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Simultaneous determination of propanil and monalide by modified glassy carbon electrode with nickel oxide nanoparticles, using partial least squares modified by orthogonal signal correction and wavelet packet transform

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ABSTRACT

In this study a Glassy carbon electrode (GCE) modified with nickel oxide nanoparticles was developed. This electrode has a good sensitivity and electrocatalytic activity toward the oxidation of propanil and monalide over a wide concentration range. The propanil and monalide oxidation mechanism on the electrode surface was investigated, and the overall number of electrons involved in the electrocatalytic oxidation was found to be 3. The detection limit of this electrode for determination of propanil and monalide was 0.05 and 0.21 μM and its relative standard deviation for 10 independent measurements was 3 and 3.7%, respectively. Finally the proposed electrode exhibited several advantageous features, including simple preparation, fast response time, and good repeatability. The electrode was successfully applied for simultaneous determination of propanil and monalide based on partial least squares (PLS) regression with orthogonal signal correction (OSC) and wavelet packet transform (WPT) as pre-processing tools with overlapping peaks. In this case, by optimization, the kind of wavelet function, the decomposition level, the number of OSC components and number of PLS factors for the OSC-WPT-PLS method were selected as Daubechies 3, 1, 1 and 4, respectively. The relative standard errors (R.S.E) of prediction obtained for two components using OSC-WPT-PLS, WPT-PLS and PLS were compared. Experimental results demonstrated that the OSC-WPT-PLS method produced the best results among the three methods.

1. Introduction

Pesticides are chemicals, which are commonly used in agriculture to protect crops from pest organisms including insects, plants, fungi, rodents and nematodes [1,2]. In their cycle, they may appear as pollutants in water sources and treat to human health due to their toxicity, carcinogenicity and mutagenicity. Most of these compounds, as well as their metabolites, represent human health and ecotoxicity threats and should therefore be removed from contaminated environments [2–4]. Propanil (3,4-dichloropropionanilide) is a highly selective post-emergence herbicide that is extensively used to control barnyard grass (*Echinochloa crus-galli*) and other grass weeds in several different crops, especially in rice [5,6]. It is a photosynthetic inhibitor which hinders photosystem II process in chloroplasts. Monalide belongs to the class of Anilide herbicides and is an important selective herbicide for the control of weeds in vegetable crops [7,8]. It is applied after the emergence of both weeds and crops. In developed countries drinking water quality is strictly regulated regarding pesticides. The National Survey of Pesticides in Ground Water, published by the U.S. Environmental Protection Agency (EPA), lists 126 polar compounds such as propanil and monalide as potential groundwater contaminants [9]. Due to the toxic effects of pesticides and herbicides, removal from environments and aquatic recourses and their assay is "an importance analytical task" [2]. One of the most widely used methods for the determination of herbicides is gas chromatography with different types of detector [10,11]. Liquid chromatography has been widely used to quantify propanil [12]. Although these methods have a high sensitivity and selectivity, there may be several drawbacks, such as being time consuming, and requiring expensive instruments and toxic solvents. Electroanalytical methods, besides offering the analytical quantification of pesticides, can provide clear information about their mechanism of degradation [13].

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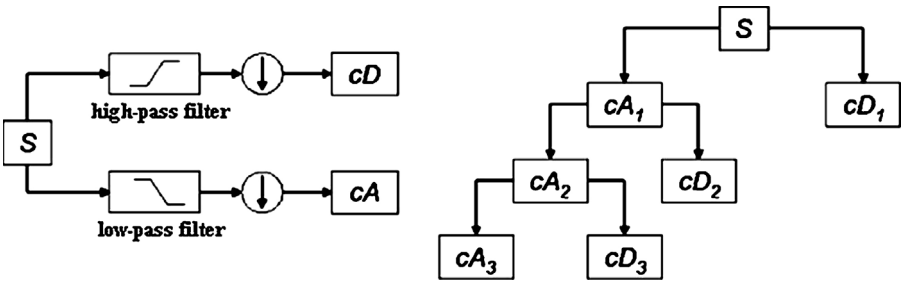

Fig. 1. Schematic diagram of Fast Wavelet Transform.

Nowadays, with the development of nanoscience and nanotechnology, there have been various trials to employ new nanomaterials in fabricating chemically modified electrodes. The electrochemical method, based on chemically modified electrodes, has shown great potentials over other techniques for the detection of organic and inorganic compounds due to its simplicity, its rapid responses, good sensitivity, high selectivity and excellent long-term calibration stability [14–17]. Among different nanomaterials, nickel oxide (NiOx) nanoparticles have received considerable attention in recent years due to their catalytic, optical, electronic and magnetic properties [18,19]. Voltammetric study of other similar compounds leads frequently to a degree of overlapping in their voltammograms due to oxidation or reduction at similar potentials. Traditionally, the peaks can be separated by choosing an appropriate electrolyte or by adding a complexing agent; however it can help in only a limited number of cases. Nowadays, due to the easy and rapid data acquisition, chemometrics methods have been widely applied to solve the problem of overlapping voltammograms peaks [20]. Several chemometric methods, such as principal component regression (PCR) and partial least squares regression (PLS), have recently emerged as fast growing techniques [21–23]; however, compared to spectrometry, there are only a few references to chemometric methods dedicated to electroanalytical problems [24,25]. In order to enhance the predictive ability of multivariate calibration models, raw data are often pre-processed for the elimination of irrelevant information prior to calibration [26,27]. So, in this work, a glassy carbon electrode (GCE) modified with NiOx nanoparticles was used for the simultaneous determination of propanil and monalide. A novel approach tested here uses orthogonal signal correction (OSC) and Wavelet packet transformation (WPT) as pre-processing methods in combination with PLS to eliminate noise and extraneous information, as well as to enhance regression quality. Additionally, the electro-oxidation mechanism of propanil and monalide at nano-NiOx modified GCE was investigated.

2. Theory

Obtaining high quality results by differential pulse voltammetry (DPV) determination of propanil and monalide requires the application of an advanced signal processing algorithm. In this work a hybrid procedure named OSC-WPT-PLS was considered. This approach is based on using partial least squares regression (PLS) with Orthogonal Signal Correction (OSC) and Wavelet Packet Transform (WPT) as pre-processing tools to analyze overlapping voltammograms.

2.1. Orthogonal signal correction (OSC)

A novel filtering technique called orthogonal signal correction (OSC) was developed in 1998 by Wold et al. [27]. The operation of this algorithm relies on the removal of systematic variations in the signal matrix **D** which is mathematically orthogonal and unrelated to the concentration matrix **C** prior to calibration. By filtering orthogonal variance, the intent is to remove most of the variation in experimental data attributed to various undesirable extraneous effects, while variance attributed to the target analyte is retained. In most cases, filtering with the OSC reduces the complexity of the model by the number of OSC components removed, without noticeable enhancement in prediction performance [28]. The number of OSC components is the number of times that OSC is applied to raw matrix **D**, and generally varying between 1 and 3.

2.2. Wavelet packet transform (WPT)

The wavelet packet transform is a powerful signal processing technique that can provide information on local time and frequency scales together. Wavelet transform (WT) can be used for the purpose of converting data from the original domain into the wavelet domain, in which the representation of a signal is spares and signal denoising is easier to be carried out. Only a brief introduction of WT is provided here [29,30]. The discrete WT has been implemented through the Mallat's pyramidal algorithm also called FWT. It operates on a single discrete signal of length M by splitting it into $M/2$ long orthogonal subspaces, called approximations and details respectively. Decomposition is made by applying two digital filters, which involves low-pass (LPF) and high-pass (HPF) versions and down sampling. The result of such decomposition is a series of approximation coefficients cA_j and detail coefficients cD_j. The cA_j set and cD_j set retain the low-frequency and high-frequency content of the signal, respectively. The procedure can be recursively applied (wavelet tree) by applying the same two filters to the approximation vector, as shown in Fig. 1. In general, conventional wavelet compression and denoise methods in signal process apply a threshold to wavelet coefficients. Only the wavelet coefficients of which absolute values are higher than a predefined threshold value are retained. For each decomposition level '*j*' a faithful reconstruction of the original signal is possible using the inverse discrete wavelet transform (IDWT) and the set of approximation coefficients obtained at level '*j*', together with all sets of detail coefficients from level '*j*' up to level 1. Wavelet packet transform (WPT) is a generalization of WT. WPT was first introduced by Coifman and Wickerhauser for dealing with the nonstationarities of the data [31]. Based on the same denoising idea, WPT can also be applied to signal denoising. The main difference between WT and WPT is that WPT decomposes not only approximations but also details. Compared to wavelet analysis, WPT has a better frequency resolution for decomposition signals, so it is possible to combine different decomposition levels to achieve the optimum time–frequency representation of the original signals.

3. Experimental

3.1. Materials and apparatus

The stock solution of each pesticide (0.01 mol L^{-1}) (with a purity of 99.5%) was prepared by dissolving suitable weight aliquots in