Novel Ce-incorporated zeolite modified-carbon paste electrode for simultaneous trace electroanalysis of lead and cadmium

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ABSTRACT

Cerium incorporated zeolite-modified carbon paste electrode (Ce-ZCPME) was studied for the anodic stripping voltammetric detection of lead and cadmium ions. The modified electrode which was fabricated in-house by a prior hydrothermal synthesis of Ce-impregnated zeolite displayed satisfactory results compared to other reported electrodes. Deposition of the metal was achieved at a potential of -1.2 V (vs. Ag/AgCl) for 120 s followed by a square wave stripping scan from $-1.6-0.0$ V. Various experimental conditions which include nature of supporting electrolyte, pH, amplitude, frequency, deposition potential and deposition time were optimized prior to the analyses. The fabricated electrode revealed a linear behavior over the metal ion concentrations with a LOD (S/N = 3) of 0.07 ppb and 0.46 ppb for lead and cadmium detection, as well as a good reproducibility (RSD 2.23%) respectively. The fabricated electrode has the potential to be used in the analysis of environmental samples due to its lack of toxicity, ease of fabrication and relative inexpensiveness.

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1. Introduction

Heavy metals are naturally occurring elements, which are found in varying concentrations in all ecosystems. Over the years through several technological advancement and industrial developments, human activities have seen the release of these metals into the environment which has today turn into an issue of extreme concern. While there is still no clear definition of heavy metal, it is sometimes referred to as any metallic element with a high relative density (>5 g/cm^3) and is toxic or fatal even at low concentrations [1]. Heavy metals include lead, chromium, nickel, cadmium, cobalt, mercury, iron, arsenic, silver, and the platinum group elements. The major health risks associated with heavy metals comes from exposure to lead, cadmium, mercury and arsenic [2].

Cadmium, a highly toxic metal contributes significantly to a number of health cases which include diabetes, cancer and heart diseases [3]. It is considered more deadly than either mercury or lead and concentrates mainly in the kidney, and liver. Exposure to cadmium is increasing today as a result of its use in batteries, in alloys for bearings and as coatings. The industries manufacturing these products, in turn, contaminate air, water and food with the metal.

Lead is another frequently encountered toxic contaminant in the environment due to its use in car batteries, in paints and in gasoline. It is associated with several health issues, such as digestive, neurological, cardiac, and mental disorders. As a matter of fact, about thirty critical health conditions have been attributed to lead, many of which affects children, infants and the unborn. Lead is believed not to have any known benefits in the body. It competes with calcium in the bones and hence delays osteoporosis (a medical condition which causes the bones to become weak and brittle).

Optical techniques which include atomic absorption spectrometry (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) have been reported for the detection of these metals over the years. However, these techniques require sophisticated instruments, a well-trained operator, consume a lot of power, and are not convenient for field applications. Electroanalytical techniques, on the contrary, offer a relatively simple approach with various advantages, which include rapid analysis, portability, high selectivity and sensitivity. In addition, stripping voltammetric techniques are preferred for the detection of trace levels of heavy metals due to their speed, simplicity, sensitivity,

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low power consumption, low cost, and minimal sample pre-treatment [3,4].

Conventionally, mercury electrodes are being used for stripping voltammetry and have been widely applied for trace metal determinations [5,6]. However, due to its toxicity, mercury has been restricted for use as an electrode material. Furthermore, it suffers some drawbacks in the detection of some metals whose oxidation potentials appear more positive than that of mercury (such as silver and gold) [3], and is not convenient for the detection of metals which are not soluble in mercury (e.g., arsenic) [4]. As a result, the development of new alternative electrode materials with comparable performances becomes necessary. A number of alternative electrode materials for various electroanalytical applications have been reported. These include bismuth-modified electrodes [7–12], silver electrodes [13–15], gold electrodes [16–20], and so on. However, the major obstacles that prevent the application of such electrodes in anodic stripping studies are due to lower cathodic potential limit and high background contributions. This has led to the further discovery of other alternative electrode materials for electroanalytical purposes. Among such materials are those who utilized zeolites for modifying carbon paste electrode for enhanced electroanalytical performances.

Zeolites as a result of their cation exchange property are being used for modifying carbon paste electrodes for the determination of several metal ions and have shown an improvement in detection sensitivity. Although a few studies were reported on the detection of heavy metals such as lead and cadmium at zeolite modified electrodes [21–25], several reports have been published on the application of this electrode for other electrocatalytic purposes [25–32]. The electroanalytical behavior of bismuth-modified zeolite doped carbon paste electrode for trace analysis of cadmium and lead was studied in 0.1 M acetate buffer (pH 4.5) by stripping technique [25]. Electrode was found to display good sensitivity towards cadmium and lead with a detection limit of 0.08 μg/L and 0.10 μg/L respectively. Various transition metal ions incorporated ZSM-5 modified electrode were studied for the electrocatalytic oxidation of glucose [26]. It was found that the sensor incorporated with Ni(II) ion displayed the highest sensitivity towards glucose oxidation. The electrocatalytic reduction of nitrate species at Cu(II) ion-exchanged ZSM-5 modified electrode was carried out using cyclic voltammetric technique [28]. The electrode was found to exhibit good electrocatalytic activity towards nitrite species reduction. Ag(I) ion incorporated zeolite-Y was investigated for electrochemical behavior in an aqueous solution containing several anions [30]. The Ag(I) ion-exchanged zeolite-Y displayed remarkable selectivity for Cl^- and Br^- ions. Ni(II) ion-exchanged zeolite Y was investigated for electrocatalytic oxidation of methanol [32]. Several methods of electrode preparation were studied, and the results showed that electrode material developed by both cation exchange and open circuit accumulation methods displayed reasonable electrocatalytic activity.

In a previous report, we studied the application of La-incorporated zeolite modified carbon paste electrode for the detection of cadmium ions [33]. It was found that the electrode was sensitive towards Cd(II) detection with a LOD of 0.12 μg/L, which was shown to compare well among various reported electrochemical sensors for Cd(II) detection [33]. In continuation of our effort towards finding alternative electrochemical sensors for various applications, we report here the fabrication of yet another novel electrochemical sensor based on Ce-incorporated zeolite modified electrode for trace level detection of lead and cadmium. The response of this sensor towards increasing concentrations of lead and cadmium ions was studied and the results compared to those from already established from literature.

2. Experimental

2.1. Chemicals and solutions

All chemicals utilized in this study were of analytical grade purity and were used as received without further purification. Silica gel, anhydrous $NaAlO_2$, and KCl were bought from Sigma-Aldrich, NaH_2PO_4, Na_2HPO_4, phosphoric acid and stock solutions of Pb and Cd, BDH chemicals, NaOH and H_2SO_4, Panreac Quimica, NH_4OH, glacial acetic acid and ammonium acetate, Fisher Scientific. All solutions used were prepared fresh using double distilled water.

2.2. Apparatus

X-ray diffraction (XRD) measurements were obtained on a Rigaku-Miniflex II diffractometer using Cu K α radiation in the 2θ angle range 5° to 50°. To determine the surface morphology, FESEM microscopy was carried out using LYRA 3 dual beam microscope equipped with energy dispersion scattering (EDS) system. Solid state ^{27}Al NMR was obtained on JEOL Lamda-500 multi NMR spectrometer equipped with MAS probe. Electrochemical measurements were obtained using a CHI 760E potentiostat (CH instruments, USA) using the three electrode configuration. The working, reference and auxiliary electrodes were the zeolite modified carbon paste, Ag/AgCl and platinum electrodes respectively.

2.3. Hydrothermal synthesis of H-MOR

An already reported procedure for the synthesis and modification of the zeolite was adopted in this study [33]. Briefly, we synthesized a gel with the molar composition $6Na_2O:Al_2O_3:30SiO_2:780H_2O$ as follows; NaOH (2.10 g) was added to deionized water (20 g) and stirred until it dissolved. $NaAlO_2$ (0.63 g) was added and further stirred. When a homogeneous mixture was formed, deionized water (34.13 g) was further added. Lastly, SiO_2 (6.95 g) was added and stirred for 1 h during which the mixture was allowed to age to form a gel. The gel was thereafter added into a Teflon-lined autoclave and was crystallized in an oven at 180 °C for 48 h. The material formed was centrifuged and washed several times with DDW until the pH drops below 9. The sample was allowed to dry overnight at room temperature so as to obtain the crystal powder. The crystal was calcined at 550 °C to expel all organic matter present.

Ion exchange of the (Na-MOR) was performed under microwave irradiation. 2 M ammonium nitrate, NH_4NO_3 was prepared by adding 16 g of ammonium nitrate in 100 ml of double deionized water (DDW). Then 20 g of this solution was added to each 1 g of the zeolite. The temperature of the microwave was ramped to 85 °C in 2 min and was later maintained at 85 °C for 10 min. The product was washed by DDW and the same ion-exchange steps were repeated. After two sequential ion-exchange steps, the product was washed, centrifuged and calcined at 550 °C to obtain H-MOR.

2.4. Metal impregnation

Ce-impregnated zeolites (Ce-MOR) were prepared by dissolving 0.2994 g, 0.7486 g and 1.4973 g of $Ce(NO_3)_3.6H_2O$ corresponding to 2 wt%, 5 wt% and 10 wt% loadings respectively in ethanol (40 g) and thereafter mixed with 2 g zeolite (H-MOR) under rigorous stirring. The resulting slurry was dried overnight in a fume hood and was later calcined in a furnace at 550 °C for 4 h in static air (temperature ramp 20 °C/min).