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PVDF–ErGO–GRC electrode: A single setup electrochemical system for separation, pre-concentration and detection of lead ions in complex aqueous samples

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ABSTRACT

An effective electrode was developed based on electromembrane extraction (EME) and square wave voltammetry (SWV) for simultaneous separation, pre-concentration and determination of lead (II) (Pb (II)) ions in complex aqueous samples. Electrochemically reduced graphene oxide–graphite reinforced carbon (ErGO–GRC) was utilized in conjunction with the SWV. Pb(II) ions were extracted from an aqueous sample solution into an acidic acceptor phase (1 M HCl) in the lumen of the polyvinylidene fluoride (PVDF) membrane bag by the application of voltage of maximum 6 V across the supported liquid membrane (SLM), consisting of organic solvent and di-(2-ethylhexyl)phosphoric acid (D2EHPA). The parameters affecting the EME were optimized for Pb(II) ions. The optimum EME conditions were found to be 20% D2EHPA in 1-octanol impregnated in the wall of PVDF membrane (PVDF17) as the SLM, extraction time of 20 min, pH of sample solution of 8 and a voltage of 5 V. The PVDF–ErGO–GRC electrode system attained enrichment factors of 40 times and 80% of extraction with relative standard deviations ($n=5$) of 8.3%. Good linearity ranging from 0.25 to 2 nM with coefficients correlation of 0.999 was obtained. The Pb(II) ions detection limit of PVDF–ErGO–GRC electrode was found to be 0.09 nM. The newly developed single setup electrochemical system was applied to complex aqueous samples such as tap, river and sea water to evaluate the feasibility of the method for applications.

1. Introduction

Water contamination is a worldwide problem which deserves attention due to its negative impact on eco-system, human health as well as economical growth. Heavy metals, as one of the pollutant categories receive particular concern due to their high toxicity even at concentration as low as parts per billion (ppb). Furthermore, the toxicity of heavy metals can be increased by transformation to more toxic compounds due to their average long-life. Among heavy metals, lead (Pb(II)) ions is considered as one of the most toxic metal affecting human health by causing damage to organs such as bones, brains, kidneys and muscles and may cause many serious illnesses or even mortality [1]. Thus, there is a need to develop an effective analytical method which allows to detect and quantify extremely low levels of Pb(II) ions in complex aqueous samples due to high matrix interferences.

The common practice in overcoming this issue is to separate and pre-concentrate the metal analyte prior to determination by any analytical technique. Several approaches such as ion-exchange separation [2], single-drop micro-extraction (SDME) [3], dispersive liquid–liquid microextraction (DLLME) [4], solid phase extraction (SPE) [5] and dispersive solid phase extraction (DSPE) [6] are available for the separation and pre-concentration of Pb(II) ions from aqueous samples. However, such procedures are time-consuming and prone to contamination. Recently, the development of hollow fiber-liquid phase microextraction (HF-LPME) and electromembrane extraction (EME) have been considered to overcome such limitations [7,8].

In HF-LPME, target analytes are extracted from an aqueous donor phase (DP), through an organic solvent immobilized in the pores of a hollow fiber as a thin supported liquid membrane (SLM),

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into a microliter volume of an acceptor phase (AP) which is filled inside the lumen of the fiber. The driving force in HF-LPME is passive diffusion of the target analytes based on the partition coefficients (log *P*) and distribution constants (log *D*) from an aqueous DP across a suitable SLM to another aqueous AP solution. Electromembrane extraction (EME) is a new concept of HF-LPME in which an electrical field serves as a driving force for the analytes to transfer between the DP and the SLM and also between the SLM and the AP [9,10].

The whole EME setup mimics a capacitor with two conducting terminals separated by SLM that behaves as an insulator which is known as capacitor dielectric [11]. This technique has been successfully applied on a wide range of metal ions followed by capillary electrophoresis (CE) with capacitively coupled contactless conductivity detection (CE-C4D) [12]. EME provides an excellent sample clean-up and pre-concentration for complex environmental matrix [13,14]. Moreover, smaller volume of AP gives higher enrichment factors (EFs) and better detection limits.

Interestingly, the combination of EME and electrochemical studies has been popular in detecting pharmaceutical active compounds (PhACs) such as sufentanil [15], morphine [7] and dextromethorphan [8]. These studies utilize modified screen printed electrode where the solution from AP is collected using microsyringe and the pH of the solution adjusted before the analyte can be detected using electrochemical techniques. This is due to the low volume and inappropriate condition of aqueous AP in EME such as pH and type of buffer solution, which is not suitable for conventional electrochemical measurements. Till date, no research was carried out on the application of EME as a part of the electrochemical electrode system that can directly separate, preconcentrate and detect heavy metal ions in complex aqueous samples.

In this study, EME was used as a part of the electrode system that can simultaneously separate, pre-concentrate and detect Pb (II) ions. The parameters affecting EME such as type of organic solvent, different PVDF membrane compositions, carrier concentration, extraction time, pH of the donor phase, effect of salt bridge and extraction voltage were optimized. Further, the selective determination of Pb(II) ions was done using electrochemically reduced graphene oxide–graphite reinforced carbon (ErGO–GRC) with a square wave voltammetry (SWV) technique as this electrode shows good recovery of Pb(II) ions for filtered tap and river water in previously reported study [16]. This study proved that the developed PVDF–ErGO–GRC electrode system might be a potential electrochemical approach for the determination of Pb(II) ions in complex aqueous samples.

2. Materials and methods

2.1. Chemicals

Polyvinylidene fluoride (PVDF) was obtained from Sigma-Aldrich (USA). Lead solution (purity > 99.90%), di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-nitrophenyl octyl ether (NPOE), 1-octanol, toluene, and N-methyl-2-pyrrolidinone (NMP) were procured from Merck (Malaysia). The deionised water obtained from Milli-Q system (Millipore, USA) was used in this study to prepare all solutions.

2.2. Fabrication and characterization of PVDF membrane

PVDF (12% (PVDF12), 17% (PVDF17) and 22% (PVDF22)) polymer was dissolved in NMP by mechanical stirring at 300 rpm until complete polymer dissolution. Then, the solution was kept in an ultrasonic bath for 30 min to remove air bubbles and was transferred to room temperature for 24 h before casting process. The polymer solution was cast on a glass plate without any non-woven support using a glass rod to obtain a defect-free flat sheet membrane. The polymer film was then immersed in a non-solvent bath of distilled water at room temperature, where the phase separation started and membrane was formed. No other components were added either to the non-solvent bath or to the polymer solution.

The surface morphology of the fabricated PVDF membrane was studied by field emission scanning electron microscopy (FE-SEM, Hitachi SU8020). The water contact angles were measured by a KRüSS DSA10-MK2 (KRüSS GmbH, Germany). The average contact angle value was obtained by measuring the same sample at five different positions. The thickness of the membrane was measured using a electronic outside micrometer SPG-Japan model DM-25. The membrane porosity was calculated according the method described by Panda and De [17].

2.3. Electroanalysis

All electrochemical measurements were done using SWV which was performed with eDAQ EA161 potentiostat (New South Wales, Australia) equipped with eDAQ EChem (v2.15) software. A conventional three electrode cell configuration was used for the voltammetric measurements. In this study, PVDF–ErGO–GRC, Ag/AgCl (3 M), and platinum wire (1.8 mm) were used as working, reference, and auxiliary electrode, respectively. All potentials were measured versus the Ag/AgCl (3 M) reference electrode.

2.4. Preparation of agarose gel

An agarose solution was prepared by heating a mixture of 2% agarose in 1 M KCl (w/v). The mixture was stirred until it boiling and formed uniform suspension. Then, the warm mixture was poured into the bottom of PVDF membrane bag using a micropipette and allowed to set overnight. Once the agarose was settled, the PVDF agarose membrane was stored in plastic bags to prevent it from drying off.

2.5. Electromembrane extraction

The EME procedure is shown in Fig. 1. A fabricated PVDF membrane was cut into two rectangular pieces (3×2 cm^2) with narrow sharp angle end and overlaid on each other. The two longer and narrow sharp angle ends were thermally sealed using a heat sealer, leaving one side open to form a membrane bag. Each individual membrane bag was immersed in organic solvents (toluene, NPOE, and 1-octanol) and D2EHPA for 24 h followed by drying at ambient temperature. Later, the PVDF agarose membrane bag was filled with 0.5 mL of 1 M HCl (acceptor phase) via a syringe (14.5 mm diameter). A GRC (HB grade, Brand Staedler) electrode (negative terminal) with a diameter of 2.0 mm was inserted through the open end of the membrane bag. Both were secured to each other with a twist tie. The EME device, containing the SLM and the acceptor phase, was then placed in the sample vial and secured by the clamps. A platinum electrode with a diameter of 0.2 mm (positive terminal) was inserted directly into a 25 mL sample solution with an inter-electrode distance of 5 mm in the sample and the acceptor phase. The two electrodes were further connected to the DC supply system using two cable wires with alligator clips. The DC power supply used was Witeg ZS3202 model (Germany) with a programmable output potential difference within the range of 0–32 V, providing currents between 0 and 2 A. Stirring of the solution was carried out by a Stuart UC151 stirrer (UK). After the extraction was completed, the GRC in the acceptor phase was substituted with ErGO–GRC electrode and