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Precision Detection Unlocked: Electrochemical Sensing of PBTC with Molecularly Imprinted Polymers

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Summary:

This study introduces a novel approach in creating sensitive and selective sensors for identifying PBTC in aqueous and real-water samples. It is based on the modified surface of Au microelectrodes with molecularly imprinted PDA polymer. The characterization of the resulting microsensor was carried out by using FTIR, CV and EIS techniques. EIS responses of the modified microelectrodes toward PBTC was well-proportional to the concentration in the range from 5−100 mg/mL indicating a good correlation. This developed device can be used for the detection of PBTC in water cooling system.

Keywords: MIPs, microsensor, PBTC, PDA, EIS

Introduction

Traditional methods for assessing orthophosphate concentrations face challenges in terms of cost, time, and complex analysis. Such limitations highlight that an on-site solution for rapid detection is needed to investigate within aquatic systems effectively [1]. In response to this analytical demand, applying molecularly imprinted polymers (MIPs) for electrochemical sensing has emerged as a significant development in environmental monitoring. MIPs are favored for their outstanding physical and chemical stability, high specificity, low-cost production, and quick responsiveness. When integrated with compact electrochemical sensors, the material enables the direct detection of specific substances in real-time with accurate results. Among various MIPs, polydopamine (PDA) stands out for its simple and mild polymerization process, versatility in adhering to a wide range of surfaces, and diverse binding mechanisms [2]. This research introduces a PDA-based MIPs electrochemical microsensor engineered for detecting PBTC—a critical orthophosphate compound used as an antiscalant in cooling water systems. Monitoring PBTC concentrations is crucial for balancing operational efficiency and environmental protection. It ensures the prevention of eutrophication and helps in complying with environmental regulations regarding phosphate discharge [3]. The sensor exhibits remarkable sensitivity and specificity for orthophosphate chemical detection under optimal conditions.

Methods

The surface of Au microelectrodes was cleaned and then immersed in an MHDA solution for an overnight incubation at 4°C. Subsequently, a mixture of EDC/NHS was applied to the prepared Au surface and allowed to react for 30 min at ambient temperature. The seed layer of PDA was then deposited onto the activated surface. Cyclic voltammetry (CV) was utilized to facilitate the electropolymerization of the NIPs and MIPs devices. To eliminate PBTC templates, the MIP chip was placed in 0.2 M H_2SO_4 for a duration of 30 min. Characterization of the resulting samples was conducted by using the CV and electrochemical impedance spectroscopy (EIS) techniques.

Results and Discussion

The surface characteristics of the modified microelectrodes were analyzed using FTIR spectroscopy (see Fig. 1). The analysis confirmed the successful binding of the PBTC template to PDA

by the electropolymerization process. The broad absorption band around 3400 cm^{-1} is attributed to the stretching vibrations of –OH bonds, indicative of the hydroxyl groups present in PDA. Additional peaks were observed, including the N–H band (3084, 1671, and 1559 cm^{-1}), C–H vibrations (2931, 2858, and 1467 cm^{-1}), and the C=O stretch at approximately 1670 cm^{-1}. Furthermore, the MIP spectra demonstrated the presence of a 1709 cm^{-1} peak for C–O stretching of carboxylic groups, and 1422 and 1205 cm^{-1} for the PO group, providing clearly evidence of PBTC incorporation.

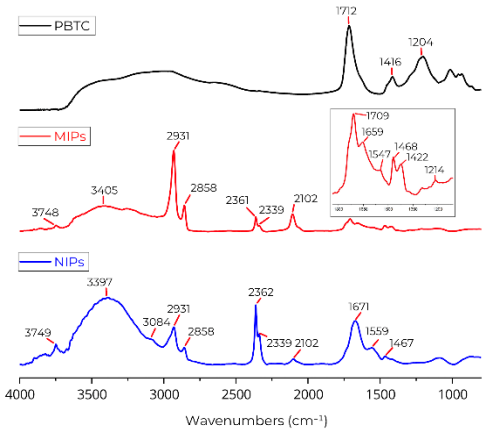

Fig. 1. FTIR analysis of the NIPs, MIPs and PBTC.

The electrochemical behaviors of the bare Au, NIPs, MIPs, extracted MIPs, and rebinding MIPs were evaluated in 5 mM $[Fe(CN)_6]^{3-/4-}$ and PBS solution using CV and EIS techniques (see Fig. 2a). CV results revealed a decrease in the current intensity of redox peaks for the modified electrodes compared to the bare Au. The redox peak of the MIPs was lower than the NIPs sensor, indicating that the reduction of the amplitude voltammogram was attributed to the presence of PBTC. After extraction of PBTC templates, a significant increase in redox peak was due to the PDA matrix providing the imprinted hole promoting the charge transfer.

EIS measurements featured a Nyquist plot where the semicircle at higher frequencies corresponds to electron transfer reactions. The bare Au electrode displayed a minimal electron transfer profile, indicative of a diffusion-driven process with swift electron transfer kinetics. The application of PBTC to the electrode's surface caused a noticeable increase in the semicircle's size on the Nyquist plot, which denotes an obstructive effect of the polymer that impedes electron transfer and increases the resistance to electron circulation. The impedance experienced a pronounced increase post-polymerization, due to the formation of the PDA film encapsulating the orthophosphate compound, which notably impedes electron transfer. The impedance was considerably reduced after the extraction of PBTC, presumably as a result of cavities left by the removed PBTC, thereby the electron transfer process. The semicircle expanded slightly after the PBTC was reintegrated, implying the effective reattachment of PBTC within the MIP at specific binding sites. Additionally, EIS graphs showed significant changes in response amplitudes as the concentration of PBTC increased. This suggests a correlation between the concentration of PBTC and the impedance of the PBTC sensor. Analyzing the data from EIS diagrams enabled the identification of a linear relationship (see Fig. 2b).

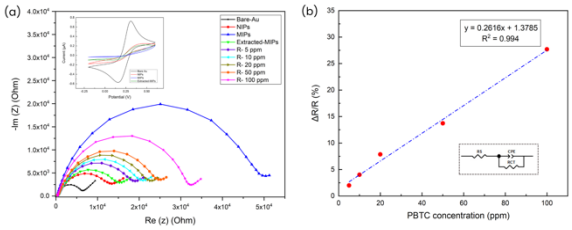

Fig. 2. (a) CV and EIS results and (b) sensitivity of molecularly imprinted microsensor based-on PDA.

Conclusions

This study highlighted the effectiveness of PDA-MIPs in achieving remarkable sensitivity and specificity in PBTC detection, crucial for ensuring operational efficiency and environmental protection against eutrophication. The electrochemical characterization through CV and EIS validated the sensor's ability to select PBTC with considerable precision. The findings, indicating a direct correlation between PBTC concentration and sensor impedance, pave the way for on-site, real-time monitoring of orthophosphate levels in aquatic systems. This breakthrough contributes substantially to the environmental monitoring field by offering a low-cost, efficient, and reliable solution to the challenges posed by traditional methods of phosphate concentration assessment.

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