In situ pre-concentration and voltammetric determination of trace lead and cadmium by a novel ionic liquid mediated hollow fiber-graphite electrode and design of experiments via Taguchi method

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ABSTRACT

In this research a single-use voltammetry sensor, incorporating a three electrodes configuration was developed, using ionic liquid mediated hollow fiber-graphite supported nanomagnetite working electrode. These electrodes coupled with differential pulse voltammetry (DPV) provided a screening tool for in-situ pre-concentration and determination of trace levels of Pb(II) and Cd(II). In this design, a two-centimeter piece of porous polypropylene hollow fiber membrane was impregnated with homogeneous mixture of nanomagnetic particles/ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate), and a graphite rod was located inside the fiber lumen. In this sensor, synthesized nanoparticles such as zero-valent Iron (ZVI), nanomagnetite (NM) and magnetic hollow spheres (MHS), dispersed in the ionic liquid, were used for one-step simultaneous purification, pre-concentration and trapping of pb(II) and Cd (II) ions from water samples. The Taguchi method was applied as an experimental design to determine optimum conditions for lead and cadmium ions removal. The experiments were designed, in two steps, according to Taguchi's method, OA_{16} L_{18} $(2^1 \times 3^5)$ and OA_{16} L_{16} $(2^1 \times 4^3)$ orthogonal were arrayed to the optimize experimental runs. Various affective parameters were investigated. The effect of all the input parameters on the output responses was analyzed using analysis of variance (ANOVA). The results revealed that the metal removal was influenced primarily by the amount of nanoparticle (52.18%) and agitation rate (19.71%). The extraction time (8.97%) and mercury acetate concentration in the electrolyte (7.6%) had little significant influence on metal removal efficiency. The performance characteristics of the developed method were evaluated by assessing response linearity and precision. The method was suitable for the quantitation of pb(II) and Cd(II) ions in the concentration range of 2–13000 ng. mL^{-1} and 0.6–6500 ng. mL^{-1} for Cd(II) and Pb(II) ions respectively. The detection limits recorded for Cd(II) and Pb (II) were 0.61 and 0.19 ng.mL^{-1} with relative standard deviation (RSD) of 4.6%, and 2.3%, respectively. Moreover, successful applications of the sensing device to real water samples were demonstrated.

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1. Introduction

Human activities through technological development and industrial events discharge heavy metals into the environment which has become a matter of concern over the past few decades, due to the characteristics of metals to cause contestable effects by reducing the quality of life in the environment [1–3]. From this perspective, removal of heavy metals is very important because they are non-biodegradable [4,5].

Among the available techniques for trace elements analysis electrochemical methods are very attractive in this field [6–8]. Different types of electrodes such as hanging mercury electrodes, mercury plated thin film and glassy carbon electrode were used in field experiments [8–10]. However, due to the difficulties in using the electrodes for field analysis, the development and application of single-use electrodes is widely reported [11,12]. Disposable electrodes are designed for one use and therefore have the advantages of not being affected by the problems associated with carryover of contaminants and this minimizes the damage often associated with a re-usable sensors [13].

Also, sample preparation techniques have been widely used for the pre-concentration and separation of trace metal ions in

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aqueous systems prior to their determination. Among the available techniques, solid phase microextraction (SPME) is one of the most interesting methods [14,15]. SPME fibers, however, are expensive and have fragile coatings and should be handled carefully. So, this study aimed to promote the SPME technique by inserting nanoparticles into the pores of polypropylene hollow fibers via an organic solvent as a solid/liquid sorbent. Hence, the idea was to have a membrane based, activated nanoparticles that acts as an analyte trap, lead in higher selectivity and enrichment, because the nanoparticles act as solid sorbents do in SPME fibers. So, the attachment of the analyte was accomplished by two different chemical approaches; non-covalent and covalent binding. Results showed significant improvement in the ordinary SPME fibers [16,17].

In the present work this μ-SLPME fiber was coupled with an electrochemical system. In this new application, the role of the background solvent is important. So the solvent would allow metal ions to penetrate into the membrane. The solvent also should be consistent with the structure of the fiber, so that would do not leave the fiber pores. Many solvents were tested and finally an ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) was selected.

Furthermore, an electrical conductor interface was needed. The electrical contact was established via a graphite pencils that were placed inside the fiber and connected to a copper wire. In this context, the used device for this study was provided by the authors. Disposable nature of the fiber (although this fiber can be reused multiple times) eliminates the risk of carry over, too. Easy preparation process, low background current, high sensitivity, stability, and small loading of nanoparticle using this combination can create new potentials and applications for fabricating robust sensors for many important species.

According to the conditions listed above, the present study aimed to couple this innovative nanoparticle assisted hollow fiber graphite sensor with 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 a pseudo electrochemical sensor for Pb(II) and Cd(II) metal ions.

2. Experimental

2.1. Chemicals and Materials

The Accurel Q 3/2 polypropylene hollow fiber membrane which was used here was obtained from Membrana (Wuppertal, Germany). The wall thickness of the fiber was 200 μm, the inner diameter was 600 μm, and the pore size was 0.2 μm.

Some of nanoparticles such as zero-valent Iron (ZVI), nano-magnetice Fe_3O_4(NM), magnetic hollow spheres (MHS) were synthesized in the authors' laboratory. Analytical $FeCl_3$ .6H$_2$O, $FeCl_2$ .4H$_2$O, $FeSO_4$.7H$_2$O, Hg(CH3COO)$_2$, NaClO$_4$, NH$_3$, sodium borohydride (NaBH$_4$), Ethylenediaminetetraacetic acid (EDTA), n-hexane, surfactants; Span-80 and Tween-80, all were purchased from Merck (Darmstadt, Germany). Ionic liquid, 1-butyl-2,3 Dimethylimidazolium hexafluorophosphate [BDMIM][PF6] was provided by Sigma-Aldrich company (St. Louis, USA). All chemicals which were used were of at least analytical-reagent grade. Triple time distilled and de-ionized water was used throughout.

Stock solutions of 100 mg.L^{-1} of each Cd(II), Pb(II) ions were prepared by dissolving appropriate amount of cadmium 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.

2.2. Instrumentation

All the voltammetric measurements were performed by trace analyzer, Metrohm Model 797 VA computerace (Switzerland), comprising three electrode arrangements such as Ag/AgCl (saturated KCl) as a reference electrode and platinum wire as an auxiliary/counter electrode and the home-made hollow fiber graphite electrode (HF-GE) as a working electrode. The voltammograms of Cd(II), Pb(II) ions were obtained by DPV mode. The volume of the solution introduced in the voltammetric cell was 15.0 mL. The solutions were de-aerated by ultrapure N$_2$ gas for 300 s. The voltammetric experimental variables such as; scan rate of the electrode potential, voltage step, voltage step time, equilibrium time, deposition time and stirring speed of the solution were optimized. The deposition time study was carried out from 0 to 3000 s as the on-line pre-concentration time of analyte.

Effect of deposition potential on peak currents of Cd(II), Pb(II) ions was tested between −0.85 to −0.41 V. The other DPV optimal conditions were as follows; equilibration time 10 s, pulse amplitude 0.09003 V, pulse time 0.01 s, sweep rate 19.8 mVS^{-1}, voltage step 0.007935 V and voltage step time 0.4 s and the operational mode was, differential pulse voltammetry.

Nanoparticles morphology, size distribution and structure were characterized by direct light scattering (DLS, Zetaplus, Brookhaven 9000 instruments), SEM (JEOL JEM2000, Nikon, Japan) and FT-IR spectroscopy (ATI Mattson, Genesis series FT-IR).

2.3. Synthesis of nanoparticles

2.3.1. Synthesis of nano zero-valent iron (ZVI)

This synthesis was stabilized by disodium salt of EDTA (Sample 1). As the zero-valent irons are very active materials in the presence of air and high potential to agglomeration, electrochemical sensor for metal ions ZVI was synthesized by EDTA because chelating agents such as EDTA can be assisted to stabilization of the ZVI [18]. The ZVI was prepared with a chemical reduction procedure. At first 75.0 mL of EDTA solution (0.15 M) was added to 100.0 mL of FeCl$_3$ (0.3 M) solution which was vigorously mixed with magnetic stirrer in the flask reactor. Then 100 mL NaBH4 (1.5 M) was added to this mixture drop-wise at room temperature under a N$_2$ atmosphere. Sweep rate of reduction was 20 mL.min^{-1} and molar ratio Fe$_3^+$/BH$_4^-$ was 1:5 because these conditions have provided maximum surface area (m^2.g^{-1}) and minimum particle size [19]. After adding the whole reagents, color of the solution changed from brown to dark-green and the black nano particles (NPs) were formed (pH 8.5). Finally, black products were rinsed by oxygen-free deionized water three times to remove residual impurities and then vacuum-dried.

2.3.2. Synthesis of the magnetic hollow spheres (MHS) iron nanoparticles

Magnetic hollow spheres iron nanoparticles were prepared according to the previously published method [20]. Briefly, an aqueous solution of NH$_3$.H$_2$O 25.00 wt % (10 mL) as precipitant was dispersed in oil phase containing n-hexane (20 mL), span-80 (1.20 g) and Tween-80 (0.90 g). After 10 min sonication, the aqueous solution containing 3.85 g of FeCl$_3$.H$_2$O and 2.00 g of FeSO$_4$ (70 mL) was added to the previous mixture. This method led to hollow structure with good spherical morphology. The reaction system maintained for 12 h at 20 °C under mechanical stirring at nitrogen atmosphere. The product was washed with deionized water several times and dried in room temperature.

2.3.3. Synthesis of Nano Magnetic Fe$_3$O$_4$ (NM)

Before the addition of any salt, 200 mL of water which was used in the experiments was bubbled with nitrogen for 15 min to remove dissolved oxygen. Then, 5.12 g ferric chloride hexahydrate