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Application of hollow fiber membrane mediated with titanium dioxide nanowire/reduced graphene oxide nanocomposite in preconcentration of clotrimazole and tylosin

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ABSTRACT

In this paper, TiO_2 nanowires and TiO_2 nanoparticles have been successfully anchored on graphene oxide (GO) nanosheets by a facile one-step hydrothermal method. The synthesized TiO_2 NWs/RGO and TiO_2 NPs/RGO nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. After comparatively studying of the as-made nanocomposites, TiO_2 NWs/RGO nanocomposite showed the best adsorbing performance and applied as an attractive efficient sorbent reinforced with microporous hollow fiber membrane through the sol–gel technology. In the following, the selected nanocomposite was utilized for simultaneous preconcentration and determination of clotrimazole and tylosin using high performance liquid chromatography (HPLC)–UV detection, respectively. In order to optimize the extraction conditions through affecting parameters (pH, stirring rate, salt addition, extraction time and volume of donor phase), response surface methodology (RSM) was employed as a powerful statistical technique. Under the optimal conditions, the limit of detection (S/N = 3) of proposed HFSPME method, was 0.67 $\mu g\,L^{-1}$ for clotrimazole and 0.91 $\mu g\,L^{-1}$ for tylosin with good linear ranges of 1.7–8000.0 $\mu g\,L^{-1}$ and 4.0–6000.0 $\mu g\,L^{-1}$. The inter-day and intra-day relative standard deviations (RSD%) at 100 $\mu g\,L^{-1}$ concentration level were in the ranges of 2.10–3.58% for clotrimazole and 3.45–7.80% for tylosin ($n = 5$), respectively. The proposed microextraction device was extended for determination of ultra trace amounts of target analytes in milk and urine samples with satisfactory results.

1. Introduction

Over the recent years, development of some modern environmentally friendly miniaturized techniques based on hollow fiber membrane such as: liquid phase microextraction (LPME) [1], solid/liquid phase microextraction [2], solid phase microextraction (SPME) [3] and stir bar sorptive extraction (SBSE) [4] has been attracted much interest for researchers. Among the above strategies, combination of solid phase microextraction as the most common sample preparation techniques with hollow fiber was first introduced by E'shaghy et al. in 2011 [5,6]. Some of the advantages of the newly so-called technique are: Simplicity, flexibility, minimal consumption of reagents (especially organic solvent and sample amount), high enrichment performance, high repeatability due to the disposable nature of device which prevents carryover effect, better convenient handling than conventional SPME fibers and easy compatibility with analytical instruments such as: liquid chromatography (LC) [5,7], gas chromatography (GC) [8] and inductively coupled plasma mass spectrometry (ICP-MS) [9]. The state of the art, graphene oxide has many unique applications including electrochemical energy devices (lithium ions battery, super capacitor, and fuel cell) [10], photoelectrochemical and photocatalytic approaches [11,12]. Moreover it can be an excellent substrate to attach with various functional groups and metal oxides due to abundant hydrophilic groups such as hydroxyl, carboxyl, and epoxyl groups bonded with carbon and other atomic scale defects [13], thereby promoting its analytical and environmental applications such as detection and removal of threatening pollutants [14]. Due to the capability of GO in trapping analytes via π−π

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stacking, van der Waals interactions, or hydrogen bonding [11], together with the inherent properties of titanium dioxide in capping and coordinating with organic species [15], the integration of GO and TiO_2 into a single composite, could be a hot topic of analytical researches respectively.

So bearing in mind that an efficient sorbent plays a critical role in SPME technique [16], we were interested to investigate the extraction behaviors of graphene-based TiO_2 nanocomposites as innovative sorbents, expecting an enhancement in recovery and extraction capacity. In our previous work, we applied functionalized TiO_2 nanoparticles dispersed in organic solvent as HF-S/LPME method [17].

In this work, two graphene-based TiO_2 nanocomposites were synthesized by a green facile one-step hydrothermal reaction [18]. It is worth emphasizing that the hydrothermal synthesis, guarantees two processes in a single step, GO reduction to RGO and decoration of TiO_2 nanoparticles (NPs) or nanowires (NWs) on RGO respectively. The extensive use of veterinary drugs in local houseplant, may leave residues in milk and other dairy products such as cheese, egg, and etc. especially if farmers do not respect the recommended withdrawal times [19]. On the other hand, after consumption of these pharmaceuticals, they are excreted via urine or feces and released into the soil and surface waters thereby leached into groundwater resulting in potential hazards to at-risk populations in receiving ecosystems [20]. In this research, clotrimazole as a topically used antifungal drug with broad spectrum antimicrobial activity, and tylosin as one of the most popular macrolide antibiotics were selected as target species (see Table S1; Supporting information). The European Union (EU) has been established maximum residual limit (MRL) of 50 ppb in milk samples for tylosin and has not allowed residue of clotrimazole in any products of animal origin, respectively [20,21]. So, developing very sensitive methods for monitoring of such organic contaminants is a matter of high priority.

Based on the mentioned facts, herein we introduced two different structures of TiO_2 anchored on graphene oxide as innovative and efficient sorbents supported by hollow fiber membrane via sol–gel technology and were investigated for simultaneous determination and preconcentration of trace amounts of clotrimazole and tylosin using HPLC–UV detection, respectively. Tetra ethyl orthosilicate (TEOS) with an acidic medium was used to create the polymeric network. To the best of our knowledge, application of TiO_2 NWs/RGO and TiO_2 NPs/RGO mediated with hollow fiber membrane as a novel microextraction device has not been reported before. Central composite design (CCD) as a fractional factorial design method was used to a rapid optimization with a minimal number of experiments for the main operating parameters. Indeed, the interaction between independent variables could be analyzed satisfactorily [22]. The results were analyzed by means of the statistical software Minitab 1410.0 for Windows.

2. Materials and methods

2.1. Reagents and materials

Graphite powder was purchased from Graphene Expert Co. (Tehran, I.R.I.) and commercial TiO_2 powder (P25), was supplied by Degussa Co. (Germany). Tylosin base and clotrimazole (with the minimum purity of 99%) were kindly donated by Erfan Daroo Co. (Tehran, I.R.I.). HPLC grade methanol (MeOH) and acetonitrile (ACN) were from Romil Co. (England). Tetra ethyl orthosilicate (TEOS, 97%) as the sol–gel precursor, 1-octanol, hydrochloric acid (37%) and the additive Triton X-100 were obtained from Merck (Darmstadt, Germany). Ultrapure deionized (DI) HPLC grade water was obtained from a purification system (Model TKA, Smart2 Pure Germany) and used to prepare mobile phase and sample solutions. All other reagents and solvents were of analytical grade.

2.2. Instrumental

All chromatographic measurements were performed with a Waters 1500 Series (Milford, MA, USA) equipped with dual λ absorbance detector (Waters Model 2487, USA). The separation was carried out on a C_{18} reversed octadecyl phase HPLC column, endcaped with 17.5% C)250 mm × 4.6 mm, 5 μm, Nucleodur; Germany). After several testing of different mobile phases consist of methanol or acetonitrile as organic phase, the elution composition of (ACN-MeOH-0.15% phosphoric acid pH 7.5) (15:60:25 V/V/V) was run in isocratic mode at a flow rate of 1.0 mL min^{-1}. The wavelengths were set at 270 and 284 nm for clotrimazole and tylosin base respectively. The mobile phase was filtered through a 0.45 μm nitro cellulose membrane prior to use. The injection volume was 50 μL and the column was thermostated at 25 °C using a column oven.

Identification of functional groups was carried out using FTIR spectrometer (Thermo; UK) in the range of 500–4000 cm^{-1}. The morphology and structure of synthesized nanocomposites was characterized by field emission scanning electron microscopy (FESEM; Model MIRA3 Tescon). X-ray diffraction (XRD) experiments were carried out using a Bruker D8 Advance X-ray diffractometer (Germany) using Cu K_α radiation (λ = 1.54060 Å).

2.3. Preparation of standard solutions and real samples

The stock standard solution (0.5 mg mL^{-1}) of each analyte was prepared separately in methanol and the mixed working solutions were prepared freshly by diluting the stock solutions with deionized water when necessary. All the solutions were stored at 4 °C and maintained in dark glass bottles. Three types of milk samples including raw full fat milk (from local farmland of University of Zanjan), pasteurized and sterilized low fat milk (from a local supermarket) were used to confirm the applicability of the method and preparation processing of milk samples was carried out according to Ref. [17]. Bovine urine samples were collected from local farmland of University of Zanjan and filtered through a 0.45 μm Minisart SRP 15 polytetrafluoroethylene membrane before using.

2.4. Synthesis of GO, TiO_2 NPs/RGO and TiO_2 NWs/RGO nanocomposites

Graphene oxide (GO) as the major substrate was synthesized from graphite via a modified Hummers' method [25], and graphene based TiO_2 nanostructures were prepared through a one step hydrothermal method according to earlier reports [18,26], by some little changes in detail. Briefly 500 mg GO was sonicated in a solution of 100 mL DI water and 40 mL of ethanol for 1 h to avoid agglomeration. Next, 150 mg Degussa P25 TiO_2 powder was added slowly to GO while stirring. The sonication and stirring was continued alternately for further 2 h until a homogeneous light gray suspension was yield. Then 10.5 g of KOH was added to the mixture and transferred into a Teflon-lined autoclave and reacted at 200 °C for 24 h, thereby cooled down naturally to room temperature. In fact the alkaline medium played the role of reduction of GO and formation of TiO_2 NWs simultaneously. The resultant product was washed with diluted HCl solution (1.2 M) and stirred slowly overnight then centrifuged for several times and dried at ambient condition. In the case of TiO_2 NPs/RGO the hydrothermal process was held just 3 h at 150 °C without adding KOH granules thereby no need was to dilute with HCl solution.