

Molecularly Imprinted Polymer (MIP) Based PVC-Membrane-Coated Graphite Electrode for the Determination of Heavy Metals

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Abstract— A PVC membrane based on molecularly imprinted polymer (MIP) coated directly on graphite electrode for determination of heavy metals in real soil sample is describes. The composite membranes have been prepared by using methacrylic acid (MAA) as functional monomer and ethylene glycol dimethyl acrylate (EGDMA) as cross linker. MAA was chosen as a functional monomer, as it capable of strong electrostatic interactions with heavy metals. The chemical behaviour of the thin film (MIP) were characterized using Scanning Electron Microscopy (SEM). The proposed electrode can be used in the pH range of 4.5-8.5 and revealed good selectivity for heavy metals over a wide variety of ions. Finally, the designed electrode was successfully applied as an indicator electrode to determine concentration of heavy metals in soil.

Keywords— molecular imprinted polymer; electrode; heavy metals.

I. INTRODUCTION

During the last decade, molecular imprinting technology has become a well-established analytical tool. It is used to produce artificial recognition elements, mimicking the highly selective recognition features of biological receptors, but with the added advantage of lower price, and higher thermal and chemical stability [1].

Molecular imprinting has been known as a polymerization technique to prepare synthetic polymers with recognition sites for given molecules [2]. Among the different methods available for the preparation of molecularly imprinted polymers (MIPs), the so-called non-covalent approach, which uses only non-covalent interactions between the template and the functional monomers, is probably the most flexible regarding the selection of the functional monomers and the possible template molecules. For the reasons, the non-covalent approach has been the most widely adopted [3].

The procedure for synthesizing an MIP is based on the chemical polymerization of a functional monomer and a cross-linking agent in the presence of a molecule used as a template. After removal of the imprinted molecule, an imprinted polymer is obtained. This polymer contains sites with a high affinity for the template molecule, due to their shape and the arrangement of the functional groups of the

monomer units. The imprinted polymers are used as antibody-like materials for high selectivity and sensitivity, owing to their long-term stability, chemical inertness and insolubility in water and most organic solvents [4,5].

Voltammetry is a powerful electro-analytical technique. The interest in voltammetry comes from the high sensitivity, multi-element measurement associated used in analytical fields. Besides the classical methods, modern techniques such as normal pulse, different pulse, square wave and stripping have become more attractive due to their significantly improved sensitivity. As a consequence, extremely low detection limit (10^{-7} - 10^{-12}) can be achieved. In addition, with the capability for automated on-line monitoring and for in situ measurements, the techniques have received increasing appreciation in many fields of application, especially in water analysis. The unique natures of voltammetry, thus, meet the growing need for to trace analysis in various kinds of samples. Voltammetry techniques can be utilized for determination of a large range of substances [6].

We chose PVC-membrane-coated graphite as the material of the electrode because the PVC-membrane-coated graphite electrode has a large active electrode surface area and is therefore able to detect low concentrations and/or volumes of the analyte. This is significant when only small amount of analyte are available. Moreover, disposable electrodes have

been used by virtue of their high electrochemical reactivity, good mechanical inertness and ease of modification, renewal, and miniaturization [7]. This electrode, when combined with a more highly sensitive and accurate voltametric technique such as differential pulse voltammetry, becomes an attractive electrode for trace analysis [8].

One of the main sources of pollution in the environments is metallic compounds. Metals and metalloids have long been mined and used in numerous application. This has led to a significant increase of metal pollutions. Metals can accumulate in all environmental matrices at either high or trace level of concentration. Therefore, in soils, in plants, air, lakes, rivers, animals, oceanic regions, even in foodstuffs and human being do present the amount of various kinds of metal. Their widespread distribution, especially heavy metals, become serious problems because of their toxicities for animals and human [9].

Heavy metals exist in man, food and various types of environment in low concentration (in a range of ng/kg-mg/kg) [10]. Thus, for the environment, ecology as well as in food control, high sensitive, accurate and reliable trace analytical methods are important. Voltametric technique have proved to be the appropriate due their unique advantages: high sensitivity, multi-elements analysis capability, and inexpensive instruments [11].

There have been a large number of application of these techniques for determinations of heavy metals in varieties of samples.

II. EXPERIMENTAL

Electrochemical studies were performed using an Hydrodynamic Voltammetry galvostat controlled by a IviumSoft version 2.2xx. A three electrode system was used for all measurement; a PVC-membrane-coated graphite electrode as the working electrode and a Pt auxiliary electrode. All measurement carried out with an Ag/AgCl reference electrode.

A. Preparation of MIP

Methacrylic acid (MAA) and ethylene glycol dimethyl acrylate (EGDMA) were mixed in a 5:1 molar ratio of cross-linking agent to functional monomer MAA. The template molecule was added in a 1:8 ratio to functional monomer, acetonitrile was the porogenic solvent used. The monomer mixture was degassed with He for 2 min in an ice bath before and after addition of the initiator.

A control electrode was prepared in every case following the same procedure, but in the absence of template molecule. The control (or non-imprinted polymer-modified electrode) had at any time the same treatment as the imprinted electrode, to ensure that the effects observed are only due to the imprinting features and not to the subsequent treatments under-gone by the electrode.

B. Electrode Preparation

The general procedure used to prepare the PVC membrane is similar to work reported by Prasada Rao [12, 13], Gupta [14] and Ganjali [15]. Exactly 60 mg PVC was dissolved in 2.5 mL of THF. A 40 mg of MIP particles were dispersed in 0.2 mL of DOP and were added to the above solution and homogenized. Graphite electrodes (3 mm

diameter and 10 mm long) were prepared from spectroscopic grade graphite. The electrodes was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water and dried in air. A shielded copper wire was glued to one end of the above graphite was dipped into the membrane solution and the solvent was evaporated. A layer was formed on the graphite surface, and it was allowed to set for 3 hours. The electrode was finally conditioned for 18 hours by soaking in a 1.0×10^{-4} M solution of heavy metals.

C. Sample Preparation

Heavy metals contaminated soils also major subject. Thus, convenient and accurate analytical processes have been developed for trace elements measurements in this kind of sample. The collected soil sample are firstly dried, homogenized, and digested. The obtained solutions are filtered; the filtrates are then diluted to appropriate volume and taken to the analysis.

A number of 0.4 grams of soil samples are weighed and put in a beaker, then added 5 mL of concentrated nitric acid, and digest. Solution formed moved into a glass beaker and add 2 ml of perchloric acid and 2 ml of hydrogen peroxide is then evaporated to dryness. Results evaporation diluted with demineralized water to obtain a solution of 10 ml. For the purposes of analysis used 2 ml of this solution and 5 mL supporting electrolyte solution was then diluted to 10 ml. Calculation of concentration by standard addition method.

An illustration for soil analysis involve simultaneous determination of Zn, Cu, Cd and Pb combining DPASV. In this method, digested soil samples are adjusted to pH 2. In another experiment, SWASV s utilized for simultaneous determination of Cu, Sn and Sb in soils.

III. RESULT AND DISCUSSION

In the analysis by voltammetry, footage should be in the form of a solution and were observed to be in the form of ions. Generally for the analysis of ions dissolved in water does not require pre-treatment except filtering. For the analysis of ions in the form of solid materials such as soil should be done dissolution and breakdown (decomposition) first. Problems in the analysis of voltammetry is usually derived from the decomposition are not perfect so there are ions that are not in the free state, is still bound to the matrix so it cannot be detected. Dissolution and decomposition of materials commonly done with a mixture of a strong acid with hydrogen peroxide.

A. Characterization of Graphite Electrode

SEM analysis aims to determine the morphology of the surface of a solid structure. Fig. 1 shows the results of characterization using SEM on carbon graphite with a magnification of 15000x. Results of SEM analysis of carbon graphite as shown in Fig. 1. It appears that the surface of the carbon graphite has a porous structure. The presence of pores that causes carbon graphite has the ability adsorbed. Carbon graphite pore size can be sized micro, meso or macro and the combination of du or third that size. Pore structure formed depends on the material forming the graphite carbon, physical activation and chemical.

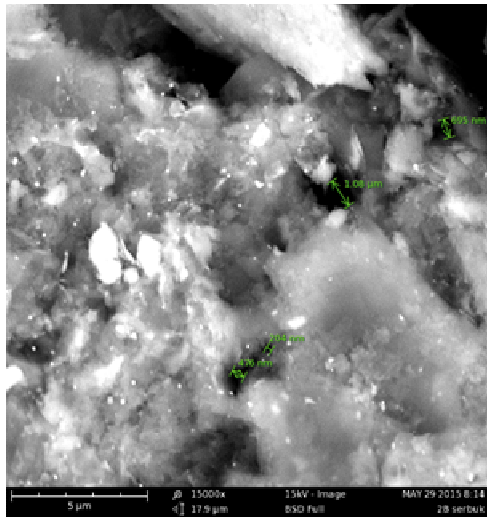


Fig. 1 Carbon Graphite Electrodes with SEM

In addition to knowing the structure of the surface morphology of carbon graphite, SEM can indicate the composition of the elements or compounds contained in the carbon graphite. From the results obtained SEM carbon graphite carbon graphite composition shown in Fig 2. The highest content of C atoms in carbon graphite, followed by the elements Si, Al, and Oxygen.

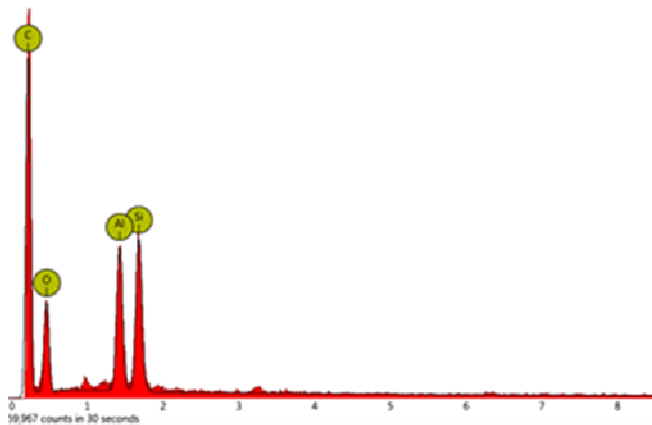


Fig. 2 The elemental composition of the carbon graphite

B. Working Potential Determination of PVC-Membrane-Coated Graphite Electrode

Advantages of elemental analysis by stripping voltammetry is no need for the provision of long samples, such as the separation between elements of major and minor and concentration prior to analysis. In voltammetry analysis, ions are separated from each other in accordance with the reduction-oxidation potential, so that the elements do not interfere major minor elemental analysis. In anodic stripping voltammetry, concentration is done at the time of the analysis conducted by the reduction observed ions into metal collected at the electrode surface, by installing a fairly negative potential of the oxidation-reduction potential ions. These conditions shorten the course of the provision of benefits for the sample, so the error analysis obtained during the sample provision does not exist.

In order to raise the sensitivity of voltammetry, in addition to use stripping technique, also used pulse technique, including normal pulse, differential pulse and pulse square wave. So far, because of the sensitivity of differential pulse voltammetry and square wave voltammetry is high enough, both of these techniques are widely used for quantitative analysis. The combination of stripping techniques and pulse techniques are very appropriate for the analysis of metallic elements. Limit of detection of ions Zn, Cd, Pb and Cu by using square wave anodic stripping voltammetry (SWASV) is smaller than the method differential pulse anodic stripping voltammetry (DPASV) and AWASV analysis time is much faster than DPASV.

Fig. 3 shows the voltammograms technique square wave anodic stripping voltammetry, after deposited for 120 seconds. Peak visible reduction $-0,98V$ Zn, Pb at $-0,60$ V, Cd at $-0,54$ V and Cu at $-0,12V$. Based on these voltammograms peaks calculating the concentration of the standard addition method.

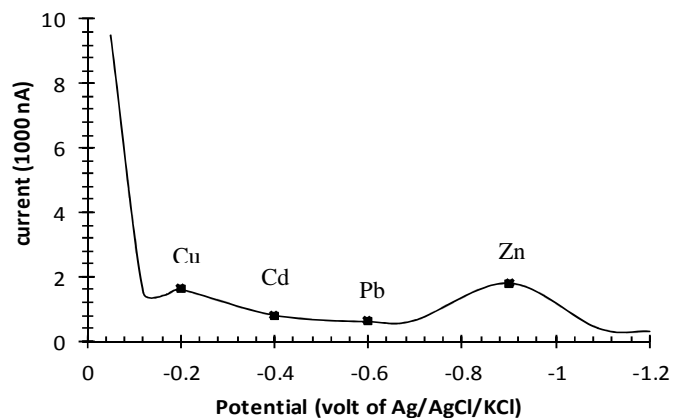


Fig. 3 Square wave anodic stripping voltammograms with deposition potential -1.3 volts/Ag,AgCl/KCl for 120 seconds

C. PVC-Membrane-Coated Graphite Electrode Test in Measurement of Heavy Metal Contents in Soil

Analysis of Cu, Cd, Pb and Zn using anodic stripping voltammetry technique with operating parameters as follows: 60 seconds deposition time, deposition potential -1.3 volts, the scanning speed of 200 mV / sec in a positive direction. Potential peak in -1.04 V Zn, Cd in -0.53 V, Pb in -0.46 V and Cu in -0.06 V. For supporting electrolyte is used acetate buffer pH 4.5.

Analysis of Ni and Co by adsorption stripping voltammetry technique using a supporting electrolyte ammonium tartrate buffer (pH 9) with complexing dimethylglyoxime (DMG). SWV method is used with the following operating parameters: 60 seconds deposition time, deposition potential -0.70 volts, the scanning speed of 200 mV/sec toward negative. DMG concentration of 2×10^{-5} M. Potential peak in -1.1 V for Ni and Co in -1.2 V. Results of the analysis of the levels of heavy metals in soil samples can be seen in Fig. 4.

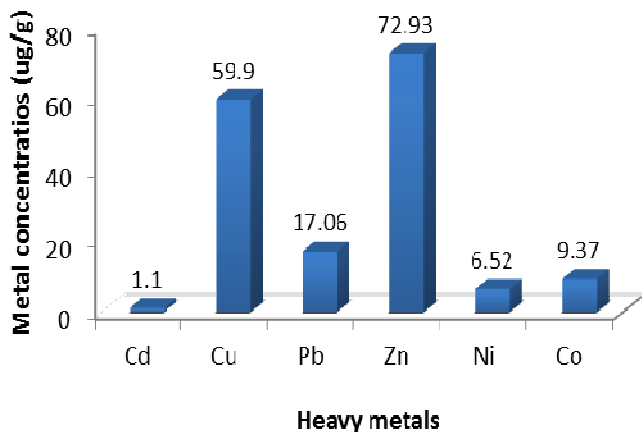


Fig 4. The concentration of heavy metals in soil samples

Percentage of recovery (% recovery) stating how much precision analytical methods to determine the concentration of ions in the material, the concentration is calculated from the results of the determination of the actual concentration divided into standard material multiplied by 100%. Recovery of heavy metals in soil samples can be seen in Fig. 5.

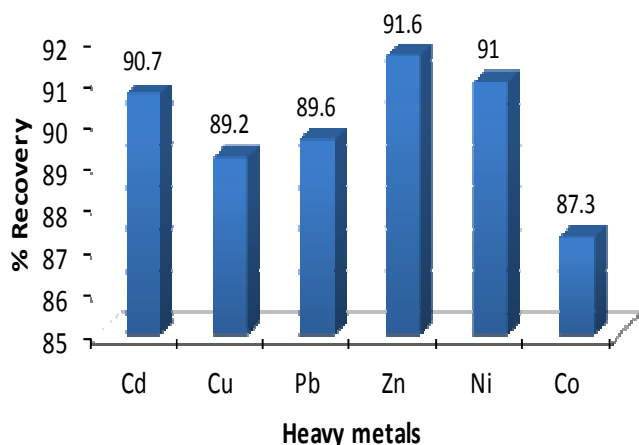


Fig. 5 Recovery of heavy metals in soil samples

IV. CONCLUSIONS

The graphite-coated membrane electrode, prepared with molecularly imprinted polymer under optimal PVC-membrane ingredients, revealed a near Nernstian response over a wide heavy metals concentration range, fast response time and selectivity over a large number of metal ions. The analytical applicability of proposed sensor was checked by

the determination and recovery of heavy metals (Cd, Cu, Pb, Zn, Ni, Co) in soils.

Voltammetry transduction adds the capacity of discriminating between species and identifying adsorption at bare electrode surface or imprinted sites, since it does not rely totally on the MIP element for the identification. The electrochemical potential is additional information enhancing the selectivity of the sensor. Therefore, it might be concluded that MIP-based voltammetric electrodes are very promising elements for highly selective analytical sensors.

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