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Synthesis and characterization of magnetic poly(acrylonitrile-*co*-acrylic acid) nanofibers for dispersive solid phase extraction and pre-concentration of malachite green from water samples

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ABSTRACT

This research describes the development of a new design of nanosorbents, magnetic poly(acrylonitrile-*co*-acrylic acid) (PAN-*co*-AA) nanofibers, for the pre-concentration of malachite green (MG) residues in water samples via dispersive magnetic solid phase extraction (d-MSPE) technique. After pre-concentration, the spectrophotometric method was used to determine MG. Magnetic PAN-*co*-AA nonwoven nanofibers was fabricated by the optimized electrospinning technique after optimization of electrospinning conditions. According to the results, increasing magnetic nanoparticles (MNPs) into polymeric matrix led to significant reduction of fiber diameter from 360 to 70 nm. This change was associated with an increase in nanofibers surface area (from 9.66 $m^2 g^{-1}$ to 12.09 $m^2 g^{-1}$). Fabricated magnetic nanofibers demonstrated suitable magnetic properties (3.6 emu g^{-1}), so it can be used for magnetic separation and easy extraction techniques. In the following step, magnetic PAN-*co*-AA nanofibers (MNFs) were used to determine MG in aquatic samples. The influence of different parameters on extraction was investigated and optimized to improve the extraction efficiency of MG. The calibration curve was linear in the range of 0.3–1.8 mg L^{-1} of MG with $R^2 = 0.9911$. The detection limit, based on three times the standard deviation of the blank, was 0.03 mg L^{-1}. The relative standard deviation (RSD) for 1, 1.5 and 1.8 mg L^{-1} of MG was 4.31%, 6.86% and 7.68% (n = 6), respectively. MG was analyzed in different water samples (urban, mineral and river waters) using the proposed method. The recoveries were 95.83–103.3% with an RSD of less than 8%. The results showed that MNFs were suitable for pre-concentration and determination of trace amount of MG in wastewater samples.

Introduction

To separate different types of analytes from various matrices, solid phase extraction technique (SPE) is used before instrumental analysis as a critical step in the analytical process. In large samples, rapid extraction is essential to lower limits of detection (LODs) [1,2]. Dispersive solid phase extraction (DSPE) has advantages over SPE including (1) the contact between sorbent and analytes does not require columns and pipette types; (2) adsorbents are in touch with analytes by stirrer or ultrasound and then separate by centrifuge; (3) using minimum organic solvent, adsorbent, operating time and laboratory workers [3,4]. Different types of nano – sorbents, due to high surface area to volume ratio, can be used in DSPE such as multi-walled carbon nanotubes (MWCNTs) [5] Cu@SnS/SnO_2 nanoparticles [6] and mesoporous silica nanoparticles [7].

Electrospinning is a technique for fabrication of nonwoven fibers. A great deal of efforts have been dedicated to use electrospun nanofibers for the extraction or removal of pollutants

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from real samples. The penetration rate of analytes onto electrospun nanofibers is high due to high surface area and porous-hydrophilic surface of nanofibers [8]. To enhance the adsorption rate of different compounds/analytes onto electrospun nanofibers, a series of strategies can be exploited to endow or improve the functional performances of electrospun nanofibers, such as 1) increasing the surface area of nanofibers; 2) modifying the surface of nanofibers; 3) preparing composite nanofibers [9] and creating complex nanostructures including core-sheath, Janus random fibers, necklace-like fibers, ribbon fibers, porous fibers, multichannel tubular fibers and their combination [10–13]. Recently there are different approaches to fabricate nanofibers in high speed production and desired properties, such as multi jet electrospinning [14], coaxial electrospinning [15] and melt electrospinning [16]. These methods can be explored for enhancing the adsorption rate of different compounds/analytes onto electrospun products. The chrome extraction was carried out using tetraphthalate electrospun nanofiber with an inner diameter of 98–504 nm [17]. Polystyrene nanofiber with 70 $m^2 g^{-1}$ surface area was used for extraction of sulfonoamides [18]. In addition, the pollutant removal was achieved using poly(vinyl alcohol-*co*-ethylene) [19], poly ethylene oxide (PEO)/chitosan [20] and polypyrrole nanofibers [3].

Magnetic solid-phase extraction (MSPE) is another sub-fields of SPE. In MSPE, the sorbent involves magnetic nanoparticles entering in a sample solution. After the adsorption of analytes, it is separated from the solution using an external magnetic field without centrifugation or filtration [21,22].

In this research, an electrospun nanocomposite was synthesized based on magnetic nanoparticle (Fe_3O_4)/poly(acrylonitrile-*co*-acrylic acid) and used for the pre-concentration and spectrophotometric determination of malachite green (MG) in dispersive-MSPE (d-MSPE) technique.

As a cationic triphenylmethane dye, MG is effectively used as an antifungal, antimicrobial and anti-parasitic agent in food industry, and a dying rubber and paper [23,24]. Due to low concentrations of the pollutant, the pre-concentration of MG was performed by micro-cloud point extraction [24], matrix solid phase dispersion [25] and molecularly imprinted solid phase extraction [26]. Also, a wide variety of nanoadsorbents have been used for pre-concentration of MG from environmental samples [27,28]. Asfaram et al. [29] reported MG extraction using Mn-doped ZnS nanoparticles loaded on activated carbon as the SPE material. Plotka-Wasylka et al. [30] used the magnetic MWCNTs with a limit detection of 0.22 ng mL^{-1} for pre-concentration of MG.

In general, there are many researches for SPE and removal of malachite green from water media by different nanostructures and techniques. But as our knowledge there is no report about the removal or preconcentration of MG using magnetic PAN-*co*-PAA nanofiber.

Because of some excellent properties, such as mechanical and thermal properties, high chemical resistant and solubility in polar solvent, acrylonitrile (AN) and AN based copolymers have been used in many applications like plastics, synthetic fibers, rubbers and so many composites [31]. However, the use of homopolymer, PAN, has been rarely reported in fiber manufacturing. Because of high melting point and high melt viscosity, spinning and dying of PAN nanofibers are too difficult [32]. Furthermore, AN homopolymer's flow temperature is higher than its decomposition temperature. Copolymerization of AN with acidic co-monomers such as itaconic acid (IA) and acrylic acid (AA) can decrease the glass transition temperature and melting point of PAN [33]. In other hand, copolymerization of AN with AA improves copolymer's capacity for pollutants adsorption which is due to presence of carbonyl groups in AA [34]. So, co-polymerization of AN with AA enhanced the properties of nanofibers for the pre-concentration of MG. The co-polymer was sensitized by radical polymerization, due to production of high molecular weight polymer.

As mentioned above in this paper, the preparation and characterization of magnetic polyacrylonitrile co acrylic acid nanofiber by electrospinning was studied. The influence of electrospinning parameters such as polymeric concentration, applied voltage, feeding rate, working distance and collector type on morphology of pure PAN-*co*-PAA nanofibers with molecular weight of 131,000 g/mol are investigated for the first time. The pure nanofiber which fabricated under the optimum electrospinning parameters were 360 nm of average diameter. The existence of magnetic nanoparticles on morphology of magnetic PAN-*co*-PAA nanofiber with different mass ratio of MNPs was studied. It was observed that nanofiber diameter reduced from 360 nm to 74 nm by increasing the amount of magnetic nanoparticles into polymeric solution, which led to the increased surface area from 9.66 to 12.06 $m^2 g^{-1}$ and also MG adsorption. The effect of different SPE parameters on extraction efficiency were studied. Low limit of detection (0.03 mg L^{-1}), and high recovery (95–103%) were obtained by use of the least magnetic sorbent. These magnetic nanofibers (MNFs) provide desirable magnetic properties, which enables convenient operations over a short time. The extraction performance of MNFs as a novel, rapid and suitable sorbent was evaluated for d-MSPE of MG from water samples prior to the spectrometric determination.

Experiments

Materials

Anhydrous ferric chloride ($FeCl_3$), anhydrous sodium acetate (CH_3COONa), ethanol, methanol, acetone, diethylene glycol (DEG), *N*,*N*-dimethylformamide (DMF), acrylonitrile (AN), acrylic acid (AA), azobisisobutyronitrile (AIBN), dimethyl sulfoxide (DMSO), acetic acid (98–100%), hydrochloric acid (HCL), sodium chloride (NaCl) and sodium hydroxide (NaOH) were of analytical grade and purchased from Merck Co., Germany. AIBN was purified by recrystallization from methanol. Other materials were used as-received without further treatment. Mili-Q water was used with a minimum resistivity of 18.2 MΩ cm^{-1}. Malachite green (MG) was purchased from Shanghai Anpel (Shanghai, China).

Preparation of magnetite (Fe_3O_4) nanosphere

The Fe_3O_4 nanoparticles were prepared by a modified solvothermal method, according to Ref. [35]. In brief, 1.35 g of $FeCl_3$ was first dissolved in 40 mL of DEG under vigorous stirring at 80 °C until a homogeneous solution was obtained. Then 3.6 g of CH_3COONa was added and stirred. Temperature was maintained at 80 °C during the procedure. Then, the obtained solution was transferred to a teflon-lined stainless steel autoclave with a volume of 100 mL. The autoclave was sealed and heated at 180 °C for 12 h. After natural cooling of the autoclave, Fe_3O_4 NPs were obtained. The black Fe_3O_4 NPs were collected by an external magnetic field and washed with ethanol and acetone. The final products were achieved after 4 h of drying in the air at room temperature.

Preparation of poly(acrylonitrile co acrylic acid)

PAN-*co*-AA were synthesized by radical copolymerization in DMSO solution in the presence of AIBN as follows [36]: AN and AA (mass ratio of 4:1) were dissolved in the DMSO (mass ratio of total monomer to DMSO 4:11). AIBN as the initiator was transferred to the mixed solution and the weight ratio of total monomers was 1:450. Then, the solution was stirred until all substances were completely dissolved. After passing nitrogen to the solution for 1 h,