

In-situ preconcentration, and electrochemical sensing of zinc(II) and copper(II) based on ionic liquid mediated hollow fiber-modified pencil graphite electrode using response surface methodology

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Abstract

A single-use electrochemical sensor using ionic liquid mediated hollow fiber-graphite working electrode was fabricated for the first time. The screening tool was developed by coupling this electrode with differential pulse voltammetry (DPV) for in-situ preconcentration and determination of Zn(II) and Cu(II). In our plot, porous polypropylene hollow fiber membrane was divided into pieces of 2 cm, then fiber's lumen and pores were satiated with homogeneous mixture of reduced graphene oxide (rGO) and three types used ionic liquids: (1-ethyl-3-methylimidazolium tetrafluoroborate), (1-butyl-3-methylimidazolium hexafluorophosphate) and (1-butyl-2,3-dimethylimidazolium hexafluorophosphate) individually. Thereafter, a pencil graphite rod was placed inside the fiber. Fabricated sensors were used for single-step simultaneous purification and determination of Zn(II) and Cu(II) ions from water samples. The response surface method (RSM) was used as the basis of the design and analysis of the experiments. Parameters that were mostly important in the separation part of the study, such as: molar mass of ionic liquids, amount of nanoparticle and sonication time have been investigated. Analysis of variance (ANOVA) and RSM contour plots were presented for effect of all factors (input parameters) on the maximum current of differential pulse voltammetry (DPV) peaks (output responses). The results disclosed that the metal removal was impressed by the molar mass of ionic liquids, amount of nanoparticle and sonication time respectively. The efficiency specifications of this procedure were evaluated by calculating precision and response linearity. Under the optimal experimental conditions linear concentration ranges of 0.9–550 $\mu\text{g L}^{-1}$ and 0.7–500 $\mu\text{g L}^{-1}$ were obtained for Zn(II) and Cu(II) ions respectively. The reported limit of detection for Zn(II) and Cu(II) were 0.27 and 0.21 $\mu\text{g L}^{-1}$ with relative standard deviations (RSD) 3.2%, and 4.4%, respectively. In addition, this sensor was successfully applied to real water samples.

Keywords: Zn(II); Cu(II); hollow fiber - pencil graphite electrode; differential pulse voltammetry; surface response method; ionic liquid.

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Introduction

As regards of environmental standards get more and more precise and because of toxicity and non-biodegradability of heavy metal ions, it is very important to measure industrial wastewaters; including, these ions such as Cu(II), Co(II), Ni(II), Zn(II), Cd(II), Pb(II), etc. [1]. Zinc is one of these heavy metals that it is a necessary paucity element in antioxidant reactions. It can uplift the human safety system. Vegetarians should receive sufficient amounts of zinc. Also, there is little amount of zinc in igneous rocks [2].

Having safe drinking water for all people, regardless of their social and economic conditions, is the primary purpose of health safekeeping societies. The amount of zinc in natural surface and ground waters are 10 and 10-40 $\mu\text{g.L}^{-1}$ respectively [2]. Due to laundering of zinc from pipes and fittings, the concentration of zinc can be found much more in tap water [3]. All living organisms have zinc as a needed element [4]. Despite this, Zinc shortage which is compensated by cadmium, may cause uncommon physiology disturbances, and, may have an impress in mouth cancer [5]. Therefore, accurate determination of zinc in the environment is very necessary and important to protecting of human life, according to the above and widespread usage of this element [6].

Cu(II) is a common pollutant in several industrial wastewaters such as mining effluents, electroplating, circuit board, printing and dyeing, etc. The removal and recovery of Cu(II) from these kinds of wastewater are essential for health, economic and environment [7]. On the other side, these heavy metals are also rare resources on the earth, so there is obvious economic

benefit to recycle and reuse them [8-10]. The water has to be purified from these contaminants before being used as drinking water or further being discharged [11]. The separation of metal ions present as contaminants in water is complicated by the number of variables that must be considered, including the solution composition, the pH, and the presence of organic substances [12]. Pre-concentration-separation methods including solid phase extraction [13], cloud point extraction [14], membrane filtration [15], liquid-liquid extraction [16], electrochemical deposition [17], etc. have been widely used for the pre-concentration-separation of heavy metal ions. Electrochemical methods compare to all existing methods for measuring elements are more attractive [18]. Different kinds of electrodes were used in electrochemical experiments such as: hanging mercury electrodes, mercury plated thin film and glassy carbon electrode [19]. Therefore, the expansion and usage of disposable electrodes is widely reported, because of the difficulties in application of the mentioned electrodes for field analysis [20]. Single-use electrodes are planned for one use and therefore have the advantages such as: no memory effect and minimizing the damage often associated with re-usable sensors [21].

Trace metal ions Pre-concentration and purification in aqueous systems before their quantification, accomplished with sample preparation techniques that have been mainly used for these purposes. Liquid-liquid extraction (LLE) and solid phase microextraction (SPME) are the most widely used in extraction techniques. In sample preparation and purification methods, SPME is more attractive compared with LLE because of

advantages such as: high-throughput analysis and considerable analytical properties containing, linearity, reproducibility, repeatability, low detection limit and quantification, high selectivity and sensitivity, eventually least matrix interposition [22,23]. SPME incorporate several stages in sample preparation and all of them are done in a single step, these stages are as follows: sampling, isolation, concentration and enrichment, sample injection into analytical instruments [24]. Solvent-based and time consuming usual methods have some problems including, multistep, large amount of samples and solvent that can make environmental contamination and be perilous to human health that SPME was developed to conquer of these problems. This study intended to advance the SPME method with incorporate nanoparticles into the pores of polypropylene hollow fibers via an organic solvents and ionic liquids as a solid/liquid sorbent because the SPME fibers are costly and have friable coatings and should be exploited attentively [25]. Therefore, our idea was based on the use of a polypropylene hollow fiber membrane with activated nanoparticles that operates as an analyte trap, among the acceptor solvent in the pores of the hollow fiber. This system caused higher selectivity and enrichment, because the nanoparticles act as solid sorbents do in SPME fibers. So, commonly the connection of the analyte was done by two various chemical effects; non-covalent and covalent binding [26, 27].

Recently, a new method called hollow fiber solid-liquid phase microextraction (HF-SLPME) was provided by Es'haghi group in which they combined hollow fiber liquid phase microextraction [28] with solid phase microextraction and benefited

from the advantages of both methods [29]. In this technique, microextraction performance was improved because of incorporation of organic solvents contained inside piece of polypropylene hollow fiber with nanocomposites refined by chemically surface modification methods. These incorporated nanoparticles in the membrane system could operate as a nanoscale solid phase extractor with high surface area. It has provided high enrichment factor of analytes [26, 29]. This method has been successfully used for separating many kinds of analytes such as drugs, environmental targets, food and beverages, etc. [30].

We used from this history and merged it with electrochemical methods to achieve and design a powerful new sensor for simultaneous preconcentration (due to the use of hollow fiber membrane incorporated with nanoadsorbent) and determination (owing to the use of electrochemical instruments) of the target analyte. We established the electrical contact between the fiber and sample solution via pencil graphite electrode (PGE) that were put inside the fiber and connected to a copper wire for electrochemical signal record. The fabricated sensor has benefits, such as high electrochemical reactivity, disposability, good mechanical hardness, ease of use, and low cost.

In addition to the mentioned factors, we require an additional component to establish electrical connection between the sample solution and the electrodes. Common organic solvents are existing which already used for HF-LPME but cannot be used here. Because these solvents cannot be able to establishing of electrical connection between the sample solution and the electrode. For this reason, we have used ionic liquids (ILs). Room-

temperature ionic liquids (RTILs) are composed entirely of positive and negative ions together and molten salt with melting point below 100°C, which have surprising properties such as: electrolytic conductivity, low volatility, adjustable viscosity and miscibility. These properties cause them to be useful for many applications in chemical analysis and nanotechnology applications [31]. RTILs have proved to be excellent materials for applications in electrochemistry and highly utilized in this field because of their matchless physicochemical properties [32, 33].

In the present work a micro solid-liquid phase microextraction (μ -SLPME) fiber was matched with a DPV method as an electrochemical system. In this innovative usage, the duty of the sonicated solvent in the hollow fiber porous was investigated because the influence of metal ions into the membrane, takes place with background solvent. Chosen solvent must be compatible and backbone with the fiber structure, so that it should be easily enter in it and would not leave the fiber pores. Many organic solvents that already used for hollow fiber microextraction goals by the researchers such as: 1-octanol, 2-octanone, n-hexane, ethyl acetate and di-n-hexyl ether were examined and eventually three kind of ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate), (1-butyl-3-methylimidazolium hexafluorophosphate) and (1-butyl-2,3-dimethylimidazolium hexafluorophosphate) was selected for this study. As inner space of HF is empty the electrical contact, needs for electrical conductor interface, was established via a graphite pencils that were fixed inside the fiber and connected to a copper wire. For the first time, authors constructed a new

electrode for this work. Recently, a new procedure called hollow fiber solid phase microextraction (HF-SPME) presented by Es'haghi and coworkers, the same as their work, have more advantages over the ordinary SPME method such as: cancellation the feasibility of sample memory effect and high reproducibility [29,30]. Many properties such as: sensitivity, stability, easy preparation process and small loading of nanoparticle using this combination can create new robust sensors for many important species. According to the above subjects, our group (especially in the present study) aimed to couple the innovative nanoparticle assisted hollow fiber graphite sensor with a DPV method as an electrochemical system. So that the fiber would play the role of a solid/liquid microextraction device and simultaneously, serve as the working electrode or an electrochemical sensor for Zn(II) and Cu(II) metal ions.

Experimental

Chemicals and Materials

We obtained the Accurel Q 3/2 polypropylene hollow fiber membrane from Membrana (Wuppertal, Germany). Its characteristics are as follow: the inner diameter was 600 μm , the wall thickness was 200 μm , and the pore size was 0.2 μm . rGO nanoparticle was synthesized in the author's laboratory. Analytical graphite, sulfuric acid, phosphoric acid, KMnO_4 , H_2O_2 , sodium borohydride (NaBH_4) were purchased from Merck (Darmstadt, Germany). A concentration of 0.05 mol L^{-1} phosphate buffered solution (PBS, prepared from NaH_2PO_4 and Na_2HPO_4) was used to control the pH of feed solution. Ionic liquids, (1-ethyl-3-methylimidazolium tetrafluoroborate) [EMIMBF_4], (1-butyl-3-methylimidazolium hexafluorophosphate) [BMIMPF_6] and

(1-butyl-2,3-dimethylimidazolium hexafluorophosphate) [BDMIMPF₆] was provided by Sigma-Aldrich company (St. Louis, USA). In all over the work we used from de-ionized and three times distilled water, and all chemicals were at least analytical-reagent grade. Stock solutions of 100mg.L⁻¹ of each Zn(II), Cu(II) ions were prepared by dissolving appropriate amount of zinc nitrate and copper nitrate (all purchased from Merck) in de-ionized (DI) water and diluted to 100 mL volumetric flask. Working standard solutions were obtained by appropriate dilution of the stock standard solution.

Instrumentation

All the voltammetry measurements were carried out by trace analyzer, μ -Autolab TYPE III, Eco Chemie BV, Netherlands potentiostat/galvanostat, and driven by the NOVA software (Version 1.8). The electrochemical cell comprised of the home-made hollow fiber - pencil graphite electrode (HF-PGE) as a working electrode, Ag/AgCl and platinum wire as a reference and counter electrodes respectively. A Metrohm pH-meter (model 691) was used for pH measurements. The DPV mode was used for take of Zn(II) and Cu(II) ions voltammograms. 15.0 mL of the sample solution was added to the voltammetric cell. The solutions were de-aerated by ultrapure N₂ gas for 300 s. We optimized the voltammetry experimental variables such as; scan rate of potential, deposition time, equilibrium time, voltage step, voltage step time and stirring speed of the solution. For the on-line preconcentration time of analyte, deposition time study was performed from 0 to 3000 s. The deposition

potential of Zn(II), Cu(II) ions was tested from -1.0 to 0.2 V.

Synthesis and characterization of rGO

Synthesis of graphite-oxide nanosheets were performed by a modified Hummers and Offeman method [39]. Then we dispersed it in water by ultrasonication for 2 h and the graphene oxide (GO) as a yellow-brown dispersion is obtained. Any un-exfoliated GO is removed by centrifugation at 3000 rpm. Afterward, the above homogeneous GO dispersion (100.0mL) was blended with 0.5 mL of hydrazinehydrate for 24 h at 90 °C (Figure 1). eventually; the black precipitation of reduced graphene oxide (rGO) was gained by filtration and water-washing cycles and then dried in vacuum.

Fabrication of the hollow fiber -pencil graphite electrode (HF-PGE)

First, 2 cm pieces of hollow fibers were cut. For eliminate of pollutions, the fiber segments were washed in acetone and dried in air, directly. The fiber segments were interpolated with 1.7 cm of a cleaned graphite pencils rod (O.D. 0.7 mm and 2.5 cm length) carefully. With the help of heat, the end of hollow fibers was blocked. Second, adequate amount of optimum rGO (3.0 mg) was dispersed with 0.5 mL of ionic liquids in the conical tube. Finally, the constructed HF-PGE was directly located on above mixture and sonicated before the analysis. The HF-PGE scheme and SEM images of fiber were shown in Figure 2. At the end, fabricated HF-PGE was bringing off the conical tube and washed twice with 1–2 mL deionized water, now it is ready for the voltammetric measurements. Because of avoiding any carry over; we used each HF-PGE only once.

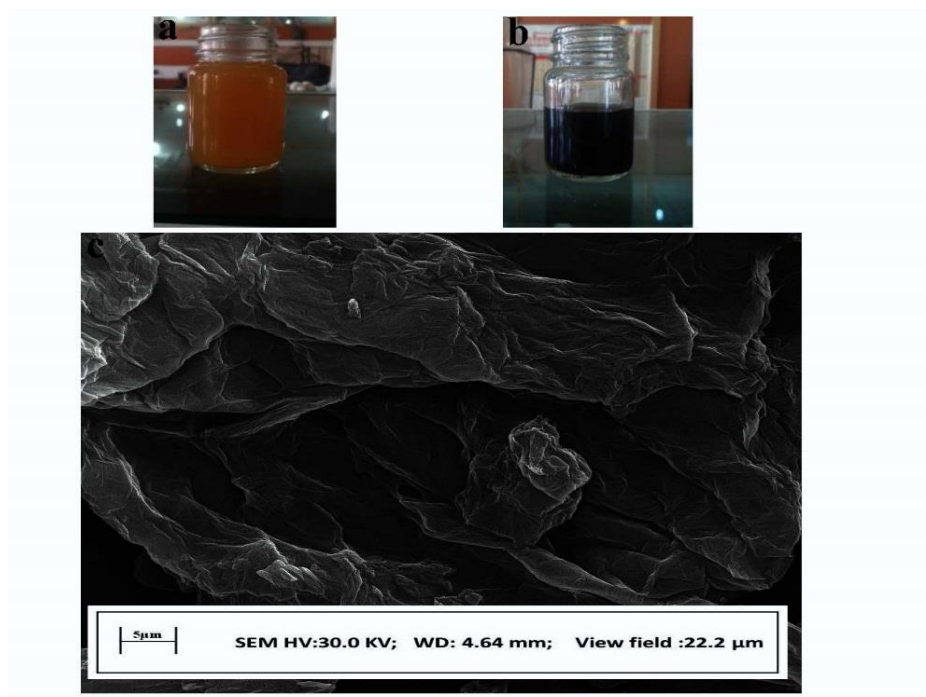


Figure 1. a) Go solution b) rGo Solution c) SEM image of rGO nanoparticle

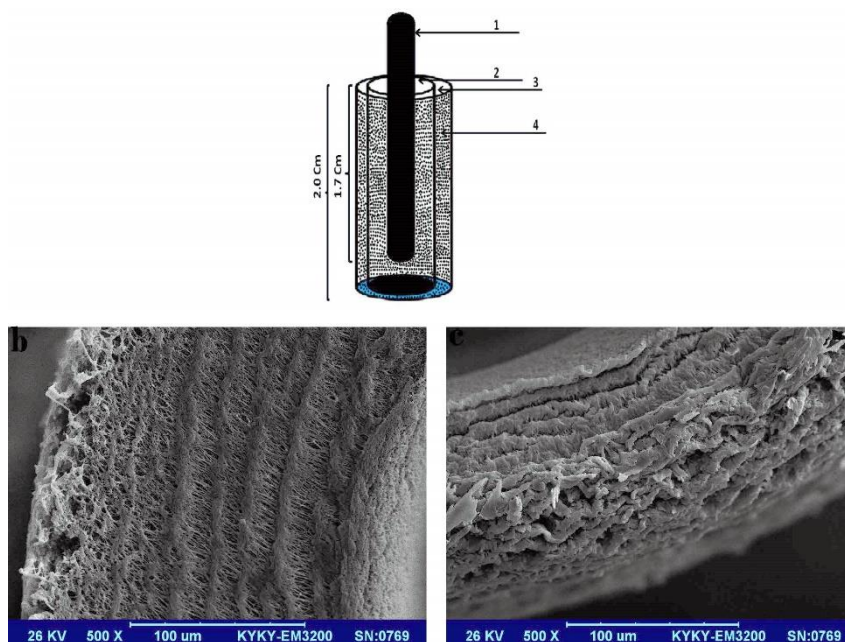


Figure 2. HF-PGE structure and characterization. (a) Electrode scheme; (1) Graphite rod:1.7 Cm (2) Lumen of the hollow fiber: 600 μ m (3) Hollow fiber surface: 200 μ m (4) mixture of ionic liquid and rGO with ratio of 3 mg per 5 mL I.L. (b) SEM image of Empty hollow fiber (c) Satiated hollow fiber with homogenized mixture of rGO and ionic liquid

Software package

Minitab 16 Software was used for optimization of conditions for zinc and copper ions removal. All plots and

diagrams were sketched by this software.

Optimization, DOE and Response surface methodology (RSM)

Because of the need to improve the quality in regulatory organization, the system of extension and validation of analytical methods cannot be investigated as an easy work. In this context, the term “optimization”, means to improve the efficiency of the analytical process, *i.e.* finding the best conditions in which we have the best response [34]. Optimization is a critical step in analytical chemistry to access the value of each factor in that the best possible response is obtained. Because of, less time, effort and resources in the multivariate design of experiments (DOE) than the univariate methods (which are being used in routine method) and easily collecting of a lot of quantitative data while minimize the number of experiments, it is an important subject [35]. It is proved that the design of experiment (DOE) and the response surface methodology (RSM) can be useful for developing, improving and optimizing processes [36]. RSM is widely used in different analytical

applications [37], industrial world [38] and in bioprocesses [39]. The flow chart provided in Figure 3 shows that DOE and RSM are frequently exploited to analytical separations and extraction methods. RSM first screening information then a response surface design is made which prepares the data that should be modeled via the least squares fitting or, exceptionally, by artificial neural networks. The utility function is the most popular tool to be used when a large number of responses should be optimized [40]. Coefficients of the response model ($\alpha_1, \alpha_2, \dots, \alpha_n$), statistical significance, and their standard errors are determined by regression analysis of the response data. Also to the constant α_0 and error (ϵ) terms, the response model interpolates linear and squared terms of the variables, and its paired first order interaction. Minitab 16 Software package were used for all calculations. For the four variables response model, the formula is come below Eq. (1): [41].

$$Y = \alpha_0 + \sum_{i=1}^3 \alpha_i X_i + \sum_{i=1}^3 \alpha_{ii} X_i^2 + \sum_{i=1}^3 \sum_{i < j=2}^3 \alpha_{ij} X_i X_j \quad (1)$$

Eq. (1) Formula for the four variables response model where: y represents the experimental response, x the independently evaluated factors, α_0 the intercept and the parametric coefficients of the obtained model.

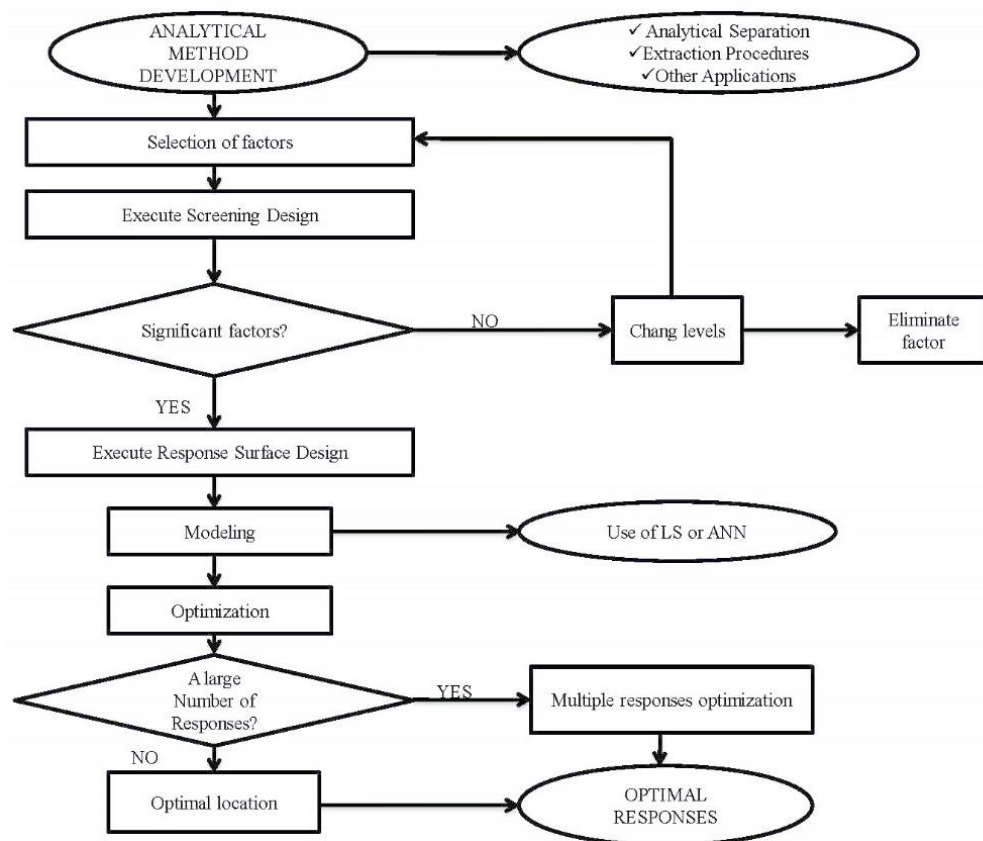


Figure 3. Flow chart which schematically exhibit application of DOE and RSM in analytical method

Results and discussion

In this literature, all of the experiments were re-do at least three times and showed data represented the mean value of these three measurements. We also considered the effect of experimental (electrochemical) variables such as potential of deposition, deposition time and the concentration dependence for each of the metal ions. In situ desorption and analysis was occurred because it simplified the experimental procedure.

Design of experiments

Maximum current of DPV peak (I_{pic}) was used for quantification of optimum conditions for zinc and copper ions removal. They are affected by several chemical or physical factors such as amount of NP, stirring speed of magnet, type of supporting electrolyte and extraction time etc [30]. Despite of above parameter, in this work we have

investigated two more effective factors else that important in separation section of work: molar mass of used ionic liquid and sonication time. Response surface methodology as a method for experimental design was employed to optimize the conditions for zinc and copper ions removal. This was carried out by applying Central Composite Face Centered (CCF) design for three independent variables of molar mass of used ionic liquid, amount of NP and sonication time. After the calculation, experimental results were analyzed with the help of performance statistics and analysis of variance (ANOVA). Following is the selection levels of process parameters. Finally, optimal process parameters were verified through the confirmation experiment. The effect of three important factors including; molar mass of used ionic liquid, amount of NP and sonication time were studied using RSM method.

In all cases it should be noted that each reported response is the average of three measurements. The used level setting values of the main factors (A–

C) and the RSM matrix employed to assign the considered factors are shown in Tables 1 and 2, respectively.

Table 1. Factors and their levels for design of experiments

Parameter	Level		
	1	2	3
(A) Sonication Time (S)	300	600	900
(B) Ionic Liquid Molar Mass (g.mol ⁻¹)	^a 197.97	^b 284.18	^c 298.21
(C) Amount of Nano Particle (gr)	0.001	0.003	0.005

a) 1-Ethyl-3-Methylimidazolium Tetrafluoroborate (EMIMBF₄)

b) 1-Buthyl-3-Methylimidazolium Hexafluorophosphate (BMIMPF₆)

c) 1-Buthyl-2,3-Dimethylimidazolium Hexafluorophosphate (BDMIMPF₆)

Table 2. Experimental parameters setting and results based the experimental design in term of peak current

Trial No.	Factors			Current(μA)
	A	B	C	Sum
1	1	1	1	9.43
2	2	1	1	9.95
3	3	1	1	9.52
4	1	2	1	22.04
5	2	2	1	21.56
6	3	2	1	21.59
7	1	3	1	17.03
8	2	3	1	17.39
9	3	3	2	16.83
10	1	1	2	14.29
11	2	1	2	14.62
12	3	1	2	13.95
13	1	2	2	26.85
14	2	2	2	26.12
15	3	2	2	25.58
16	1	3	2	22.19
17	2	3	2	22.06
18	3	3	2	20.56
19	1	1	3	9.25
20	2	1	3	8.87
21	3	1	3	8.12
22	1	2	3	21.67
23	2	2	3	21.23
24	3	2	3	19.93
25	1	3	3	16.43
26	2	3	3	16.32
27	3	3	3	14.93
28	2	2	2	26.20
29	2	2	2	26.34
30	2	2	2	25.86

Variables study in the HF-PGE method

To take the optimum advantages of the procedure, various experimental parameters must be studied to obtain an optimized scheme. These parameters were optimized in the present research by an RSM method, all three-factors

have three-levels and the experimental data were evaluated using Minitab 16 Software. Each selected factor has centered value of the levels that showed the effect of factor changes on the extraction efficiency. Results showed in Tables 3 and 4.

Table 3. Model regression coefficients and their probability of (p-value) in the second-order polynomial of the peak current

Current	Coeff. SC	Std. Err.	P	Conf. int(±)
Constant	29.885	0.192042	1.21E-33	0.399375
Sonication Time	-0.411585	0.0619181	1.40E-06	0.128766
Type of Ionic Liquid	3.65222	0.0597558	3.84E-25	0.124269
Gheraphene	-0.482224	0.0597558	7.16E-08	0.124269
Son*Son	-0.270624	0.0968154	0.0108445	0.201339
I.L*I.L	-11.8708	0.220036	5.20E-24	0.457591
Ghe*Ghe	-4.93896	0.0968154	1.67E-23	0.201339
Son*I.L	-0.176245	0.0675783	0.0164253	0.140537
Son*Ghe	-0.317501	0.0731856	0.000289341	0.152198
N = 30	Q2 =0.997	Cond. no. =9.874	R2 adj. =0.998	
DF = 21	R2 =0.999	RSD =0.2535	Conf. lev. =0.95	

Table 4. The ANOVA result showing lack of fit (p=0.374) and high regression (p=0.000)

Current	DF	SS	MS (variance)	F	p	SD
Total	30	11002.5	366.751			
Constant	1	9966.34	9966.34			
Total corrected	29	1036.18	35.7302			5.97748
Regression	8	1034.83	129.353	2012.54	0	11.3734
Residual	21	1.34974	0.0642736			0.253522
Lack of Fit(Model error)	18	1.22774	0.068208	1.67725	0.374	0.261167
Pure error(Replicate error)	3	0.122	0.0406667			0.20166
N = 30	Q2 =0.997	Cond. no. =9.874	R2 adj. =0.998			
DF = 21	R2 =0.999	RSD =0.2535				

Influence of the used ionic liquid molar mass

In this section we describe the effect of used ionic liquid molar mass on maximum current of DPV peak (I_{pic}) in three levels. Common organic solvents that already used for HF-LPME cannot be used here. Because the used solvent must be able to establish electrical connection between the solution and the electrode. Therefore, three type of ionic liquid such as: 1-ethyl-3-methylimidazolium tetrafluoroborate ($197.97 \text{ g mol}^{-1}$), 1-buthyl-3-methylimidazolium hexafluorophosphate ($284.18 \text{ g mol}^{-1}$), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ($298.21 \text{ g mol}^{-1}$) were selected according to their molar mass. The results shown in Table 3

demonstrate that the molecular weight of ionic liquid compared with other factors, has the greatest impact on maximum current of DPV peak (I_{pic}). The contour plots in Figure 4 presents the effects of ionic liquid molar mass on I_{pic} in three levels listed above: $197.97 \text{ g mol}^{-1}$ (4a), $284.18 \text{ g mol}^{-1}$ (4b) and $298.21 \text{ g mol}^{-1}$ (4c) when the value of the other factors maintained at a choice levels according to Table 2. The numbers inside the Figures represent the maximum current of DPV peak (I_{pic}) along each line. The results show that with increasing the molecular weight of ionic liquids, I_{pic} is too high. But, if the molecular weight of ionic liquid to raise more, I_{pic} will be reduced.

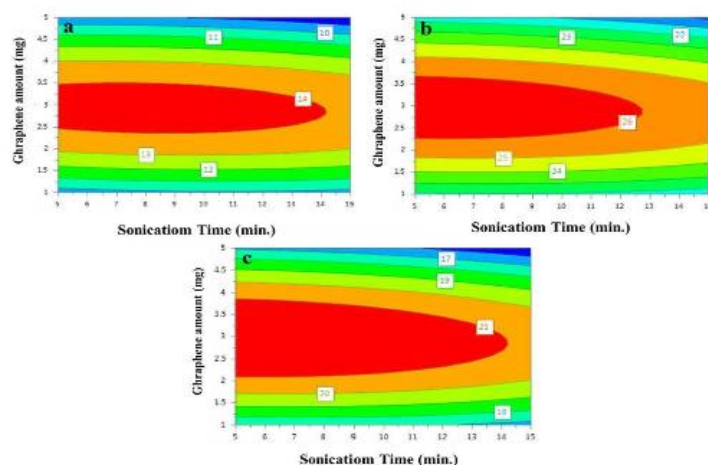


Figure 4. Contour Plots of maximum current of DPV peak (I_{pic}) as a function of ionic liquid molar mass, (a) $197.97 \text{ g mol}^{-1}$ (b) $284.18 \text{ g mol}^{-1}$ (c) $298.21 \text{ g mol}^{-1}$

Amount of nanoparticle effect

At this standpoint, three levels of 0.001, 0.003 and 0.005 g were considered for amount of rGO nanoparticle. First, constant volume of selected ionic liquid in the previous section (0.5 mL) was added to a tube and then electrodes were put in that and ultrasonicated for ten minutes. By this action, we led to gentle dispersion of rGO nanoparticles in the ionic liquid and nice permeation into the fiber pores. The results show that increasing the amount of

nanoparticles, decrease fluidity of the mixture, thus the connection between the analytes and the ionic liquid and make deliver them to the electrode surface will be difficult. The contour plots in Figure 5 presents the effect of nanoparticle amount on I_{pic} in three levels: 1mg (5a), 3 mg (5b) and 5 mg (5c) when the value of the other factors maintained at a choice levels according to Table 2. The numbers inside the Figures represent the maximum current of DPV peak (I_{pic}) along each line.

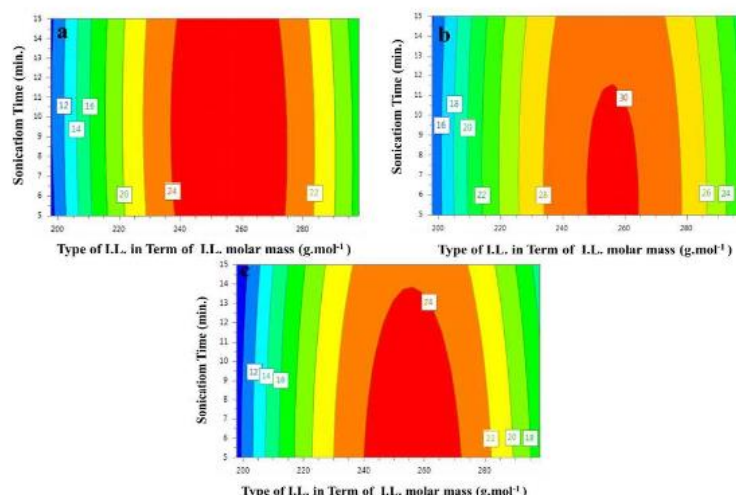


Figure 5. Contour Plots of maximum current of DPV peak (I_{pic}) as a function of rGO amount, (a) 1 mg (b) 3mg (c) 5 mg

Impression of sonication time

Sonication time of hollow fiber in ionic liquids has a direct effect on the extraction process. Because of increases in the sonication time, the amount of ionic liquid inside the hollow fiber increases and the contact area between two phases enhances and causes the mass transfer is well done. Also, the electrical connection between the electrodes and the solution from the electrical point of view is better established. But if too much time is spent for sonication, hollow fiber holes are completely filled and increasing the time will be ineffective. The contour

plots in Figure 6 presents the effects of sonication time of hollow fiber in mixture of ionic liquids and rGO in three levels: 5 min (6a), 10 min (6b) and 15 min (6c) when the value of the other factors maintained at a choice levels according to Table 2. The numbers inside the Figures represent the maximum current of DPV peak (I_{pic}) along each line. The results show that with increasing the sonication time, I_{pic} is too high. But, if the sonication time exceeds the optimum value, I_{pic} will be reduced. The overall optimized factors are shown in Table 5.

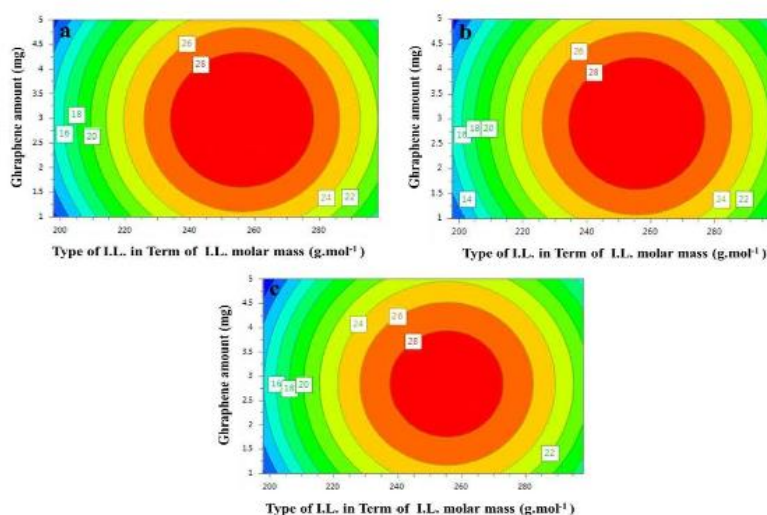


Figure 6. Contour Plots of maximum current of DPV peak (I_{pic}) as a function of sonication time of hollow fiber in mixture of ionic liquids and rGO, (a) 5 min. (b) 10 min (c) 15 min

Table 5. Optimized factors of proposed method

Number of factors	Factor	Level			Selected level
		1	2	3	
1	Sonication Time (S)	300	600	900	600
2	Ionic Liquid Molar Mass (g.mol ⁻¹)	197.97	284.18	298.21	284.18
3	Amount of Nano Particle (gr)	0.001	0.003	0.005	0.003

Analytical figures of merit

In the optimized conditions which were obtained after one steps experimental designed, the calibration equations are derived by regression analysis between measurements of peak current and standard concentrations of analytes. Calibration curves were linear in the range of 0.9–550 µg L⁻¹ and 0.7–500 µg L⁻¹ for Zn(II) and Cu(II) ions respectively with correlation coefficients 0.998 and 0.997. The limit of detection (LOD) of the new method for determination of Zn(II) and Cu(II) was studied under the optimal experimental conditions. The LODs were obtained from $C_{LOD} = (K_b S_b / m)$, where m is the slope of the calibration graph, K_b is the numerical value of 3 and S_b is the standard deviation of five

replicates of the blank measurement. LODs were 0.27 and 0.21 µg L⁻¹ of Zn(II) and Cu(II) respectively. The relative standard deviations (RSD) were bellow of 5% (3.2%, n=5, $C_{Zn}=50 \mu\text{g L}^{-1}$ and 4.4%, n=5, $C_{Cu}=50 \mu\text{g L}^{-1}$). It clearly shows that the proposed method of this study has good sensitivity and precision with a wide dynamic linear range.

Effect of interfering ions

In this section the effects of prevalent interfering ions on determination of Zn (II) and Cu (II) by HF-PGE extraction method were checked. In these experiments, mixed solutions of 50 µg L⁻¹ Zn(II) and Cu(II) containing the interfering ions were treated. Table 6 shows results.

Table 6. Tolerance ratio of interfering ions in the determination of 50 µg.ml⁻¹ of Zn(II) and Cu(II)

Interfering ions	5% tolerance ratio ($W_{ions}/W_{\text{target metals}}$)	
	Zn (II)	Cu(II)
PO ₄ ³⁻ , SO ₄ ²⁻ , Cl ⁻ , F ⁻ , Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	1000	1000
Fe ³⁺ , As ³⁺ , Hg ²⁺	500	500
Pb ²⁺ , Cd ²⁺	200	200
Co ²⁺ , Ni ²⁺	25	25
Cu ²⁺	25	-

Real samples analysis

To do the analysis of real samples we applied the presented method for the designation of Zn (II) and Cu (II) in different water samples. Well, mineral and tap waters were gathered from the different parts of the city of Kermanshah, Iran and wastewaters were collected from the industrial region of Kermanshah, Iran. Filtration was performed for all samples prior to use. We spiked from Zn (II) and Cu (II) ions to some of samples because they were lacking ions. The relative recovery studies were conducted by three times spiking real water samples at a concentration level of $50\mu\text{g.L}^{-1}$,

before extraction. Then the real samples diluted by supporting electrolyte for simultaneous pre-concentration and determination, and analyzed by spiking with adequate concentrations of standard metal ion solutions. All electrochemical measurements are repeated three times. We also spiked the standard solutions of cations into real samples to illustrate the ability of HF-PGE method to extraction of ions. The relative recovery of real waters was determined as the ratio of the concentration in the real water and distilled water samples spiked at the same concentration level. Table 7 and Figure 7 show the results.

Table 7. Determination of the Zn(II) and Cu(II) ions in various water sample

Sample	Spiked level ($\mu\text{g.ml}^{-1}$)		Found ($\mu\text{g.ml}^{-1}$)		Recovery (%) [*]	
	Zn ²⁺	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺	Cu ²⁺
Mineral Water	0.00	0.00	ND	ND	-	-
	50.00	50.00	48.7±0.21	48.1±0.41	97.4	96.2
Tap Water	0.00	0.00	31.4±0.27	2.3±0.19	-	-
	50.00	50.00	79.65±0.34	50.1±0.26	96.5	95.6
River Water 1	0.00	0.00	14.5±0.43	4.7±0.21	-	-
	50.00	50.00	61.6±0.52	56.4±0.37	94.2	103.4
River Water 2	0.00	0.00	18.3±0.37	3.2±0.22	-	-
	50.00	50.00	65.8±0.65	54.1±0.41	95.0	101.8

^{*} Calculated using, $\%R = [(F - I)/A] \times 100$ where F and I are the determined concentrations of spiked and unspiked samples, and A is the concentration of analyte added to spiked sample.

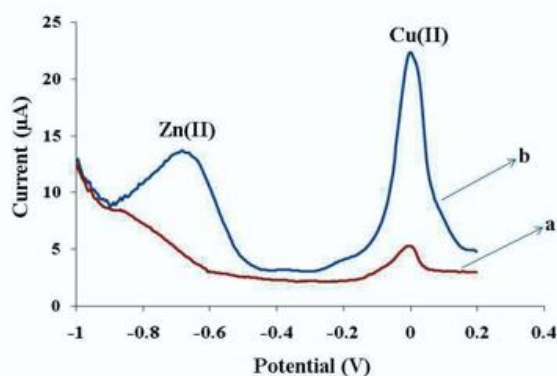


Figure 7. Differential pulse voltammogram (DPV) of real sample (a) before (b) after spike, by HF-PGE method in optimum conditions

Conclusion

This research presented the results achieved by in-house fabricated electrode (HF-PGE) for electrochemical DPV analysis of Zn (II) and Cu (II) ions. The coupling of three-electrode configuration system with differential pulse voltammetry has prepared tools of a comparatively cheap in place sensor for trace levels of zinc and copper. In this work, target metal ions detected with using the optimized method for modules. By the optimized conditions mentioned above, obtained results show that the HF-PGE electrochemical sensors have an enough sensitivity and reproducibility for DPV determination of zinc and copper in the parts per billion ranges. The linear dynamic range acquirable with HF-PGE/DPV was wide.

Real water samples were evaluated for the environmental samples and it was observed that suggested method was usefulness for the determination of zinc and copper and this showed that the success in developed HF-PGE electrochemical sensors on matrices effect for analytes monitoring. The used nanosorbent has properties such as: small particle size and its homogeneous dispersion within the ionic liquid background that enhanced its sorbent capacity. The intense interplay between analyte and nanosorbent is one of the main advantage of our suggested method. Wall pores of hollow fiber are

the kennel which the nanosorbent and analyte molecules were trapped in there and conflict with each other. Meantime, the size exclusion selectivity to the analyte molecules is done by pores. New design device has many useful properties such as: Flexibility, simplicity, disposable nature that overcome on the facility of sample carry over, and these properties increase efficiency of this method as a one of its main advantages. Our research illustrated that electroactive analytes such as metal ions exist in the feed can be measured at one step simultaneous purification and determination by the HF-PGE/DPV. Polar analyte from the same sample often cannot be measured by conventional SPME coatings and this allows by HF-PGE/DPV that this is another advantage for suggested method. In addition, we easily use of all kind of nanoparticles in HF-PGE/DPV method as well as retouch ability of the nonabsorbent structure; these caused that we could determine a wide range of electroactive analytes with high level of selectivity and specificity. This method is comparable, although we don't use of modern and costly tools. Table 8 is a review of selected methods which used in the designation of Zn (II) and Cu (II) in real samples.

Table 8. Comparison between proposed and other methods of determination of Zn(II) and Cu(II) ions in real samples

Metal ions	Date	Type of real samples	Extraction method	Detection method	LOD ($\mu\text{g.ml}^{-1}$)	DLR ($\mu\text{g.ml}^{-1}$)	RSD%	Ref.
Zn	2016	Tap and river water	HF-SLPME	DPASV	0.015	-	3.6	[42]
Cu	2011	Rice	HF-SLPME	DPASV	0.007	0.01-100	<5	[43]
Zn	2015	Ointment and collyrium	MCPE	DPASV	11.11	19.6-3269	-	[44]
Zn	2016	Drinking water	MSPCE	SWASV	0.09	0.1-100	-	[45]
Zn	2016	Pharmaceutical	BIA-SWV	SWASV	8.50	-	<1	[46]
Zn	2015	Freshwater	SPE- μ SILOV	Colorimetric	2.39	-	-	[47]
Cu					0.11	-	-	
Zn	2016	Water and food	SPE	FAAS	0.13	-	3	[48]
Zn	2014	Freshwater, hemodialysis solution and tuna fish	CPE	FAAS	2.3	0.37-2.6	2-2.6	[49]
Zn	2012	Water and cereal	SPE	FAAS	1.02 and 0.48	-	2.5 and 3.4	[50]
Zn	2013	Water (tap, dam and well water), biological (hair and nail), liver samples	SPE	FAAS	2.2	-	1.2	[51]
Zn	2016	Mineral, tap and river water	HF-PGE	DPV	0.27	0.9–550	3.2	Present work
Cu					0.21	0.7–500	4.4	

HF-PGE: Hollow fiber - pencil graphite electrode, HF-SLPME: Hollow fiber solid-liquid phase microextraction, MCPE: Modified carbon paste electrode, MSPCE: Modified screen-printed carbon electrode, BIA-SWV: Batch-injection analysis system with square-wave voltammetry, SPE- μ SILOV: Solid phase extraction in a micro sequential injection lab-on-valve, SPE: Solid phase extraction, CPE: Cloud point extraction, DPASV: Differential pulse anodic stripping voltammetry, SWASV: Square wave anodic stripping voltammetry, FAAS: Flame atomic absorption spectrometry.

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