



Iron oxide functionalized graphene nano-composite for dispersive solid phase extraction of chemical warfare agents from aqueous samples



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ARTICLE INFO

Article history:

Received 17 November 2014
Received in revised form 16 March 2015
Accepted 16 March 2015
Available online 23 March 2015

Keywords:

Chemical warfare agents
Nerve agents
Sulfur mustard
Magnetic dispersive solid phase extraction
Graphene
Magnetic nano particles

ABSTRACT

Present study deals with the preparation and evaluation of graphene based magnetic nano-composite for dispersive solid phase extraction of Chemical Weapons Convention (CWC) relevant chemicals from aqueous samples. Nano-composite, $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-G}$ was synthesized by covalently bonding silica coated Fe_3O_4 onto the graphene sheets. Nerve agents (NA), Sulfur mustard (SM) and their non-toxic environmental markers were the target analytes. Extraction parameters like amount of sorbent, extraction time and desorption conditions were optimized. Dispersion of 20 milligram of sorbent in 200 mL of water sample for 20 min. followed by methanol/chloroform extraction produced average to good recoveries (27–94%) of targeted analytes. Recoveries of real agents exhibited great dependency upon sample pH and ionic strength. Sarin produced maximum recovery under mild acidic conditions (56% at pH 5) while VX demanded alkaline media (83% at pH 9). Salts presence in the aqueous samples was found to be advantageous, raising the recoveries to as high as 94% for SM. Excellent limits of detection (LOD) for sulphur mustard and VX (0.11 ng mL^{-1} and 0.19 ng mL^{-1} respectively) proved the utility of the developed method for the off-site analysis of CWC relevant chemicals.

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1. Introduction

Nerve agents (NA) and vesicants belong to a group of weaponized synthetic chemicals which exhibit their devastating power due to their inherent toxicity [1–3]. Chemically, NA belongs to a class of organophosphorus chemicals which severely affect the transmission of nerve impulses in the nervous system by irreversibly inhibiting acetyl cholinesterase enzyme [1,2]. Notable examples of this class include Sarin (isopropyl methylphosphonofluoridate, GB), Soman (pinacolyl methylphosphonofluoridate, GD), Tabun (O-ethyl N,N-dimethylphosphoramidocyanidate, GA) and VX (O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate). Vesicants include toxic sulfur (bis(2-chloroethyl)sulphide, SM) and nitrogen mustards (tris(2-chloroethyl)amine, NM) and arsenicals and bear toxicity due to their alkylating properties [1]. These chemicals have shown their horrifying capabilities in many incidents related to the military and terrorist activities [2]. To save

the mankind and the world from these deadly chemicals, an international treaty, known as chemical weapons convention (CWC) came into the existence in April 1997 [2–4]. The CWC prohibits proliferation of CWA through its verification regime and it is administered by an international organization known as the Organization for the Prohibition of Chemical Weapons (OPCW) [3,4]. Verification of CWC involves the inspection and on-site analysis of samples collected from suspected sites. In case of any ambiguity, collected samples are forwarded to the laboratories designated by the OPCW for the off-site analysis of the environmental samples.

Water serves as an important environmental matrix for the verification analysis of CWC in deliberate or inadvertent spread of CWA. A rich database is available in the open literature dealing with the analysis of CWC relevant chemicals present in aqueous samples. Amongst various reported techniques, gas chromatography coupled to a suitable detector, such as mass spectrometer (GC-MS), nitrogen-phosphorus detector (GC-NPD) and flame photometry (GC-FPD) is the most preferred one [5,6]. The analytical protocol for gas chromatographic analysis demands an efficient sample preparation step to transfer the desired analytes from aqueous samples to a GC compatible organic solvent. Mostly this involves liquid–liquid extraction (LLE) [7–9], solid-phase micro-extraction

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(SPME) [10,11], liquid-phase micro-extraction (LPME) [12–15], and solid-phase extraction (SPE) [7–9]. Each type of sample clean-up procedure has its own merits and demerits, and adoption of a particular method depends on the type of analytes and nature of the water sample.

Magnetic dispersive solid phase extraction (MDSPE) is one of the most important sample preparation methods gaining importance in present research. It involves dispersion of magnetized sorbents in the samples for a pre-defined time followed by its magnetic retrieval with the help of an external magnet [16]. Analytes present in the sample come in close contact with the finely dispersed sorbent and enrich on the sorbent surface due to hydrophobic or ionic interactions. MDSPE is convenient, economical and eliminates various problems associated with conventional SPE (i.e. handling of dirty and/or large-volume samples).

Hitherto, various materials such as polymers, silica, C18, carbon nanotubes, graphene and MOF (metal organic framework), etc. have been functionalized by magnetic nanoparticles for subsequent application to the enrichment of pollutants from different environmental sources [16–20]. Amongst these, graphene has gathered great attention in the scientific community because of multiple exceptional properties derived of its one atom thick carbon sheet with a hexagonal packed lattice structure [19,20]. The large surface area (theoretically 2630 m²/g, [19]), extremely high surface to volume ratio, light weight nano-sheet structure and delocalized π - π electron system makes it an excellent sorbent material for analytical applications [19,20]. Its sorbent properties have been exploited for the extraction of various analytes such as pesticides, aromatic hydrocarbons, phenolic compounds, proteins, inorganic metal ions and dyes [19,21].

In present study, an effort has been made to exploit graphene based magnetic nano-composite for the extraction of CWA and relevant chemicals (Fig. 1) from aqueous samples. Nano-composite was synthesized by covalently binding graphene to the silica coated Fe₃O₄ nano particles (Fe₃O₄@SiO₂-G). To the best of our knowledge, this is the first investigation, evaluating the efficiency of Fe₃O₄@SiO₂-G magnetic nano-composite sorbent for the extraction of CWA agents and their markers from aqueous samples.

2. Experimental

2.1. Reagents and chemicals

Graphite powder (<45 μ m), Potassium persulfate (K₂S₂O₈), Iron (II,III) oxide (<50 nm particle size), Tetraethyl orthosilicate (TEOS), (3-aminopropyl) triethoxy silane (APTES), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxysuccinimide (NHS), Tributyl phosphate (TBP) were purchased from Sigma Aldrich, New Delhi. All other reagents and solvents were purchased from E. Merck, India and were used as received. Microgram quantities of dialkyl methylphosphonates, GB, GF, VX and SM were synthesized in our laboratory as per reported procedures [22].

Caution: Chemical Warfare Agents are extremely toxic chemicals; they should be prepared and handled by trained professionals in an efficient fume hood equipped with an alkali scrubber. Individuals handling them should wear a facemask, gloves, and protective suit.

2.2. Synthesis of graphene oxide

Graphene oxide was synthesized by a modified Hummers method [23]. Briefly, 2 g natural graphite was pre-oxidized in the presence of 15 mL of concentrated H₂SO₄, 3 g of K₂S₂O₈ and 3 g of P₂O₅ at 80 °C for 5 h. After completion, the reaction mixture was cooled and diluted with 500 mL of deionized (DI) water. Finally, it

was filtered through the 0.22 μ m filter and dried under vacuum at 60 °C for 24 h.

In the second step, pre-oxidised graphite was added slowly to the cooled concentrated sulphuric acid (100 mL) with vigorous stirring. Ten grams of KMnO₄ was added in small quantities over a period of 2 h maintaining the reaction temperature below 10 °C. After complete addition the contents were stirred at 40 °C for 72 h during which, the initial dark green coloured solution slowly converted into light brown pasty mass. The oxidation process was quenched by the addition of 160 mL of DI water, maintaining the temperature below 50 °C. The reddish brown solution was further stirred for 2 h followed by the addition of 500 mL of DI water and 14 mL of 30% H₂O₂. Thus obtained brilliant yellow coloured solution was centrifuged and washed with 3% HCl to remove metal ion impurities. Residue was washed repeatedly with DI water until the pH became neutral. The brown coloured graphene oxide sheets were collected by drying in rota vapour.

2.3. Synthesis of Fe₃O₄@SiO₂-NH₂

Fe₃O₄@SiO₂-NH₂ was synthesized by Stober's method by single step functionalization [24]. Five hundred milligram of Fe₃O₄ nano particles were sonicated for 30 min. in a solution containing 320 mL of ethanol and 80 mL of water and 10 mL of 30% NH₄OH solution to achieve a fine dispersion. To this, a mixture of 2 mL APTES and 1 mL TEOS was added in 45 min. and the contents were allowed to stir at room temperature for 24 h. Thus produced amino functionalized silica coated nano particles (Fe₃O₄@SiO₂-NH₂) were magnetically separated, washed with copious amount of water and ethanol and finally dried under vacuum at 70 °C for 24 h.

2.4. Synthesis of Fe₃O₄@SiO₂-G

The covalent coupling of graphene oxide to Fe₃O₄@SiO₂-NH₂ was carried out by inducing the amide bond formation [25]. Briefly, 200 mg of GO was first exfoliated in 400 mL of DI water under sonication for 2 h. Activation of -COOH groups on the GO was carried out by the addition of 200 mg of EDC and 160 mg of NHS for two hours. To this, 400 mg of Fe₃O₄@SiO₂-NH₂ particles dispersed in DI water were added slowly with vigorous stirring and allowed to stir at 50 °C for one hour. Thus prepared Fe₃O₄@SiO₂-GO nano-composite was retrieved with external magnet, washed thoroughly with DI water and dried under vacuum.

In the final step, Fe₃O₄@SiO₂-GO composite was reduced to Fe₃O₄@SiO₂-G with 200 μ L of hydrazine hydrate in 200 mL of water at 98 °C for 2 h. Obtained material was washed thoroughly with water and ethanol and re-suspended in known amount of water for further applications.

2.5. Standards and spiking solutions

Individual stock solutions of selected analytes (1000 μ g mL⁻¹) were prepared in acetonitrile (ACN). Mixed intermediate standard solutions of 10 μ g mL⁻¹ were prepared by the dilution the stock standard solutions in ACN. Stock and intermediate standard solutions of chromatographic standard, tributylphosphate (TBP) were prepared in the same way in ACN. The final concentration of internal standard was kept at 200 ng mL⁻¹. Water samples were spiked at a concentration of 3 ng mL⁻¹ with intermediate standard solutions. To avoid the loss of analytes by hydrolysis, samples were prepared freshly just before the experiments.

Extraction conditions and quantitative studies were performed in glass distilled water (DW). For validation purposes, samples were collected from laboratory tap and untreated municipal waste of our city. The pale yellow alkaline (pH 8.7) waste water

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