

Study Modification Parameters for Electrochemical Detection of Benzotriazole

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Summary:

Benzotriazole (BZT), a widely used corrosion inhibitor, poses environmental and health risks. In this study, we developed an electrochemical sensor based on screen-printed electrodes modified with a Vulcan–polymer composite for detecting BZT. The influence of synthesis parameters, including sulfonation time of the polymer, concentrations of Vulcan and sulfonated poly(ether ether ketone), and suspension volume for electrode modification, was investigated. The Vulcan nanoparticles enhanced electron transfer, while the sulfonated polymer provided a stable matrix for better adsorption of BZT.

Keywords: Benzotriazole, screen-printed electrode, Vulcan XC-72-R, polyether ether ketone, electrochemical sensor.

Background, Motivation an Objective

Benzotriazole (BZT) is a polar chemical extensively utilized as a corrosion inhibitor for copper and its alloys, forming a protective layer that prevents undesirable surface reactions. It is also found in applications in household dishwashing products as a protection agent for silver [1]. Its applications span various industries, including aerospace, automotive, and oil and gas, due to that it discharges into receiving waters or is runoff from roads due to tire abrasion [2]. The widespread use of BZT has raised environmental concerns, as it is highly water-soluble and not readily biodegradable. It is classified as harmful for aquatic life and is under assessment as an endocrine disruptor, meaning that it influences hormonal status [3]. Therefore, the development of sensitive and reliable electrochemical sensors for BZT detection is essential for environmental monitoring. Screen-printed electrodes (SPEs) offer a promising, cost-effective, and portable alternative to conventional electrochemical systems. Their sensitivity can be significantly enhanced through surface modification using materials that improve the conductivity of the working electrode. In this study, we investigate the effect of synthesis parameters of Vulcan–polymer composite materials used to modify SPEs for the electrochemical detection of BZT.

Description of the New Method or System

A screen-printed electrode (SPE) comprising a carbon working electrode, a platinum counter electrode, and a silver reference electrode was used for sensor fabrication. The working electrode was modified with a composite of Vulcan XC-72-R and sulfonated poly(ether ether ketone) (SPEEK). Vulcan was first functionalized using nitric acid (HNO₃), while poly(ether ether ketone) (PEEK) was sulfonated in sulfuric acid (H₂SO₄), following the procedure reported by Kuila et al [4]. The effects of sulfonation duration and polymer concentration on sensor performance were systematically investigated. The Vulcan–SPEEK composites were prepared by mixing the components and sonicating the dispersions until fully homogenized. Modification of the working electrode was performed by drop-casting various volumes of the prepared dispersion (ranging from 2 μL to 10 μL) onto the electrode surface, followed by drying at room temperature overnight. BZT solutions were prepared in 0.1 M H₂SO₄. Electrochemical measurements were conducted using cyclic voltammetry (CV) and square wave voltammetry (SWV) with a PalmSens4 potentiostat.

Results

The synthesized Vulcan–SPEEK composite particles are shown in *Fig. 1*. Transmission electron microscopy (TEM) images reveal that the Vulcan

XC-72R nanoparticles exhibit an average size of approximately 100 nm.

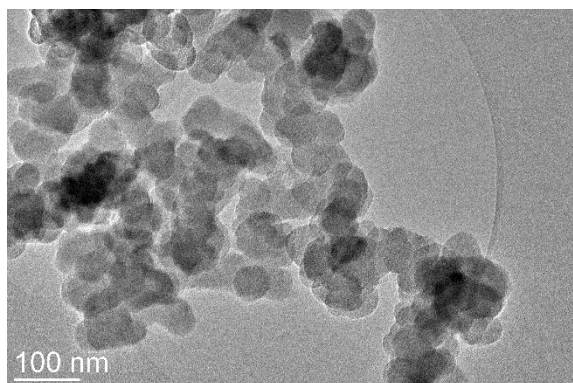


Fig. 1. TEM image of the Vulcan nanoparticles modified with polymer.

The electrochemical behavior of BZT on the modified screen-printed electrode (SPE-V-SPEEK) was evaluated using CV and SWV. A distinct reduction peak was observed at approximately -1.4 V vs quasi-Ag electrode, indicating the electrochemical activity of BZT at the modified electrode surface. The effect of synthesis parameters on the electrochemical reduction of BZT was systematically investigated, as shown in Fig. 2.

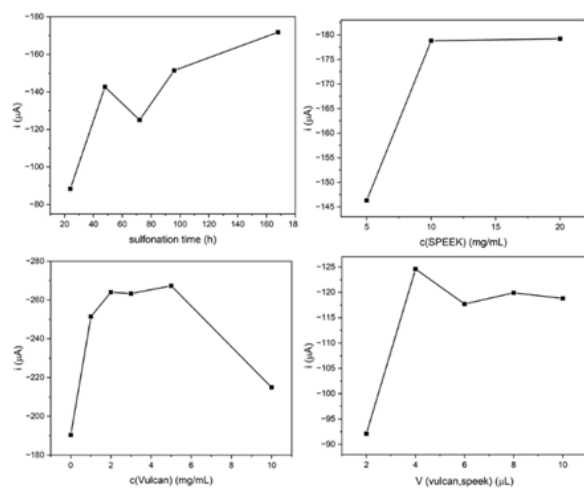


Fig. 2. Influence of the modification parameters on the maximum peak current of the reduction of BZT: sulfonation time, concentration of SPEEK, concentration of Vulcan, and volume of drop-casted dispersion on the working electrode.

The degree of sulfonation of the polymer significantly influenced the electrochemical response. With increased sulfonation time, a higher reduction peak current was observed, suggesting improved adsorption of BZT on the surface of the electrode by adding sulfonate groups. The concentration of sulfonated poly(ether ether ketone) also affected sensor performance. Peak current increased with SPEEK concentration from 5 to 10 mg/mL, after which further increases had no significant effect, indicating a saturation point.

Similarly, optimization of Vulcan content showed that concentrations between 2 and 6 mg/mL provided the highest current response. Higher concentrations led to a decrease in current, likely due to nanoparticle agglomeration, which can hinder electron transfer. The volume of suspension used for electrode modification was also optimized. The best electrochemical response was obtained with a 4 μL volume, suggesting an optimal coating thickness that balances conductivity and surface coverage. Overall, the careful adjustment of Vulcan and polymer content, as well as sulfonation degree, enabled the development of a sensor with a low limit of detection (LOD) of 1.4 μM . The Vulcan particles enhance electron transfer during the redox reaction, while the sulfonated polymer provides a stable matrix for electrode modification and better adsorption of the BZT on the surface of the electrode. These features make the proposed SPE-based sensor a promising platform for reliable BZT detection in real environmental samples.

References

- [1] S. Weiss, T. Reemtsma, Determination of Benzotriazole Corrosion Inhibitors from Aqueous Environmental Samples by Liquid Chromatography-Electrospray Ionization-Tandem Mass Spectrometry, *Analytical Chemistry* 77, 7415–7420, (2005); <https://doi.org/10.1021/ac051203e>.
- [2] A. Klopfer, M. Jekel, T. Reemtsma, Occurrence, Sources, and Fate of Benzothiazoles in Municipal Wastewater Treatment Plants, *Environmental Science and Technology* 39, 3792–3798 (2005); <https://doi.org/10.1021/es048141e>.
- [3] Y. Sakuragi, H. Takada, H. Sato, A. Kubota, M. Terasaki, S. Takeuchi, A. Ikeda-Araki, Y. Watanabe, S. Kitamura, H. Kojima, An analytical survey of benzotriazole UV stabilizers in plastic products and their endocrine-disrupting potential via human estrogen and androgen receptors, *Science of The Total Environment* 800, 149374 (2021); <https://doi.org/10.1016/j.scitotenv.2021.149374>.
- [4] T. Kuila, A.K. Mishra, P. Khanra, N.H. Kim, Md.E. Uddin, J.H. Lee, Facile Method for the Preparation of Water Dispersible Graphene using Sulfonated Poly(ether-ether-ketone) and Its Application as Energy Storage Materials, *Langmuir* 28, 9825–9833 (2012); <https://doi.org/10.1021/la301469u>.

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