



# Development of zirconia nanoparticles-decorated calcium alginate hydrogel fibers for extraction of organophosphorous pesticides from water and juice samples: Facile synthesis and application with elimination of matrix effects



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## ARTICLE INFO

### Article history:

Received 1 August 2016

Received in revised form 16 October 2016

Accepted 26 October 2016

Available online 29 October 2016

### Keywords:

Zirconia nanoparticles

Alginate

Organophosphorous pesticides

Micro solid phase extraction

Gas chromatography

## ABSTRACT

In this research, novel zirconia nanoparticles-decorated calcium alginate hydrogel fibers (ZNAHF) were synthesized through a simple, green procedure. ZNAHF were used as an adsorbent in the micro–solid-phase extraction (MSPE) of methyl parathion (MP), fenitrothion (FT) and malathion (MT) as model pesticides prior to gas chromatography–mass spectroscopic detection (GC–MS). The composition and morphology of the prepared fiber were characterized by Fourier transform–infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive X-ray diffraction (EDX), and differential scanning calorimetry (DSC). Various parameters affecting fabrication of the fiber (weight ratio of components) and relative extraction recovery (pH, amount of adsorbent, extraction time, salt addition, and desorption conditions) were investigated and optimized. Under optimized conditions, the calibration curves were obtained in the concentration range of 0.01–500 ng mL<sup>-1</sup> with regression coefficients between 0.9997 and 0.9999. The limits of detection (LOD) ( $S/N=3$ ) and limits of quantification (LOQ) ( $S/N=10$ ) of the method ranged from 0.001 to 0.004 ng mL<sup>-1</sup> and 0.003 to 0.012 ng mL<sup>-1</sup>, respectively. The intra-day and inter-day relative standard deviations (RSDs) were 2.2–5.9% and 3.2–7.8%, respectively. The applicability of the fabricated adsorbent was investigated by extraction of selected organophosphorous pesticides (OPPs) from real samples of juice and water. The obtained relative recoveries were in the range of 90.6–105.4%, demonstrating elimination of matrix effects which can be attributed to the remarkable affinity of OPPs toward ZNAHF.

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## 1. Introduction

In general, sample preparation is a key step in the trace analysis of environmental samples. Extraction as a part of sample preparation is necessary prior to any instrumental analysis. Solid phase extraction (SPE) [1] and related new miniaturized techniques such as solid phase micro extraction (SPME) [2], dispersive micro solid phase extraction (DMSPE) [3], micro solid phase extraction (MSPE) [4] and, stir-bar sorptive extraction (SBSE) [5] have been employed for effective cleanup and preconcentration procedures. In these sorbent-based extraction methods the selection of adsorbent plays an important role in analytical techniques; thus, a promising direc-

tion of sample preparation is the development of new adsorbents. However, separating sorbent from sample solutions after extraction and elution is a laborious, time-consuming step. Magnetic sorbents [6], stir-bars [7], stir disks [8], encapsulated sorbent in polypropylene membrane bags [9] and fibers with or without modified surfaces [10,11] have been used to overcome these difficulties, because they are easily isolated from matrices.

Alginates (sodium, potassium and ammonium salts of alginic acid) are water-soluble, natural polysaccharides extracted mainly from brown algae. Industrial applications of alginates are based on their gelling, viscosifying and stabilizing characteristics. Alginates are extensively used in biotechnology, medicine and food industries. They are binary, linear copolymers composed from  $\beta$ -D-mannuronic acid (MA) and  $\alpha$ -L-guluronic acid (GA) and are known as nontoxic, biodegradable and non-immunogenic biopolymers (Fig. S1). Differences in M/G ratio and block configuration account for the differences in alginate properties and functionality, especially gelling capability and gel strength. The most important

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chemical property of alginates is the selective binding of multi-valent cations, which is the basis for their sol/gel transition of alginates. A controlled introduction of cross-linking cations such as  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  can form stabilized hydrogels with the formation of a three dimensional network (3D-N) [12–16]. Because of their ability to form stable hydrogels, alginates are widely used for the immobilization of different materials, such as algal biomass, microorganisms and enzymes. In entrapment of living cells within Ca-alginate beads, a cell suspension is mixed with a sodium alginate solution, the mixture dripped into a calcium chloride solution and the droplets instantaneously form gel-spheres entrapping the cells in a 3D-N [16]. Typically, alginates with higher calcium contents (between 3 and 10%, w/w) are nearly or totally insoluble, The proportion and sequence of G blocks in alginate affect the mechanical and swelling properties of the gel beads of Ca-alginate ionic cross-links formed because G-blocks are responsible for specific ion binding with multivalent cations [12,16]. Generally, hydrogels made with synthetic and natural polymers usually have porous surfaces, large specific surface areas and strong loading capacity. The swelling property of hydrogels in water allows the free movement of water and solutes through the inner cavities of hydrogels [17,18]. Recently, metal oxides such as  $\text{TiO}_2$  and  $\text{ZrO}_2$  supported by alginate-based hydrogels have found applications in the analysis of pharmaceuticals and photo-catalytic and adsorption de-pollution of water bodies [14,15,19–22].

Zirconia acts as a hard Lewis acid because of the zirconium (IV) vacant 3d orbital. Lewis acid sites on the surface of zirconia interact strongly with Lewis-based functional groups (e.g.,  $\text{R}-\text{SO}_3^-$ ,  $\text{R}-\text{PO}_3^-$  and  $\text{R}-\text{O}-\text{O}^-$ ), creating coordination bonds [23,24]. This inorganic material with high mechanical property is used as biomaterial for hip prosthesis, tooth crown, and dental implants, and is a candidate for new bone restorative  $\text{R}-\text{SO}_3^-$ ,  $\text{R}-\text{PO}_3^-$  and  $\text{R}-\text{O}-\text{O}^-$  material due to its low toxicity. Recently, zirconia based sorbents are used for DMSPE of pesticide residues in fish and edible oils [25,26]. The use of zirconia nanoparticles (ZNPs) with high surface area, lack toxicity, physicochemical stability over the whole pH range, and selective affinity to phosphorous groups, is an attractive approach for the capture of phosphate groups. Moreover, it has been employed in water treatments and electroanalytical methods [27–33]. However, the small size and possible release into the treated solution restrict their practical applications. Immobilization and encapsulation of nanoparticles with supports such resin, chitosan and alginate have been effectively used to prevent their leakage into the environment [22].

Organophosphorus pesticides (OPPs) are still used extensively throughout the world to improve yield and quality of fruits, grain crops, and vegetables during the entire period of growth [34]. These pesticides are an important contamination source in the environment because of their widespread application, and their residues become a potential threat to human beings. European Union regulations have established maximum residue limits (MRLs) for OPPs in food and water samples in the ranges of  $0.01-0.5 \text{ mg kg}^{-1}$  and  $0.02-0.1 \text{ mg L}^{-1}$ , respectively [35]. Therefore, the effective extraction of these pollutants from complex matrices such as food and environmental samples is necessary and often requires extensive clean-up treatments to isolate target analytes from sample interferences. A wide variety of modern miniaturized sample preparation methodologies in various modes such as dispersive liquid-liquid micro extraction (DLLME) [34,35], SPME [36], and magnetic solid phase extraction [37] coupled with chromatographic techniques have been employed to extract and determine the OPPs. The chemical structures of the examined OPPs are illustrated in Fig. S2.

The object of this work was to develop a facile synthesis methodology for zirconia nanoparticle/calcium alginate hydrogel fiber (ZNCAHF) as novel sorbent for OPPs. The fabricated sorbent with skein shape as a selective, green, and more environmentally-

friendly sorbent was easily applied for simultaneous micro extraction and determination of methyl parathion (MP), fenitrothion (FT) and malathion (MT) (the three most toxic and widely-used OPPs) as model analytes in water and juice samples in off-line conjugation with gas chromatography-mass detection (GC-MS). The 3D-N Ca-alginate provides a suitable environment for the immobilization of ZNPs as an adsorbent to OPPs as well as the easy mass transfer of analytes into the network. With the aid of this hydrogel fiber, there is no need for centrifugation or filtration techniques or the use of magnetic fields for magnetic adsorbents, because it is a floating, fibrous solid phase which is easily withdrawn from the solution using forceps.

## 2. Experimental

### 2.1. Reagents and standards

Certified standards of MP, FT and MT were supplied by Fluka. Stock solutions of these compounds were prepared in methanol at a concentration of  $500 \text{ mg L}^{-1}$  and were stored at  $-20^\circ\text{C}$ . ZNPs were purchased from Inframat Advanced Materials (Farmington, CT, USA). Sodium alginate (SA) from brown algae with an approximate viscosity of 3500 cps was purchased from Sigma. Methanol (MeOH), toluene, *n*-propanol, dichloromethane (DCM), acetone, acetic acid (HOAC), hydrochloric acid (HCl), sodium hydroxide (NaOH), calcium chloride ( $\text{CaCl}_2$ ), and sodium chloride (NaCl) were purchased from Merck (Darmstadt, Germany).

### 2.2. Instrumentation

GC analysis was carried out on an Agilent 7890A instrument (Palo Alto, CA, USA) with split/splitless injection port, and an Agilent 5975C mass detector system were used. The MS detector was operated in electron impact (EI) mode with ionization energy of 70 eV. Helium (99.999%) was used as the carrier gas at a flow rate  $1 \text{ mL min}^{-1}$ . OPPs were separated on a  $30 \text{ m} \times 0.320 \mu\text{m}$  HP-5 MS column with  $0.25 \mu\text{m}$  film thickness. The GC column temperature was first  $70^\circ\text{C}$  ( $t=0 \text{ min}$ ), then increased to  $150^\circ\text{C}$  by  $25^\circ\text{C min}^{-1}$ , next raised to  $180^\circ\text{C}$  by increments of  $3^\circ\text{C min}^{-1}$ , and finally increased to  $200^\circ\text{C}$  by increments of  $1.5^\circ\text{C min}^{-1}$ . The split/splitless injection port was set at  $250^\circ\text{C}$  and in splitless mode. The GC-MS interface, ion source and quadruple temperatures were set at 280, 230 and  $150^\circ\text{C}$ , respectively. The solvent delay and total run time for analysis were 7 min and 22 min, respectively. For quantitative determination, MS detector was operated in the time-scheduled selected ion monitoring (SIM) mode. Data acquisition was conducted using Chemstation software. Field emission scanning electron microscopy (FESEM) and energy dispersive x-ray diffraction (EDX) were used to show the morphology, dimension and composition of the ZNCAHF (Mira 3-XMU, Germany). FTIR spectrum was recorded by a vertex 70 FTIR spectrometer (Bruker, Germany). Differential scanning calorimetric (DSC) analysis was performed using a DSC1 STAR system (Mettler Toledo, Switzerland). 10 mg of sample was put in an aluminum pan and heated from 0 to  $400^\circ\text{C}$  at a constant heating rate of  $10^\circ\text{C min}^{-1}$  under constant purging of nitrogen at  $20 \text{ mL min}^{-1}$ . Solution pH values were measured by a pH-meter E520 (Metrohm Herisau, Switzerland). Fibers were prepared using a probe sonicator with the power output of 400 w (TOPSONICS, Iran). Solvent desorption of OPPs was performed by an ultrasonic bath (Elma, Germany). All sample solutions were stirred using a CAT M 6.2 magnetic stirrer (Germany).

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