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A novel polythiophene – ionic liquid modified clay composite solid phase microextraction fiber: Preparation, characterization and application to pesticide analysis

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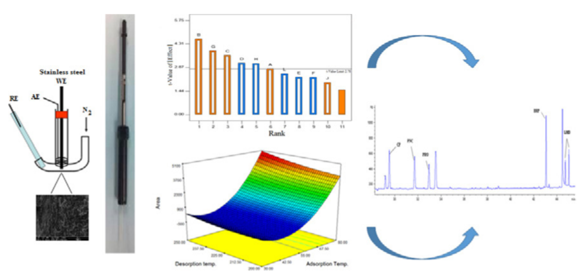
HIGHLIGHTS

- A novel polythiophene – ionic liquid modified clay surface has been prepared.
- Polymerization was performed electrochemically on a stainless steel wire.
- This material was used as a SPME fiber in head space mode.
- This new SPME fiber was applied for analysis of pesticides in juice samples.
- Fiber adsorption properties were improved by modification of ionic liquids.

GRAPHICAL ABSTRACT



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ABSTRACT

This report comprises the novel usage of polythiophene – ionic liquid modified clay surfaces for solid phase microextraction (SPME) fiber production to improve the analysis of pesticides in fruit juice samples. Montmorillonite (Mmt) clay intercalated with ionic liquids (IL) was co-deposited with polythiophene (PTh) polymer coated electrochemically on an SPME fiber. The surface of the fibers were characterized by using scanning electron microscopy (SEM). Operational parameters effecting the extraction efficiency namely; the sample volume and pH, adsorption temperature and time, desorption temperature and time, stirring rate and salt amount were optimized. In order to reveal the major effects, these eight factors were selected and Plackett–Burman Design was constructed. The significant parameters detected; adsorption and temperature along with the stirring rate, were further investigated by Box–Behnken design. Under optimized conditions, calibration graphs were plotted and detection limits were calculated in the range of 0.002–0.667 ng mL^{-1}. Relative standard deviations were no higher than 18%. Overall results have indicated that this novel PTh-IL-Mmt SPME surface developed by the aid of electrochemical deposition could offer a selective and sensitive head space analysis for the selected pesticide residues.

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1. Introduction

Pesticides are widely used in agricultural production but their residues in food are harmful to human health because of their potential mutagenicity and carcinogenic properties [1]. Thus, it is of great significance to develop an accurate and reliable analytical method for their determination in food and the environment in trace level. Conventional multi-residue analytical methods based on liquid–liquid extraction (LLE) [2] and solid-phase extraction (SPE) [3] are time-consuming and necessitate a large amount of toxic solvents.

Alternatively, solid phase microextraction (SPME) provides a simple, fast and solvent-free technique which eliminates some disadvantages such as solvent-consumption and analyte loss [4–6]. In this technique, target analytes are preconcentrated on the thin polymer film coated SPME fiber and then are rapidly delivered to a capillary GC column. For complex matrices, cleaner extracts can be obtained by this means than conventional methods and analysts do not always need sophisticated or expensive instrumentation [7]. The selection of a suitable fiber coating for a particular extraction enhances the selectivity towards the targeted analytes.

An ideal fiber for SPME application should display high adsorptive capacity, good thermal, and mechanical stability along with the acceptable reproducibility [8]. However, the sample components with matching polarity might adsorb on the fiber creating a capacity problem in direct immersion conditions. Head space sampling, on the other hand, provides a kind of selectivity as the volatiles and semi volatiles can only be collected on the fiber thus, providing a long life and reproducible performance.

Beyond that low cost, ease in preparation and the ability to extract various classes of compounds with different polarities are required. Commercial fibers in a range of polarity have been applied in a vast number of analyses but, they suffer from short lifetime and high cost. Therefore, recent studies have been focused on fabricating low cost, simple, robust and long-life fiber with enhanced selectivity for the target analyte by introducing novel materials as functional coatings [9–12].

Conducting polymers meet greatly these requirements due to their mechanical and chemical stability and high porosity with increased surface area. By electrochemical polymerization, the film thickness can easily be controlled, and polymers with different functional groups can be formed conveniently under controlled electrochemical conditions. In early studies, mostly polypyrrole (Ppy) [9,10] and polyaniline (PANI) [13] fibers and their derivatives have been coated on a metallic fiber for this purpose. Increasing attention has recently focused on polythiophene (PTh) coatings that display a higher extraction efficiency toward some analytes in comparison to other conducting polymers [12]. A recent trend is to

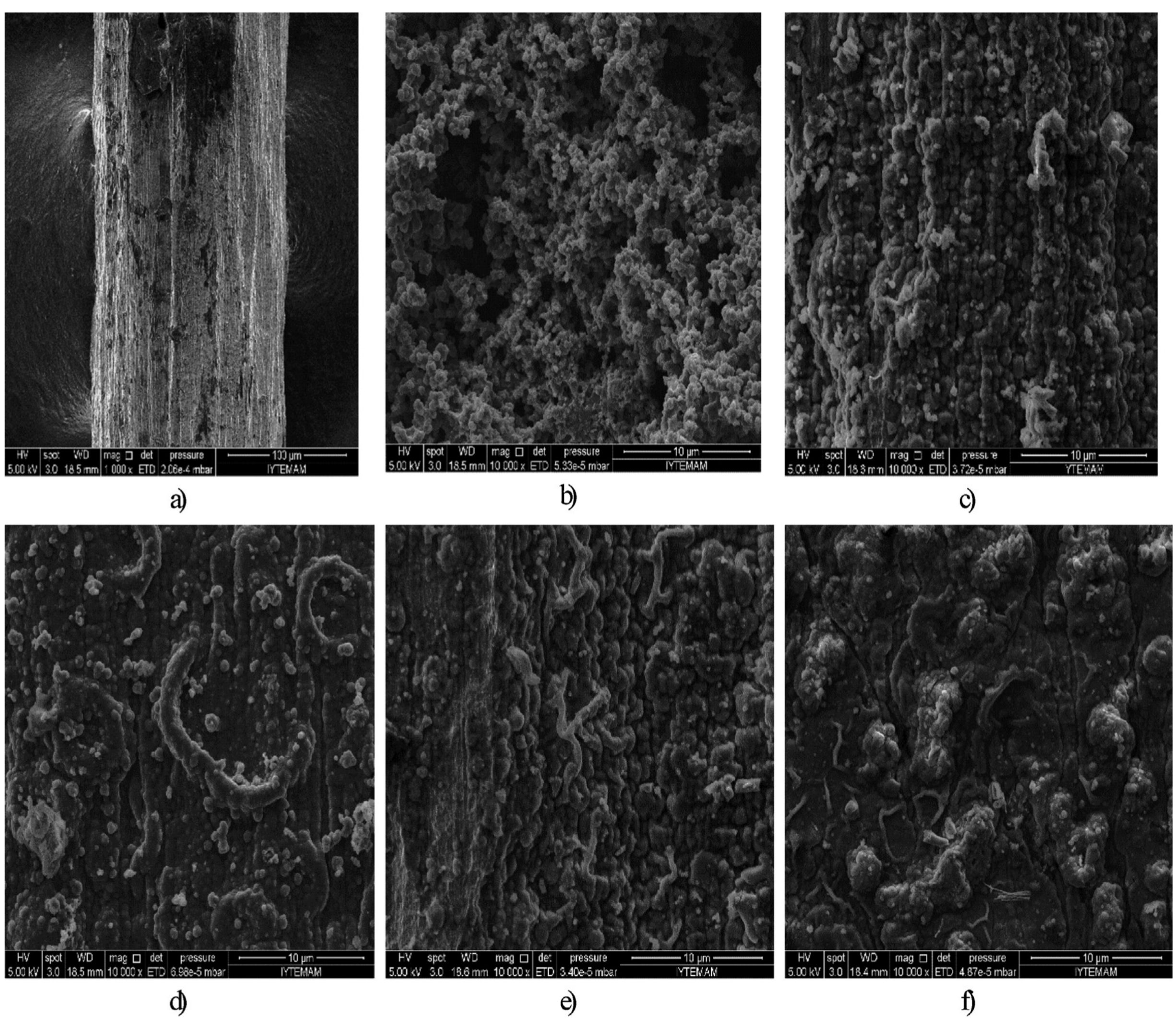

Fig. 1. SEM images of (a) stainless steel (b) PTh (c) PTh-Mmt (d) PTh-Mmt-C8mimBr (e) PTh-Mmt-C12mimBr (f) PTh-Mmt-C18mimBr (10.000× magnification).