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Environmental Monitoring by Eco-Friendly-Fabricated Carbon-Modified Electrode Sensors

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Mohd Azmuddin Abdullah,[1] Aamir Amanat Ali Khan,[2] Huma Ajab[3]

[1]Universiti Malaysia Terengganu, Malaysia
[2]Department of Chemical Engineering, Universiti Teknologi Petronas, Malaysia
[3]Department of Chemistry, COMSATS Institute of Information Technology, Pakistan

Correspondence: Mohd Azmuddin Abdullah, Institute of Marine Biotechnology, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia, Tel +609-6683104/3661, Fax +609-6683105,
Email azmuddin@umt.edu.my, joule1602@gmail.com

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Abstract

Environmental monitoring is necessary to understand and evaluate the extent of pollution and eco-system disturbances and to work out remedial strategies. Electrochemical methods are attractive for environmental monitoring due to their capability for remote and *in situ* applications. The electrode-based sensors are prone to fine-tuning and modification to improve the selectivity and sensitivity for trace analystes detection. Different types of modifiers have been applied which include hydroxyapatite, montmorillonite, ionic liquids, chitosan, bismuth and plant-based materials and their composites with graphites can be optimized utilizing cyclic and square-wave voltammetric techniques. These may have wide appeal in the analyses and detection of heavy metal ions, pharmaceuticals or biomolecules, airborne particulate matter, fly ash, rocks, minerals and sediments. Screen-printed electrodes especially enable portable systems for real-time, non-invasive analysis of a sample. The fabrication into microelectrodes and the preparation in machine-controlled manufacturing make screen-printed electrode more versatile for mass production at low costs. The small dimensions, and planar configuration with lab-on-chip, point-of-care applications are attractive features for the future development of eco-friendly-based sensors for multi-dimensional utilities.

Keywords: environmental monitoring, lab-on-chip, microelectronics, screen-printed electrode, Voltammetry, heavy metal ion

Introduction

Environmental monitoring has become an integral component to achieve Global Sustainability Goals especially in the context of understanding and observing disturbances to environmental cycles to allow strategies to be devised to mitigate potential disaster. One of the Principal of Green Chemistry is to promote analytical methodology development for real-time analysis, in situ monitoring and management before hazardous substances formations.[1],2 Innovative green technologies are pertinent to reduce or eliminate the use or generation of hazardous substances in the design, manufacturing and use of chemical products.[3] Among the most recalcitrant and hazardous environmental contaminants are heavy metals where lead, cadmium, and mercury being listed as priority pollutants.[4] One parts per billion is the maximum allowable limit for lead, cadmium and mercury in water by the US Environmental Protection Agency.[4] Some metal ions have toxicological effect in selected group of enzymes affecting heme synthesis and mitochondrial energetics, causing oxidative phosphorylation disruption and mitochondrial ion transport modifications.[5] With all the associated problems due to excessive exposure, trace level heavy metal monitoring has become increasingly imperative.[6] Whether in simple media such as water quality determination, or complex media such as blood serum or industrial waste effluent, real-time monitoring and point-of-care diagnosis is needed so that corrective actions and quick decisions can be taken to ensure remediation and restoration to safety levels.

Heavy metal ion monitoring and detection

Traditionally, heavy metals ion detection is carried out by discrete sampling, followed by laboratory analyses with storage in between. Stability of natural samples during long-term storage is questionable, as they are subjected to various biological, chemical and physical effects.[7] The bulky, expensive and sophisticated analytical equipments such as Atomic Absorption Spectrometry, Atomic Emission Spectrometry with Inductively coupled Plasma Excitation, Electro analytical methods, X-ray Fluorescence or Neutron Activation analysis, require dedicated specialist and trained personnel for analyses of heavy metal ions.

Electrochemical methods, particularly stripping analysis and voltammetric methods are attractive for remote application and trace metal determination. The common stripping voltammetry technique involves hanging mercury drop electrode or mercury film electrode.[8] The sensitivity of stripping analysis is a result of unique coupling of analytes pre-concentration steps on the electrode and the advanced measurement technique, where metal analytes are stripped away from the electrode during the potential scan. Such combination offers convenient quantization of trace metals down to the sub-nanomolar concentration levels,[9,10] and good selectivity and reproducibility due to the in situ pre-concentration step.[9,11] Although, the mercury electrodes forming amalgam with reduced metal, have high sensitivity and excellent reproducibility, they are hazardous and efforts are being made to replace mercury with a more eco-friendly materials for sensor fabrication.

Micro-engineering and micro-fabrication technology

Micro-engineering and environmental science link the tools and methods needed to address environmental concerns, and pave the way for portable and robust analytical devices. The push towards miniaturization brings together fields as diverse as chemistry, engineering, physics, microelectronics and electrochemical technology into miniaturized and microfluidic platforms to facilitate on site and *in situ* environmental monitoring and pollution control. Electrical sensors allow remote deployment with near-real time monitoring capability, along with highly sensitive and selective detection capabilities. A vast array of electrochemical devices has been developed in recent years for monitoring of numerous inorganic and organic contaminants such as heavy metals.[12–14]

Micro-fabrication technology allows sample preparation, mixing steps, chemical reactions, and detection to be performed in a miniaturized device. The miniaturization of analytical assays or on-chip assays use reduced volumes of reagents (2-3 orders of magnitude as compared to traditional bench approaches) and reduce cost per reaction and improve reaction kinetics.[15,16] Integration of several assay functions on a single chip leads to assay automation and elimination of operator involvement. Microchip devices have become increasingly important for rapid diagnostic applications in hospitals and on site environmental detection. Printable materials and printing processes such as the nanomaterial concentration and its corresponding viscosity allow selective deposition, repair, and re-print capability. However, printed features with desired properties, thickness, and tolerance may pose significant challenges. Generally, dilute solutions are used for thin ink-jet printing, and pastes are used for thick screen and contact printing. Low viscosity, in the range of 7-10 cp for the generation of submicron thin structures is preferable for ink-jet printing processes. Screen and contact printing are better performed using higher viscosity (100,000-150,000 cp) thixotropes and generate 10-25 mm thick features.[16]

The development of disposable, field-based size and low cost screen-printed electrode (SPE) is a new dimension in electrochemical-analysis especially in assisting rapid and sensitive monitoring of various substances with different properties, for pollutant characterization at the contaminated sites.[17] SPE enables detection method incorporated in portable systems, an important requirement for real-time, non-invasive analysis of a sample, without alteration of the "natural environmental conditions". The recent possibility of designing and fabricating SPE, including microelectrodes and chemically modified electrodes and incorporating these in a variety of highly sensitive biosensors, has increased industrial, clinical, and environmental interest.[15,18] SPEs are more versatile in practical preparation machine-controlled manufacturing thus enabling possible mass production at low costs, small dimensions, and planar configuration.[15] These make carbon ink-based electrodes and similar assemblies particularly attractive as the single-use and on site sensors.

Development of eco-friendly biosensors

Micro-fabrication of thick film electrodes through the use of screen-printing technique for field-base analyses involves sequential deposition of layers of different conductive or non-conductive inks through a mesh screen which defines the shape and size of the desired electrode on a variety of inert substrates.[19] A good and reliable electrochemical sensor very much depends on the materials that constitute the detection platform. The synergy between electrochemical sensors technology and the nanomaterials should confer great advantages for new transducing platforms, beside their use as labels or tags for signal enhancement.[20] Modification of bare Carbon Paste Electrode (CPE) has been developed, known as chemically-modified carbon electrodes (CME), by combining CPE with some other unique substances. These are highly selective sensors for both inorganic and organic analyses. The advantages include ease of manufacturing, mercury-free, low cost, low back ground current, wider operational window, renewable surface, stability in various solvents and the freedom in choosing the composition of carbon/components to tailor for expected analytical use.[21–23] Bismuth (Bi) nanoparticles.[24] Hydroxyapatite (HA)[25] and Bi-HA[26,27] have been used as modifiers, with improved sensitivity.

Bi is environmentally-friendly with widespread pharmaceutical use.[28] Modification of carbon electrode with HA and Bi(II) has been carried out to enhance Cd^{2+} and Pb^{2+} deposition through HA ion-exchange. Stripping voltammogram shows the current peaks corresponding to limit of detection (LOD) of 5μg/l for Pb^{2+} and 10μg/l for Cd2+, far more sensitive and selective than the CPE.[26] The analytical properties of Bi(II) are due to the property of Bi to form "fused alloys" with numerous heavy metals, analogous to the amalgams that mercury forms.[28] HA is the main constituent of bones and teeth, and a bioactive ceramic material with high bio-affinity and biocompatibility. HA consists mainly of calcium phosphate, with sorption capacity for divalent heavy metal ions. Heavy metal ions interact with HA-modified electrode by pre-concentration with surface complexation, followed by simultaneous adsorption on HA, and the calcium ion substitution coupled with diffusion on the electrode surface. The interacting ability of the Bi film and HA on the electrode surface holds the key to the performance of the SPE developed.

There has also been an increased preference to use plant tissue for the preparation of CMEs which may be used directly with minor preparation. Advantages include simplicity for biosensor construction, environmentally-friendly and less hazardous.[29,30] mechanical testability, high rigidity, long shelf-life, and a sensing surface that can be renewed by a simple polishing procedure.[31] Plant tissues-based CME has been firstly developed for the determination of L-glutamate.[32] In the plant material, there may be different sites present on which the analyte will bind or the presence of enzymes of attention in its natural environment showing the activity towards the analyte.

Table 1 shows the plant materials used as modifiers for Pb(II) detection.[33,34] The modifiers based on plant parts for electrode construction comprise of various chemical constituents that serve as active components for binding with the analytes. Amino acids in protein can help as a very active ligand for a multiplicity of metal ions because they have a great number of potential donor atoms through the peptide backbone and an amino acid side chains. Similarly, lignocellulosic materials and lignins can be useful as binding sites for metals. Lignins comprise large amount of oxygen-containing functional groups such as, alcoholic, phenolic and carboxylic structures which may possibly form lignin-metal macromolecular complexes with high stability through hydrogen, ionic and co-ordinate covalent bonding. The polysaccharide constituents like cellulose may serve as binding sites of metals by carbonyl and hydroxyl groups.[41]

Table 1 CPEs modified with plant and animal materials for Pb(II) detection

Modifier	Detection limit (ppb)	Reference
Plant based		
Kapok fiber	1000	35
Pennisetum (grass weed)	10	36
Pineapple	-	37
Banana tissue	100	38
Animal based		
Feather	121	39
Feather	590	40

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Conclusion

Research effort has been geared towards developing more sensitive analytical techniques to detect and remove toxic pollutants and analytes such as heavy metal ions. Having access to robust, sensitive, selective, low-cost and environmentally-friendly chemical sensors is fast becoming an important consideration in any environmental monitoring effort. Substitutions of traditionally hazardous mercury-based electrodes with electrodes which are disposable, with inert electrochemistry, wide potential window, and electrocatalytic activity for a range of redox reactions, via carbon-modified electrode, glassy-carbon electrode or screen printed carbon electrode, are among popular routes explored. For these, selection of proper sensing and modifier materials such as the eco-friendly plant-based materials, cellulose and hydroxyapatite are of paramount importance. Coupled with process optimization, reproducible and reliable analyses for informed decision making should safeguard public health, facilitate advances in technology and improve the quality of the environment.

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Conflict of interest

The author declares no conflict of interest.

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