was investigated. Besides, 1g of commercial polyurethane foam (PUF) was finely shaved and soaked in HCl 3M for 24h. After being washed with distilled water, it was placed in HCl 0.1M and cooled in an ice bath. During the strong stirring process of PUF, 10 ml of ethyl iodide was added dropwise to it and was left in the fridge for 24 h [23]. The obtained Polyurethane foam ion exchange (PUFIX) was air-dried and blended in an agate mortar. FTIR spectrum of primary PUF and PUFIX were recorded.

Synthesis of nanocomposite PUFIX-MWCNT

In order to synthesize PUFIX-MWCNT nanocomposites, the PUFIX and functionalized MWCNT were refluxed for 6 h under 55⁰ C in 40 mL ethanol. The produced black powder MWCNT-PUFIX was washed with distilled water and acetone, respectively and dried at room temperature. The product was blended in an agate mortar. FTIR spectrum of consecutive steps was obtained and SEM test was performed for finding nanocomposite particle size. Finally, the synthesized nanocomposite was used for new sensor fabrication.

Fabrication HF-GE electrode for LSSPME procedure

First, in order to remove the pollutions of graphite pencil rods, they were cleaned with water and acetone. Besides, segments of the polypropylene hollow fiber with 15.0 mm length were

prepared and cleaned with distilled water and acetone. It was dried at room temperature and one end of the hollow fiber segment was closed with the help of heating. By an Ultrasonic Processor, 10 mg of the synthesized nanocomposite was dispersed in 2.0 mL of existing solvent until the uniform mixture was obtained. The graphite pencil rod was placed in this mixture for 8-10 min and, then, was carefully inserted into the hollow fiber segment and placed as a one-use working electrode without carryover, in a voltammetry cell for preconcentration and extraction of cadmium in one step as a new approach. For obtaining an appropriate peak analyte, the four various statements were investigated:

1- The PGE (O.D 0.7 mm) which was covered by hollow fiber, was sonicated in n-octanol solution containing dispersed nanocomposite, and placed in the apparatus on which no peak was observed.

2- The PGE (O.D 0.5 mm), covered by hollow fiber, was sonicated in n-octanol solution containing dispersed nanocomposite, and used as a working electrode, again no peak was observed.

3- The PGE (O.D 0.5 mm) was placed in n-octanol solution containing dispersed nanocomposite and sonicated for about 10 minutes, after that, the fixed PGE was covered by hollow fiber. In this case, a relatively intense peak was observed.

4- The PGE (O.D 0.5 mm) was placed in n-octanol solution containing dispersed nanocomposite and then was sonicated for about 10 minutes, besides, the hollow fiber segment was soaked at n-octanol for 10 min in order to fill cavities of the hollow fiber. Finally, the prepared PGE was covered by filled hollow fiber. In this sense, there was no peak.

So, the third statement was selected as the optimum and the sensor was prepared in this way. For LSSME procedure, the standard working solution of cadmium in phosphate buffer at pH 7 was added to voltammetry cell with working electrode HF-GE. The scanning was carried out in the range of -0.5 to -1.5 volt and the related cadmium peak was observed and recorded.

In this process, the analyte molecules were extracted into the outer wall of the hollow fiber. Then to aid air molecules, the analyte was crossed from cavities and brought to infixed nanocomposite on the graphite pencil rod and the analyte peak was observed. Several parameters such as environment pH (from 3 to 11), type of supporting electrolyte and its concentration, nanocomposite concentration, dispersive organic solvent, scan rate and the effect of some additives were optimized. Finally, the calibration curve and LOD and LOQ were investigated and the real samples were studied under optimized parameters' condition.

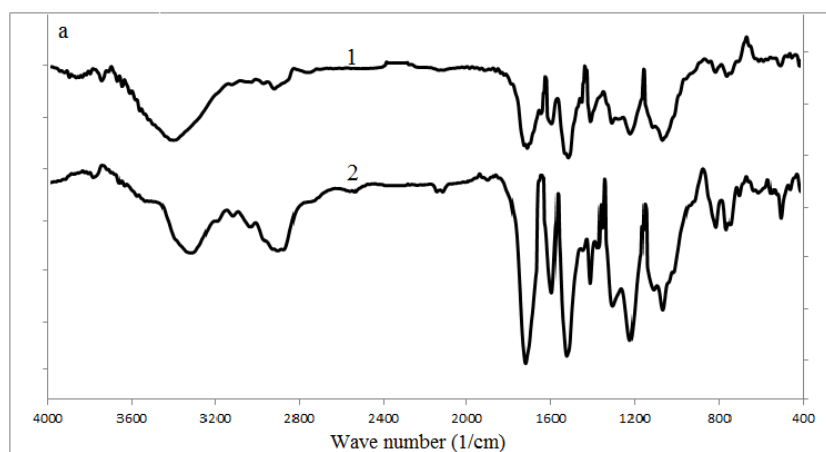
Results and discussion

Characterization of synthesized nanocomposite

Structure confirmation with FT-IR spectrum

The functionalization and chemical structure of MWCNT which were identified by FTIR. Typically 30 scans over the range of 4000–400 cm^{-1} were taken from each sample. As seen in Figure 1, the presence of the oxygenated groups was confirmed by the broadband of FTIR spectra between 3000 and 3700 cm^{-1} [24]. And it could be detected the presence of C=C bond at around 1645.2 cm^{-1} as a percentage of the nanotube functionalization product is visible. The peaks at 1519.8 and 1415.2 cm^{-1} can be attributed to the presence of NO_2 as a result of nitric acid and sulfuric acid application for functionalization procedure. As can be seen in spectra of PUF and PUFIX, the bands at 3402.2 are due to free NH and the peak at 1580.4 cm^{-1} corresponds to the presence of urethane ($-\text{NHCOO}-$) groups.

Two bands at 1527.5 and 1410 cm^{-1} for a NO_2 group, and 1072.3 cm^{-1} are due to a carbonyl group which shifted to lower energy because of conjugated double bonds in PUF and PUFIX [25,26].



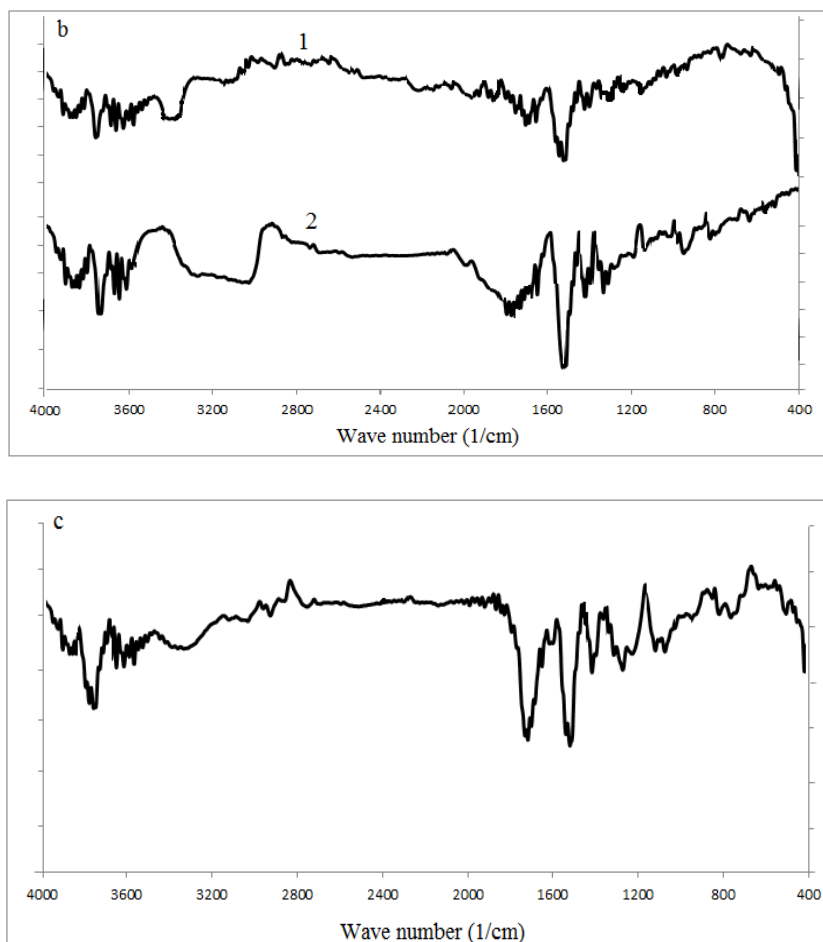


Figure 1. FTIR spectrums of a) Polyurethane foam 1: Initial PUF and 2: functionalized PUF (PUFIX) b) Multi-walled Carbon Nanotube 1: Initial MWCNT and 2: functionalized MWCNT c) Nanocomposite (PUFIX-MWCNT)

Structure confirmation through SEM images

Scanning electron microscopy (SEM) imaging of synthesized nanocomposite was performed. As can be seen in Figure 2, the threaded structure of MWCNT (Figure 2, b) and porous particles of PUF (Figure 2, a) have been

used in the manufacture of MWCNT-PUFIX (Figure 2, c) helping to capture the analyte and as a result increase the preconcentration and extraction yield. It is clear from (Figure 2, c) that nanocomposite has been obtained with $\approx 53\text{nm}$.

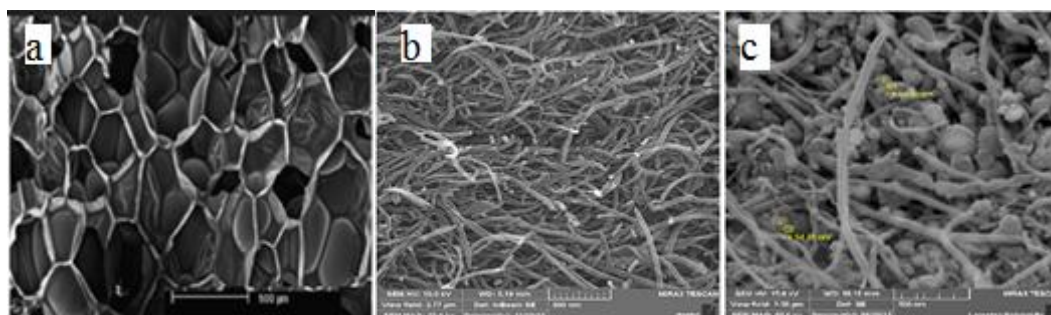


Figure 2. SEM imaging of a) Polyurethane foam (PUF) [27] b) Functionalized MWCNT [28] c) Nanocomposite (MWCNT -PUFIX)

*Optimization of parameters***Effect of pH**

The effect of pH on the preconcentration, determination, and extraction of Cd (II) ion from aqueous donor phase was investigated by adjusting the pH of a phosphate buffer solution at the required values over the

range of 2.0–11.0. As shown in Figure 3, the current and thus the electrode response were increased with the increase of analyte acidity up to pH 6 and in continuing decrease. Thus pH 6 is comfortable to continue the experimentation.

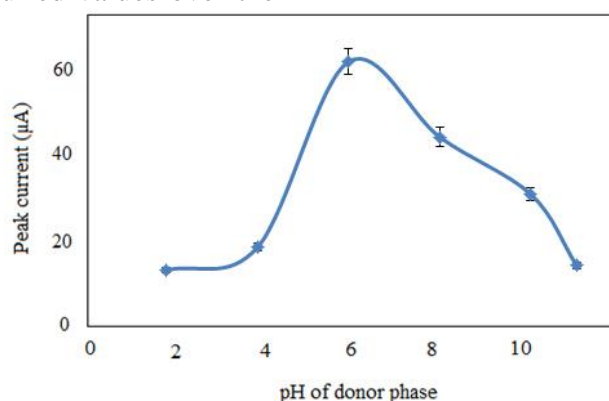


Figure 3. Effect of pH of donor phase on the peak current

The pK_a value of phosphate buffer 0.05 M is 6.86 [29]. Thus the extracted value of Cd to sensor surface increases at the pH of about 6-7 [30]. Besides, a decrease is observed at adsorption of Cd to nanocomposite due to the positively charged cadmium species with the electrostatic repulsion of the protonated active sites on the MWCNT-PUFIX [31].

Effect of organic solvent

The effect of organic solvents on the process efficiency was investigated using several solvents with consecutive carbon numbers containing acetone, 1-butanol, cyclohexanol, 1-octanol, and 2-decanol. Dispersion process was carried out, but in acetone and 1-butanol there was no dispersion as well. Therefore, three electrodes were prepared with the use of cyclohexanol, 1-octanol, and 2-decanol. Moreover, they were separately used as working electrodes in a three-electrode system. The sensor-made using 2-decanol did

not show any peak, but the sensor made using cyclohexanol showed a low current peak with high background effect. Finally, the sensor was prepared with the use of 1-octanol and a sharp peak with no background current. Therefore 1-octanol was selected as the optimum organic solvent.

Concentration of nanocomposite

The influence of the nanocomposite concentration in the organic solvent on the peak current was investigated and shown in Figure 4. For this purpose, nanocomposite concentration over the range, 0.5 to 10 mg/mL were dispersed. The results indicated that the peak current is increased with the increase in the amount of nanocomposite due to the increase in binding sites facilitating the accumulation of cadmium at the electrode surface. However, the highest peak currents were obtained with 7.5 mg/mL of the nanocomposite in n-octanol.

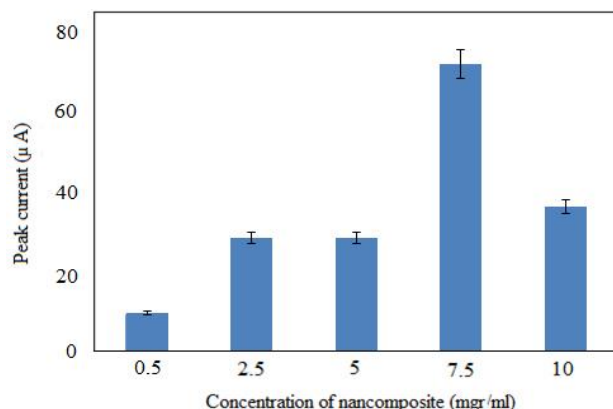


Figure 4. Effect of nanocomposite concentration on peak current

Effect of scan rate

The scan rate is an important and effective parameter in voltammetry technique with considerable impact on peak current. The scan rates were investigated from 10 to 100 mv/S. By increasing the speed of scanning, peak current was clearly reduced. Therefore, the highest peak with the lowest rate was observed. This could be explained as the slow scan gives more opportunities to the analyte for path

wending from voltammetry cell to hollow fiber cavities and then transferring to the nanocomposite vicinity. Thus, the simultaneous slowing down in the preconcentration and measure processes could increase the efficiency of the sensor

To check that, the difference between peak currents is due to random error or significant difference, carried out the one-way ANOVA test. Its data and calculations are present in Table 1.

Table 1. The data and calculations of one-way ANOVA for studying effects of scan rate on peak current

Peak current (10^{-5} A)				
Scan Rate (V/S)	Average 1	Average 2	Average 3	Average 4
0.01	6.14	5.70	4.89	4.64
0.02	2.90	4.00	3.84	3.56
0.04	2.52	2.41	2.53	2.27
0.06	5.02	5.39	4.09	5.18
0.08	4.38	5.27	4.11	6.14
0.1	4.94	4.45	4.20	4.49

$\sum T_i$	$\sum T_i^2$	T	T ²	CF
1.03E-03	1.87E-07	1.03E-03	1.06E-06	4.42E-08
Crude SS	SS _{Total}	SS _{Between}	SS _{Within}	df of Between
4.72E-08	3.00E-09	2.40E-09	6.04E-10	5
df of Within	MS _{Between}	MS _{Within}	F _{Calc}	F _{Crit}
18	4.79E-10	3.35E-11	14.30	3.38

SS; Sum of squares
 MS; Mean of squares
 df; degree of freedom
 F_{Calc}; F_{Calculated}
 F_{Crit}; F_{Critical}

As can be seen, the calculated F (14.30) is bigger than critical $F_{0.95}$ (3.38). As a result, the difference between peak currents is not due to random error, and results have a significant difference. So, with 0.95 confidence and $P < 0.05$, lowest scan rate, has best results.

Effect of supporting electrolyte

As supporting electrolyte has an important role in the electroactivity of the ions and thus on the electrochemical process efficiency, its type and concentration should be optimized. For this purpose, the three most commonly

used electrolytes containing sodium perchlorate, Robinson buffer and phosphate buffer were tested. In a differential pulse voltammetry technique (DPV) the best result of cadmium peak current was shown at the presence of phosphate buffer as a supporting electrolyte. In the following, phosphate buffers 0.05 and 0.1 M showed a better effect on the extraction process in phosphate buffer 0.05 M. Results of supporting electrolyte optimization are well depicted in Figure 5.

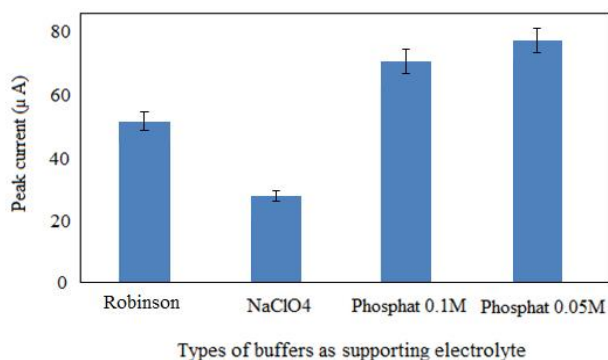


Figure 5. Effect of the type and concentration of supporting electrolyte on cadmium peak current

Effect of some additives

The impacts of the non-ionic surfactant charged polyelectrolyte solution and salts on the determination of Cd (II) with designed sensor were examined using the addition of Triton X-100, chitosan, potassium chloride and sodium chloride respectively. The solutions with different concentrations of additives were prepared in 10 mL of

the buffer solution containing cadmium in voltammetry cell. The peak currents were recorded in the presence of different amounts of them. Overall, all of the additives showed a positive effect on extraction efficiency and peak current. As can be seen in Figure 6, the best peak current in the presence of KCl 2.0 mM was observed.

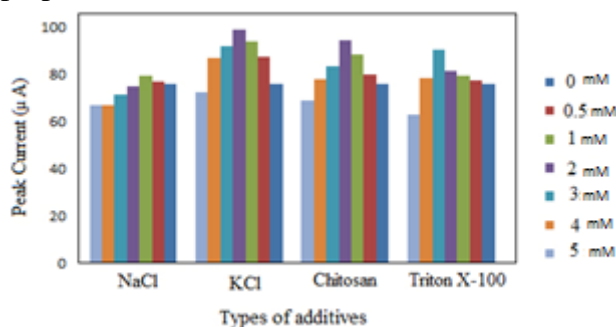


Figure 6. Effect of type and concentration of additives on peak current

For investigating the reason for the difference between peak currents, the two-way ANOVA test was done. The

data and calculations for this study are presented in Table 2.

Table 2. The data and calculations of two-way ANOVA for investigation of the effect of additive concentration and additive type on peak current (μA)

Additive Concentration (mM)	Additive type			
	Triton – X 100	Chitosan	KCl	NaCl
0	76	76	76	76
0.5	77.4	80	87.6	77.1
1	79.3	88.4	94.1	79.6
2	81.4	94.3	99.1	74.8
3	90.3	83.6	91.7	71.2
4	78.6	77.9	86.8	66.8
5	63.1	68.8	72.5	66.7

$\sum T_i^2$	$\sum T_j^2$	T	T ²	CF
718030	1253756	2235.1	4995672	178416.9
Crude SS	SS _{Total}	SS _{Columns}	SS _{Rows}	SS _{Remaining}
180625.7	2208.84	691.13	1090.64	427.07
df of Column	df of Row	df of remaining	MS _{Columns}	MS _{Rows}
3	6	18	230.37	181.77
MS _{Remaining}	F _{Column}	F _{Crit-Columns}	F _{Rows}	F _{Crit-Rows}
23.73	9.71	3.16	7.66	2.66

SS; Sum of squares
 MS; Mean of squares
 df; degree of freedom
 F_{Crit}; F_{Critical}

As the results show, in the columns, the calculated F (9.71) is bigger than critical F_{0.95} (3.16) and in the rows, the calculated F (7.66) is bigger than critical F_{0.95} (2.66) too. So, the results of the type and concentration of additives with 0.95 confidence and P 0.05, have a significant difference. And the difference between peak currents is not due to random error.

Calibration curve and linear range

For plotting the calibration curve, the optimum condition of DPV technique

was applied and concentration of Cd (II) versus the peak height was drawn. The HF-PGE electrode response was linear from 2.39 to 47.6 μM , with a correlation coefficient of 0.9933. The LOD was obtained 0.399 μM was based on three times of standard deviation divided by the slope of the calibration graph, and the quantification limit was 1.00 μM . The results were shown to be appropriate for the determination of cadmium (Figure 7), indicating that the method could be

employed for the analysis of cadmium (II) in biological and water samples. Also, a comparison between the

designed method and the previously reported method is presented in Table 3.

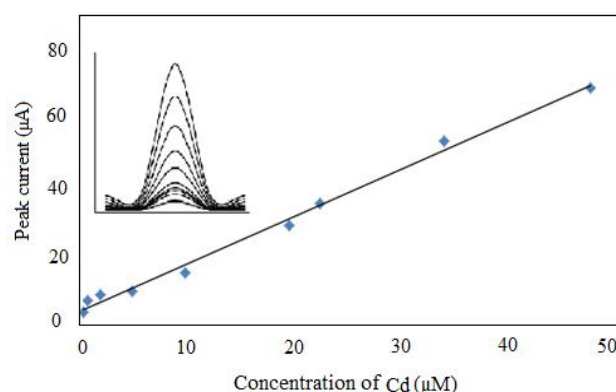


Figure 7. The calibration curve of cadmium in the concentration range of 0 to 47.6 μM

Table 3. A comparison between previously reported method and the proposed method for Cd determination

Method	Detection	LOD	DL	R2	RSD%	Ref
Column pack	FAAS	0.05ng/ mL	0.1–90 ng/mL		2.4	31
With sorbent MWCNT	ICP-AES	0.30 ng/ mL	-	-	1.63	32
Extraction with HF-GE	DPV	0.61 ng/ mL	2–13000 ng/mL	-	<5	33
Modified carbon paste electrode	DPASV	105 $\mu\text{g/L}$	200-650 $\mu\text{g/L}$	-	<5	14
Flow- through analysis	ASCP	<0.02 $\mu\text{g/L}$	-	-		34
Fluorescence Spectroscopy	ICP-OES	0.038 $\mu\text{g/L}$ (0.03 μm)	-	0.978	-	35
	ICP-MS	0.012 mg/kg	1.2-24 $\mu\text{g/L}$	0.9997	-	36
Deproteinization of samples	ICP-MS GF-AAS	0.08 $\mu\text{g/L}$ 0.02 $\mu\text{g/L}$	-	0.9949	-	37
Solvent separation	FAAS	0.002 mg/L	-	0.9999	-	38
HF-PGE electrode	DPV	0.399 μM	2.39 to 47.6 μM	0.9933	4.27	Present work

The effect of interferences

In the DPV technique, interfering molecules in the sample solution may be co-deposited on the active sites of the electrode surface, resulting in changes in the stripping peak current.

The interference may be the result of two main factors: (i) intermetallic compound formation and (ii) the competition between analytes and interfering ions for active sites on the electrode surface.

The interference study was performed by adding various potentially interfering metal cations including different fold excess with target metal ions into a standard solution containing 2 μM Cd^{2+} under the optimized working conditions. As

listed in Table 4, the change in the peak current of Cd^{2+} was less than 10% after adding interfering ions up to the values listed. Thus, the fabricated sensor displayed appropriate selectivity for Cd^{2+} in the heavy metal analysis.

Table 4. The effect of ion interferences on the analyte peak current in cadmium determination

Interfering ion	Maximum tolerance ratio
Fe^{+2}	100
Cu^{+2}	25
Zn^{+2}	50
Na^{+}	500
K^{+}	500
Cl^{-}	500
ClO_4^{-}	500

Real sample treatment

Three wastewater samples, collected from chemistry laboratories, were analyzed by this sensor. The samples were filtered and adjusted to pH 6 with the addition of HCl 0.1 M solution. Urine samples often do not require pretreatment [39], for urine studies the initial pH of urine was checked and adjusted to pH 6 with NaOH 0.1 M and diluted with a phosphate buffer of the optimum pH to one-tenth. In order to prepare nail sample, it was cleaned by the solution of water and acetone with a ratio of 1:1. In this sense, the aim was to remove all the pollutions and fats. Then, it was dried and the 0.01 g of it

for 24 h soaked in 1 mL concentrated HCl. The 0.1 mL of obtaining mixture was diluted with 25 mL of optimum buffer. After real sample treatment, specified amounts of cadmium were spiked and the HF-LSSPME procedure with the mentioned sensor by differential pulse voltammetry technique was carried out.

It is notable that, recognition and determination of cadmium in nail samples with PGE electrode was impossible due to high background effects and broadening peaks. But by application of this sensor, a peak without background effects was observed. Results are shown in Table 5.

Table 5. Analytical results for determination of cadmium in real samples

Sample name	Spiked amount (μM)	Detected amount (μM)	RR %*	RSD %
Waste water (lab 1)	0.769	0.830	107.95	3.21
Waste water (lab 2)	0.769	0.820	106.74	5.9
Waste water (lab 3)	0.769	0.758	98.69	7.9
Urine 1	0.769	0.734	96.03	6.4
Urine 2	0.769	0.771	100.39	4.29
Nail	0.769	0.790	102.77	2.63

* Relative Recovery%

Conclusion

In this work designing a sensitive and simple disposable electrode for use in an electrochemical three electrode system has been carried out for detection and determination of heavy metal cadmium. This research suggests that the MWCNTs properties can be improved by being combined with functionalized polyurethane foam. The PUFIX-MWCNT, as infixed nanocomposite, would increase the preconcentration, extraction, and determination of Cd in a simultaneous approach. It is noticeable that the designed sensor is fast and requires very low organic solvents. The method has satisfactory LOD and LOQ and results show that the new sensor is useful to develop the cadmium analysis method with the acceptable response.

Acknowledgements

The authors wish to thank Payame Noor University for supporting this research.

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