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Construction a magneto carbon paste electrode using synthesized molecularly imprinted magnetic nanospheres for selective and sensitive determination of mefenamic acid in some real samples

Tayyebeh Madrakian*, Esmaeel Haghshenas, Mazaher Ahmadi, Abbas Afkhami

Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

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ABSTRACT

A novel magneto multiwalled carbon nanotube/carbon paste electrode (MMW/CPE) for the determination of mefenamic acid (MFA) was introduced. Magnetic molecularly imprinted polymer nanoparticles (MMIPNPs) were synthesized and then added to the solution of MFA. After stirring for 20 min, the MMW/CPE was immersed in the solution of MFA (contain MMIPNPs) and the MMIPNPs were captured by it. Then oxidation of MFA was analyzed by differential pulse voltammetry (DPV). Electrochemical impedance spectroscopy, cyclic voltammetry, and DPV were employed to characterize the MMW/CPE. The MMIPNPs exhibited a high selectivity and sensitivity toward MFA. The effect of various experimental parameters including pH, MMIPNPs dosage, stirring time, accumulation potential and time on the voltammetric response of MFA were investigated. Under the optimal conditions, selective detection of MFA in a linear concentration range of 2.0–1000.0 nmol L^{-1} was performed with the detection limit of 1.2 nmol L^{-1} (3S/N). To further study the practical applicability of this method, it was applied to the analysis of some real samples and the obtained results were satisfactory.

1. Introduction

Mefenamic acid (MFA), *N*-(2,3-xylyl)anthranilic acid, is a nonsteroidal anti-inflammatory drug (NSAID) used as potent analgesic and anti-inflammatory agent in the treatment of osteoarthritis, rheumatoid arthritis and other painful musculosketal illnesses (Evangelos et al., 2009; Rouini et al., 2004). MFA blocks certain substances in the body that are linked to inflammation. It is used in cases of mild to moderate pain, including headache, dental pain, postoperative and post-partum pain, and in musculoskeletal and joint disorders such as osteoarthritis (Heli et al., 2009). A number of analytical methods have been developed for the quantitative determination of MFA in dosage forms and in biological samples. Those include spectrophotometry (Raza, 2008; Alarfaj et al., 2009; Kumar et al., 2009), titration methods (Kobzar et al., 2006), flow injection (Aly et al., 2000), chromatography (Ankam et al., 2010). These methods are time consuming, expensive and often need the pretreatment step. Also, some of them suffer from low sensitivity and selectivity in the corresponding determinations. To overcome these defects, electrochemical methods are used extensively for the elegant and sensitive properties such as selectivity, reproducibility, low cost and simplicity of this approach.

Over the last few years, molecular imprinting technique has received considerable attention in the fields of polymer science and chemical analysis, owing to its predetermined selectivity for target molecular, high affinity and robustness (Haupt and Mosbach, 2000; Liang et al., 2009). The highly selective recognition characteristics of the MIPs are comparable to those of the natural biological species such as receptors and antibodies. The advantages of MIPs, such as stability at extremes of pH and temperature, ease of preparation, low cost, and reusability, have led to the development of various MIP applications in chromatographic separation (McNiven et al., 1997; Ou et al., 2007), chemical and electrochemical sensors (Kirsch et al., 2001; Afkhami et al., 2013), capillary electrochromatography (Vallano and Remcho, 2000), solid phase extraction (SPE) (Madrakian et al., 2013a; Sun et al., 2008; Chen et al., 2009)

Recently, a technique based on magnetic polymer has received increasing attention. Generally, magnetic polymer is prepared by encapsulating inorganic magnetic particle with organic polymer. The magnetic polymer adsorbing analytes can be easily collected by an external magnetic field without additional centrifugation or filtration, which makes separation easier and faster (Chen et al., 2009). Recently, using of magneto electrodes in electrochemical sensing of various compounds was improved. Ability of magneto electrochemical sensors to capture different functionalized

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* Corresponding author. Fax: +98 811 8257407.
E-mail addresses: madrakian@basu.ac.ir, madrakian@gmail.com (T. Madrakian).

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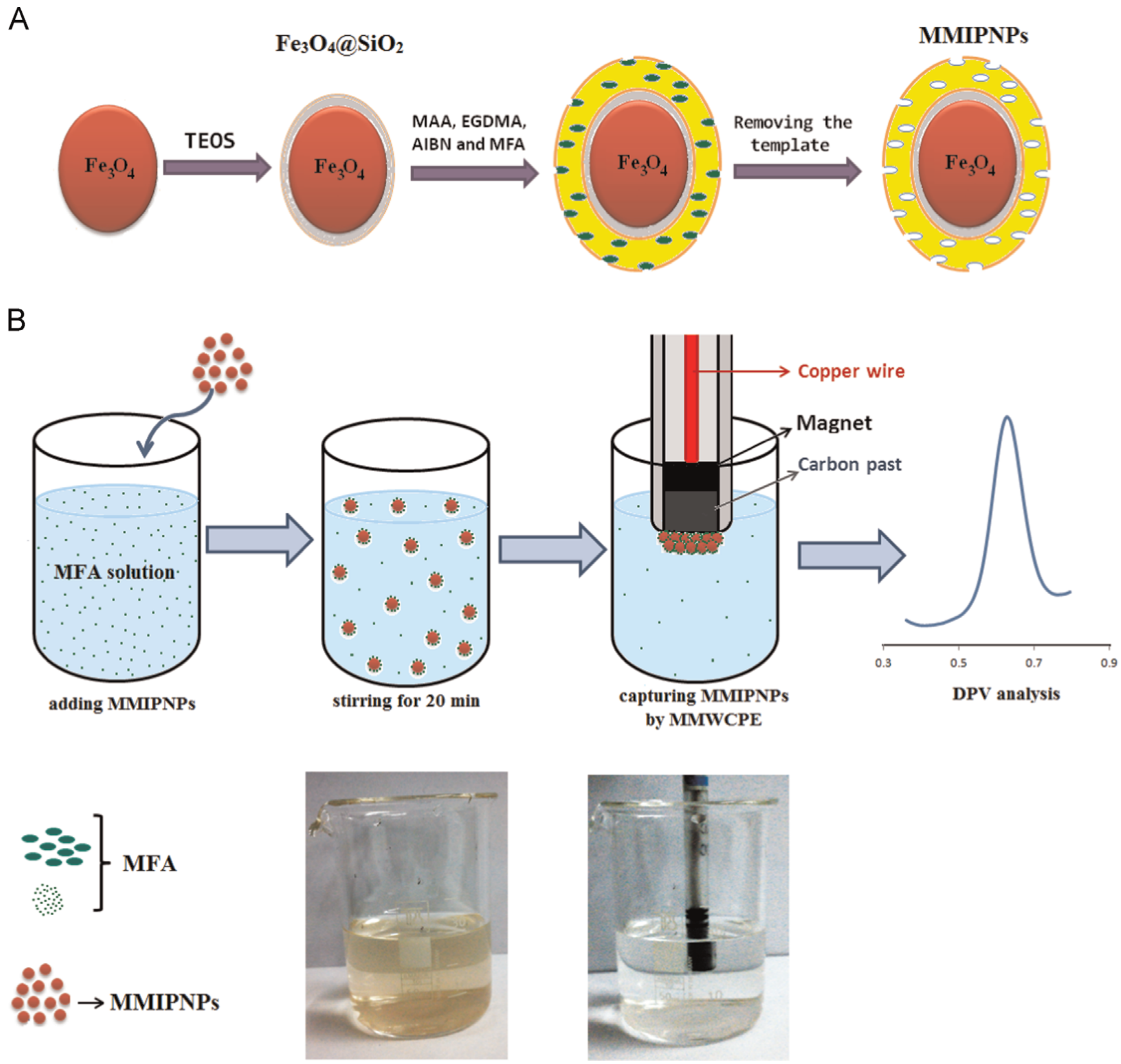

Scheme 1. Schematic illustration showing the preparation of MMIPNPs (A), the stepwise procedure and electrochemical detection of MFA (B).

magnetic beads from solution makes it an excellent devise for determination of molecules and biomolecules in recent years (Yang and Li, 2001; Conzuelo et al., 2012; Kergaravat et al., 2013).

In the present study, we describe a magneto multiwalled carbon nanotube/carbon paste electrode (MMW/CPE) for selective and sensitive MFA detection in pharmaceutical and urine samples. The present strategy is based on two steps: firstly, suitable amount of MMIPNPs was added in the solution of MFA and stirred for 20 min. At this step, MFA molecules were selectively adsorbed on MMIPNPs. In the next step, the MMIPNPs are captured by a MMW/CPE. This work cause MFA concentration increase on the magneto electrode surface. The electrochemical response is measured using differential pulse voltammetric (DPV) method. A schematic illustration of the stepwise procedure and electrochemical detection of MFA was presented in Scheme 1. The developed sensor was successfully applied to the determination of MFA in pharmaceutical and urine samples.

2. Experimental

2.1. Chemicals

All reagents and materials, such as ethylene glycol dimethacrylate (EGDMA), methacryl amide (MAA), $FeCl_3 \cdot 6H_2O$ and tetraethoxysilane (TEOS) were of analytical grade and purchased from Merck Company (Darmstadt, Germany) or Aldrich Company (USA). Multiwalled carbon nanotubes (10–20 nm in diameter, length of 30 μm, purity of 95%) were purchased from Neutrino Company (Iran). A Briton–Robinson buffer solution (BRBS) of pH 5.0 served as a supporting electrolyte solution.

2.2. Apparatus

Electrochemical measurements were performed on a potentiostat/galvanostat (Autolab PGSTAT302 N). It was controlled by a computer using Nova version 1.7 software. A platinum wire was used as the auxiliary electrode. MMW/CPE and Ag/AgCl were used as the working and reference electrodes, respectively. A Knauer 1050 HPLC pump and a Knauer 2850 PDA detector with Macherey nagel column C18 (150 mm × 2.5 mm, particle size 4 μm) was used. For instrumental control, data collection and processing chromgate software was employed. A Metrohm Model 713 pH lab (Herisau, Switzerland) was used for pH measurements.

2.3. Preparation of modified carbon paste electrode

The MW/CPE was prepared via mixing graphite powder,