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Multivariate optimization of molecularly imprinted polymer solid-phase extraction applied to parathion determination in different water samples

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ABSTRACT

In this work a parathion selective molecularly imprinted polymer was synthesized and applied as a high selective adsorber material for parathion extraction and determination in aqueous samples. The method was based on the sorption of parathion in the MIP according to simple batch procedure, followed by desorption by using methanol and measurement with square wave voltammetry. Plackett–Burman and Box–Behnken designs were used for optimizing the solid-phase extraction, in order to enhance the recovery percent and improve the pre-concentration factor. By using the screening design, the effect of six various factors on the extraction recovery was investigated. These factors were: pH, stirring rate (rpm), sample volume (V_1), eluent volume (V_2), organic solvent content of the sample (org%) and extraction time (t). The response surface design was carried out considering three main factors of (V_2), (V_1) and (org%) which were found to be main effects. The mathematical model for the recovery percent was obtained as a function of the mentioned main effects. Finally the main effects were adjusted according to the defined desirability function. It was found that the recovery percents more than 95% could be easily obtained by using the optimized method. By using the experimental conditions, obtained in the optimization step, the method allowed parathion selective determination in the linear dynamic range of 0.20–467.4 $\mu g\,L^{-1}$, with detection limit of 49.0 $ng\,L^{-1}$ and R.S.D. of 5.7% ($n = 5$). Parathion content of water samples were successfully analyzed when evaluating potentialities of the developed procedure.

1. Introduction

Organophosphate pesticides have played an important role in increasing agricultural productivity. Due to their high toxicity and widespread uses in agricultural areas, the residues could be left in our environment [1,2]. For human health protection and environmental control, it is important to develop a selective and sensitive method for the detection of organophosphate pesticides in water, plants, soil and foodstuff, etc.

Due to the popularity of solid-phase extraction, new sorbents have recently appeared as alternatives to conventional solid-phase extraction sorbents with the aim of achieving a more selective preconcentration or extraction of the analytes. Immunosorbents which rely upon reversible and highly selective antigen–antibody interactions and synthetic antibody mimics, such as molecularly imprinted polymers (MIPs) appear as excellent candidates to accomplish such requirement. In particular, MIP offers important advantages such as the possibility of synthesizing polymers with a predetermined selectivity for a particular analyte. MIPs are reusable and have higher stability and shorter preparation times than antibodies. They are fabricated by synthesizing highly cross-linked polymers in the presence of a "print" molecule. After removal of the print molecule, the polymer can be used as a selective binding medium for the print molecule or structurally related compounds. The mechanisms by which these polymers specifically bind the print molecule are attributed to the formation of functional groups in a specific arrangement within the polymer that corresponds to the print molecule and to the presence of shape-selective cavities [3–5].

Introduction of MIPs into SPE [5,6], a technique commonly referred to as MISPE, is emerging as a very popular tool. The fact that MIPs can bind a particular analyte from a mixture of similar structures makes MISPE a very desirable technique for the development of selective and sensitive methods for trace analysis. During recent years there have been several publications describing the success of MISPE for the extraction of a whole range of compounds from different matrices. These include, amongst many; the extraction of triazine herbicides [7], steroids [8], nicotine [9], clenbuterol [10,11], propranolol [12], darifenacin [13], local anaesthetics [14], sameridine [15], caffeine [16], coumarins [17] and even nerve agents degradation products [18].

The overall aim of this study was to investigate the potential use of MIPs as SPE sorbents for the direct extraction of parathion.

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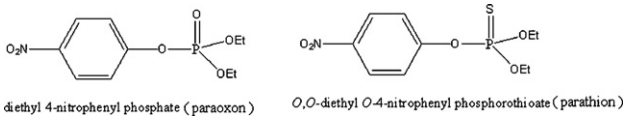

Fig. 1. Chemical structure of parathion and paraoxon as main neurotoxins.

In this work we developed a MIP based solid-phase extraction-square wave voltammetry for parathion determination. In fact, the simple and high selective MIP based batch SPE was coupled with square wave voltammetry as a sensitive and selective determination method in order to measure this important compound in real samples at very low concentrations. We also focused on the enhancement of the recovery percent and pre-concentration factor of parathion by using screening and response surface experimental designs as improved optimization methodology. A multivariate approach to the optimization of the SPE process led to simultaneous study of various factors, and allowed us to find the best compromise between potential conflicting criteria in a faster and more cost-effective manner.

2. Experimental

2.1. Instruments and reagents

Electrochemical measurements were carried out with a three-electrode system using a potentiostat/galvanostat model PGSTAT302, Metrohm. A glassy carbon electrode was used as a working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Methacrylic acid (MAA) (Sigma–Aldrich, Germany) was purified by passing it through a short column of neutral alumina, followed by distillation under reduced pressure. Ethylene glycol dimethacrylate (EDMA) was obtained from Fluka (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at 4°C until use. 2,2′-Azobisisobutyronitrile (AIBN) were supplied by Sigma–Aldrich (Munich, Germany), and used as received. Paraoxan, Parathion, Ethion, Atrazine and Malathion, was supplied from Supelco/Chem (USA). Other chemicals were of analytical grade and were purchased from Merck (Germany).

2.2. Polymers preparation

Molecularly imprinted polymer for parathion was prepared according to the following procedure: parathion (1 mmol), MAA (3.2 mmol) and 70 mL of dry chloroform were placed into a 100-mL round-bottomed flask and the mixture was left in contact for 10 min. Subsequently, EDMA (20 mmol) and AIBN (0.2 mmol) were added. The flask was sealed and the mixture was purged with nitrogen for 15 min. Polymerization took place in a water bath at 60 °C for 24 h. The final polymer was simply powdered and the template was removed by Soxhlet extraction with methanol for 16 h.

Non-imprinted polymer was prepared in the conditions similar to those of imprinted polymer except that in this case, parathion was not present in the polymerization composition.

Complete removal of the template from the polymer was traced by the square wave voltammetry method.

2.3. Square wave voltammetry analysis

The voltammetric determination of organophosphonate such as parathion and paraoxon (Fig. 1) having electroactive ph-NO_2 group is well-known and has been discussed in some articles [19]. In this work, at first, the potential of −0.6 V was applied to the glassy carbon electrode for 20 s which resulted in reduction of the nitro group of the parathion (–NO_2) to the hydroxyl amine group (–NHOH) via an irreversible four-electron reaction. Then the square wave potential with frequency of 100 Hz was swept from 0.2 to 0.5 V to start an oxidation reaction in which the previously produced product was oxidized via a reversible two-electron redox reaction. The current of anodic peak of square wave voltammetry was used for parathion determination.

2.4. Data analysis

ANOVA statistical toolbox of Matlab (version 6.5) and Minitab 14.1 were used for the experimental design, mathematical model development and regression analysis of the experimental data. The quality of the fit of the polynomial model equation was expressed by the coefficient of regression R^2, and its statistical significance was checked by a Fisher *F*-test. The level of significance was given as values of the probability less than 0.05.

2.5. Proposed analytical procedure

430 mL of different parathion aqueous solution containing 5 mL acetonitrile are contacted with 0.05 g of MIP for 20 min at the stirring rate of 200 (rpm). Then the mixture was passed through sintered glass filter forced by a vacuum pump. The remained MIP on the filter was firstly washed with 10 mL distilled water and subsequently retained target molecules on the MIP were eluted with an optimum volume of methanol (7 mL). The eluent was then dried with nitrogen gas in water bath at 40 °C. Then the residue was redissolved in 4 mL buffer solution (pH 1.5) and then the square wave voltametry was carried out as described above.

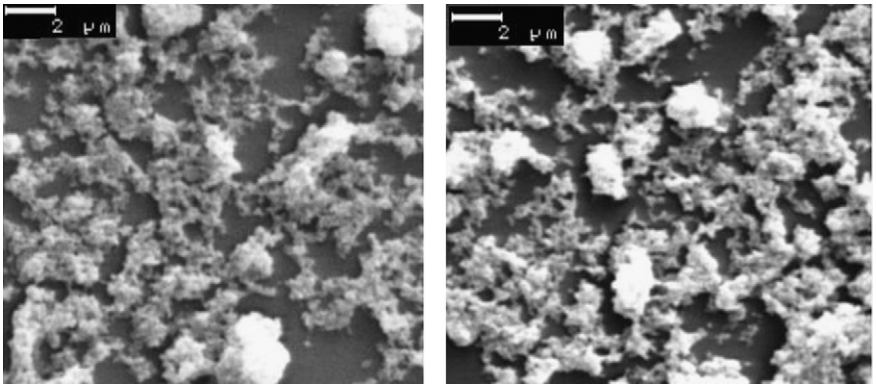

Fig. 2. Scanning electron micrographs of the parathion imprinted polymer (left) and corresponding non-imprinted polymers (right) (the images magnified by 5000-fold).