



Graphene-derivatized silica as an efficient solid-phase extraction sorbent for pre-concentration of fluoroquinolones from water followed by liquid-chromatography fluorescence detection



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ABSTRACT

This work presents a novel analytical method based on graphene for the determination of five widely used fluoroquinolones (FQs) in aqueous matrices. The procedure entails solid-phase extraction (SPE) on graphene-derivatized silica (200 mg), followed by liquid chromatography with fluorescence detection. Monolayer graphene oxide (GO) flakes were covalently bonded onto aminopropyl silica microparticles, and then treated with aqueous hydrazine to obtain the reduced GO (RGO). The final material (RGO–silica) was characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and BET analysis, and for the first time evaluated as mixed-mode sorbent for the SPE of FQs from natural waters. Accuracy was studied on tap/raw river water in the concentration range 5–10,000 ng L⁻¹, obtaining mean absolute recoveries from 72 to 118%. The inter-day precision was good, showing relative standard deviations (RSDs) in the range 5–15%. Sample volumes up to 1 L provided enrichment factors up to 1000, achieving accurate quantification of concentrations as low as 5 ng L⁻¹. The analytes were simultaneously and quantitatively eluted from the RGO–silica cartridge in a single fraction by using acetonitrile combined with aqueous tetrabutyl ammonium hydroxide. The batch-to-batch reproducibility was verified on three independently prepared RGO–silica samples. RGO–silica was advantageous in terms of adsorption capacity and reusability with respect to commercial sorbents; the cartridge proved to be reusable for at least 10 consecutive extractions, with no significant loss of efficiency (recovery >70%). The analytical procedure was applied to the determination of FQs in actual environmental waters.

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1. Introduction

Since the first experimental evidence of its unique electronic properties in 2004 [1], graphene (GN) has become the most intensively studied material. GN represents a new form of carbonaceous material, consisting of single-layer or few-layer thickness of sp²-hybridized carbon atoms forming a honeycomb structure. Due to the high surface area and outstanding physical–chemical properties, GN has attracted great interest in the recent years in many research fields, including analytical chemistry [2]. In particular, GN appears as the ideal candidate to prepare novel sorbent materials for solid-phase extraction (SPE), a technique that has gained great popularity for trace determination of a variety of analytes in view of its low cost, high enrichment factors and reduced consumption

of organic solvents [2]. As described in the recent review by Sitko et al. [2], graphene oxide (GO) and reduced graphene oxide (RGO) – obtained by exfoliation of graphite and from GO reduction, respectively – have been tested for pre-concentration of metal ions and organic compounds, due to the possibility to establish various interplays with the target species, viz. π–π stacking, cation–π bonding, electron donor–acceptor interaction, hydrogen bond, hydrophobic interaction etc. With regard to organic analytes (i.e. chlorophenols, phthalate esters and sulfonamides) better performance was observed in respect of carbon nanotubes, graphitic carbon, and commercial sorbents [3–6], owing to the special morphology of GN wherein both sides of the planar sheets are easily accessible for molecular adsorption, enabling fast adsorption equilibrium and analyte elution [4].

A recent work [7] investigated in batch the sorption affinity of RGO/magnetite for two fluoroquinolone (FQ) antibiotics, reporting adsorption capacities in water around 20 mg g⁻¹. However, to the best of our knowledge, no analytical methods focusing on the use of

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GN or GN-based materials for SPE of FQs from water are currently available in the literature.

FQs are antibiotics for human and veterinary medicine, endowed with broad activity spectrum against Gram bacteria, and good oral absorption [8]. Their occurrence in the environment is issue of great concern and has been assessed in the last years, both in aquatic [9] and soil [10] compartments at concentrations in the ranges $\text{ng}/\mu\text{g L}^{-1}$ and $\mu\text{g}/\text{mg kg}^{-1}$, respectively [9,10]. The environmental diffusion of these anthropogenic compounds is due to various reasons. First, FQs are excreted in pharmacologically active form [11]; moreover, their removal in wastewater treatment plants (WWTPs) is only partial [12,13], consequently variable quantities of drugs are regularly released into aquatic basins, affecting FQs transformation and removal rates. On this account, FQs can be defined as “pseudo-persistent” emerging contaminants [14]. Additional sources of contamination are the custom of recycling liquid manure from livestock farming and sewage sludge from WWTPs as fertilizers [11], animal medication in fish farming [15] and recycling of sludge for the production of compost, widely employed as soil conditioner/fertilizer [16]. Although photodegradation represents the major natural FQs decontamination pathway both in water [17,18] and soil [19,20] systems, the presence of these antibiotics in the environment involves serious threats to the ecosystem and human health due to their ability to stimulate bacterial resistance [21,22], and due to the formation of pharmacologically active photoproducts contributing to the environmental impact [22,23]. For these reasons, FQs environmental monitoring is an important task, requiring accurate and sensitive analytical methods. With regard to water systems, the low concentrations usually detected (from tens ng L^{-1} to few $\mu\text{g L}^{-1}$) necessitate a pre-concentration step prior analysis, usually performed by reversed-phase SPE on hydrophobic or mixed-mode sorbents such as C18-silica and HLB (hydrophilic/lipophilic-balanced polymer), respectively [9].

On the basis of the current state of the art, we deemed interesting to test GN for SPE of FQs from natural waters. A hybrid material consisting of silica microparticles modified with GN was prepared, characterized by scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and BET measurement, and tested as a fixed-bed SPE sorbent for the simultaneous pre-concentration of five widely employed FQs, viz. Ciprofloxacin (CIP), Enrofloxacin (ENR), Levofloxacin (LEV), Marbofloxacin (MAR) and Norfloxacin (NOR), from tap water and not tampered river water. After SPE, separation and quantification was performed by high performance liquid chromatography coupled with fluorescence detection (HPLC–FD). The main figures of merit of the proposed analytical method have been explicated. Cartridge reusability and batch-to-batch reproducibility have been assessed. The analytical procedure has also been applied to the determination of FQs in actual environmental water samples.

2. Experimental

2.1. Chemicals and materials

All the chemicals employed were reagent grade or higher in quality. Graphene oxide (flake size 0.5–5 μm , thickness $1.1 \pm 0.2 \text{ nm}$, 80% atomic layer, C 79% O 20%) was purchased from Graphene Laboratories Inc. (New York, USA). Silica (<63 μm , 230 mesh; surface area $550 \text{ m}^2 \text{ g}^{-1}$; cation exchange capacity $0.43 \text{ mequiv. g}^{-1}$) from Merck (Darmstadt, Germany) was used. Analytical grade FQs standards, tetrabutyl ammonium hydroxide (TBAH, 1 M in H_2O), anhydrous N,N-dimethylformamide (DMF, 99.8%), N,N'-dicyclohexylcarbodiimide (DCC, 99%), aminopropyltriethoxysilan (99%), ethanol ($\geq 99.8\%$), toluene ($\geq 99.9\%$), Schleicher&Schuell® filter paper, polypropylene

tubes and polyethylene frits were supplied by Sigma–Aldrich (Milan, Italy). Oasis® HLB (200 mg) cartridges were purchased from Waters (Milan, Italy). HPLC gradient grade acetonitrile (ACN) and methanol (MeOH) were purchased by VWR (Milan, Italy). H_3PO_4 (85%, w/w), HCl (37%, w/w), NH_3 (30%, w/w), anhydrous NaOH (97%) and hydrazine ($\geq 99\%$) were obtained from Carlo Erba Reagents (Milan, Italy). Ultra-pure water (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25°C) was produced by a Millipore Milli-Q system. pH was measured by an Orion 420A pH meter (Thermo Electron, Rodano, Italy). FQs stock solutions of $200 \mu\text{g mL}^{-1}$ were prepared in MeOH containing 0.1% (v/v) 1 M NaOH and stored in the dark at 4°C . FQs working solutions of $0.1\text{--}1 \mu\text{g mL}^{-1}$ in 25 mM H_3PO_4 were renewed weekly. All the laboratory operations involving use of standard solutions were conducted under red light.

2.2. Synthesis of RGO–silica

Silica microparticles were firstly silanized to obtain aminopropyl silica (APS). Silica (5 g) was stirred overnight in 300 mL 3% (v/v) aminopropyltriethoxysilan toluene solution and then refluxed at 100°C for 2 h. Large part of the solvent was removed under vacuum and the remaining suspension was filtered by means of a Büchner funnel on a paper filter; the solid was washed with 200 mL ethanol and then dried at 60°C for 4 h.

GO was covalently grafted on silica by a coupling reaction between the amino groups of APS and the carboxyl groups of GO using DCC as the coupling agent, similarly to the procedure by Liu et al. [24]. GO (250 mg) was dispersed in 150 mL anhydrous DMF by sonication (10 min) and then 2.5 g of APS and 100 mg DCC were added. The mixture was stirred at 60°C for 24 h. The suspension was filtered and the solid material (GO–silica) was washed with 200 mL ultrapure water followed by 100 mL MeOH to remove any residual coupling agent or unbound GO, and finally dried at 60°C for 4 h. RGO–silica was prepared by reduction of GO–silica with aqueous hydrazine. GO–silica (2 g) was stirred at 90°C for 3 h in 200 mL aqueous hydrazine (1%, v/v). The solid was collected by filtration, washed with ultrapure water (200 mL) followed by MeOH (100 mL), and finally dried at 60°C for 4 h.

2.3. Characterization of RGO–silica

SEM images were acquired by a Cambridge S360 microscope (Cambridge Instruments, Cambridge, UK); powders were inserted in special stubs and coated with gold under low vacuum (2×10^{-2} mbar) to obtain a conductive material (Au layer thickness 10 nm). For BET analyses, carried out using an ASAP 2010 physisorption analyzer (Micromeritics Instrument Corporation, Norcross, USA), samples were heat-treated at 200°C under vacuum before measurement.

TGA measurements have been performed with a TGA 1 Star System from Mettler Toledo (Novate Milanese, Italy). Heating rate was $10^\circ\text{C min}^{-1}$ and the range of temperature was from 25°C to 1000°C . Reactive gas was air (Sapio, Monza, Italy) at a flow rate of 100 mL min^{-1} . For each experiment about 10 mg of materials were weighted, and put into an alumina crucible. The TGA furnace was conditioned for 2 h to provide a suitable atmosphere for combustion.

2.4. Water samples

Tap water from the Pavia municipal waterworks (pH 7.7, conductivity at 20°C $271 \mu\text{S cm}^{-1}$, Ca^{2+} 35 mg L^{-1} , Mg^{2+} 10 mg L^{-1} , Cl^- 5 mg L^{-1} , NO_3^- 0.6 mg L^{-1} , SO_4^{2-} 5 mg L^{-1}) and surface water collected in July 2014 from Stàffora River (pH 7.5, conductivity at 20°C $430 \mu\text{S cm}^{-1}$, Ca^{2+} 62 mg L^{-1} , Mg^{2+} 12 mg L^{-1} , Na^+ 7 mg L^{-1} , K^+

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