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The environment has been exposed and subjected to the increase of global energy usage and unwanted release of pollutants. The health and economical risks caused by the environmental pollutants have attracted several studies unfolding and assessing the pollution threat. Despite several efforts, the detection techniques of harmful chlorine-based pollutants are hardly available in developing countries, especially Namibia due to their high cost and maintenance. Electrochemical sensors are reliable for quantitative and qualitative detection of harmful environmental pollutants, such as volatile organic compounds (VOCs). This study aimed at the electrochemical evaluation of synthesized sensing materials, namely Polyaniline (PANI) and Tin (IV) oxide nanoparticles (SnO₂ NPs), for the detection of chloroform, free chlorine, and polychlorinated biphenyls (PCBs). The synthesis of polymeric materials (Polyaniline (PANI) and Tin (IV) oxide nanoparticles (SnO₂ NPs) was conducted both by chemical oxidative polymerization and electrochemical polymerization. Tin (IV) oxide nanoparticles (SnO₂ NPs) were incorporated into the polymer matrix to form PANI/SnO₂ nanocomposites. Various characterization techniques such as, Thermogravimetric Analysis (TGA), Fourier-transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Ultraviolet Visible Spectroscopy (UV-Vis), were employed for analysis of the synthesized sensing materials. Positive identification of functional groups for the sensing materials was achieved with excellent conductivity properties suitable for chemical sensors development. The sensors were fabricated using both glassy carbon electrodes (GCE) and screen-printed electrodes (SPE), modified with the synthesized materials. Cyclic voltammetry (CV) was employed to investigate the electrochemical behavior of the sensors toward the selected analytes. Parameters such as sensitivity, limit of detection, linearity, and stability were assessed. The results confirmed the applicability of the synthesized materials in electrochemical sensing, with PANI/(SnO₂ NPs)-modified electrodes showing enhanced performance characteristics.

Introduction

Environmental pollutants risks and effects has inspired various research efforts aimed at pollution remedy applications. Organic compounds such as Hydrocarbons (HCs) also known as persistent organic pollutants (POPs) or Volatile Organic Compounds (VOCs) are non-degradable and toxic, enabling them to be the primary cause of environmental pollutants. The development of nano technology based chemical sensors models have been considered effective towards detection and remediation approaches for several environmental pollutants including VOCs, CO, and other inorganic compounds. Nano-chemical sensors are composed of important sensing properties including primary transducers which is comparable to chemical size scale, and shape of metal-metal oxides for better selectivity, sensitivity, and reproducibility . In addition, semi-conductor nanostructures such as polymers, are understood to play an important role in developing smart materials that can simultaneously sense and destroy harmful chemical contaminants from the environment. Polymer-based materials participate in sensing mechanisms whereby their chemical composition is modified to enhance their reactivity, flexibility, biocompatibility as well as their resistance to degradation . Polymeric materials are utilized in the form of thin films due to their high surface area and high selectivity . Therefore, in the overview of the above, the aim of the present study was to develop a sensitive electrochemical based Nano-chemical sensor for the detection of chloroform, a by-product of chlorination in water treatment as well as Volatile Organic Compounds (VOCs) in pesticides formulation, using conducting polymeric nanomaterials.

Methodology

Synthesis (Chemical Oxidative and electrochemical polymerization) and characterization of polymeric materials (PANI, PANI/ SnO₂ nanoparticles), electrochemically and spectroscopically using cyclic voltametric mode, UV-Vis, TGA, SEM and FTIR.

Fabrication of a NanoChemical Sensor on Glassy carbon electrode GCE, and Screen printed electrodes (SPEs).

Detection and Investigation of target analyte (chloroform) using the fabricated NanoChemical Sensor (s)

Development of a Nano-Chemical Sensor for the detection of Volatile Organic Compounds using polymeric materials in aqueous media

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Results and Discussion

Sensing materials	Solvents						
	Tetrahydr ofuran	DMS O	ethanol	water	methanol	acetone	chloroform
PANI	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
PANI/SnO ₂	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble
SnO ₂	Soluble	Soluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

Table 1: Solubility of synthesized sensing materials

Figure 2: TGA of PANI/

Figure 3: SEM images of pure PANI (a) & (b), PANI/ SnO₂ NPs (c) and SnO₂ NPs (d)

Figure 4: Variation of absorbance with wavelength for PANI, PANI/ SnO₂ NPs and SnO₂ NPs

Figure 5: Cyclic voltammograms for pH optimization study of the fabricated NanoChemical sensor (GCE/PANI/ SnO₂ NPs) in 1x Phosphate buffer saline (PBS) solution

Figure 1: FTIR spectrum of monomer aniline (a), polyaniline (PANI) (b), PANI/ SnO₂ NPs (c) and SnO₂ NPs (d)

Figure 6: Cyclic voltammograms for the characterization of bare GCE and the fabricated sensor (GCE/PANI/ SnO₂ NPs) against in 1x Phosphate buffer saline (PBS) solution pH 7.2 at a scan rate of 50 mV/s.

Figure 7: Cyclic voltammograms for electrochemical activities of chloroform increasing concentrations using: (a) bare GCE, (b) NanoChemical sensor (GCE/PANI/ SnO₂ NPs)

Figure 8: Cyclic voltammograms for the electrochemical evaluation of chloroform against fabricated nanochemical sensor (s) (GCE/PANI/ SnO₂ NPs), and (SPE/PANI/ SnO₂ NPs) at different scan rates

Conclusion

This study provided significant insights into the synthesis and properties of conducting polymer-metal oxide nanocomposites for application in chemical sensors.. The synthesized materials were successfully incorporated on glassy carbon electrodes (GCE) and screen-printed electrodes (SPE) for electrochemical detection. The detection of the selected pollutants was evaluated using cyclic voltammetry (CV). The modified GCE and SPE demonstrated a linear response to varying concentrations of the pollutants with remarkable sensitivity and good reproducibility. The composite sensing material (PANI/SnO₂) exhibited a better electrochemical response compared to individual components. The modified GCE sensors showed higher sensitivity and detection efficiency towards chloroform than SPE, although both platforms were effective. These findings confirm the potential of the synthesized composite sensing materials for application in the fabrication of sensitive, selective, and cost-effective nano-chemical sensors for the detection of chlorine-based pollutants in aqueous media.

Reference(s): Kant T, Shrivas K, Dewangan K, Kumar A, Jaiswal NK, Deb MK, et al. Design and development of conductive nanomaterials for electrochemical sensors: a modern approach. Mater Today Chem. 2022 June 1;24. .