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Magnetic hydrophilic–lipophilic balance sorbent for efficient extraction of chemical warfare agents from water samples

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ABSTRACT

Magnetic hydrophilic–lipophilic balance (MHLB) hybrid resin was prepared by precipitation polymerization using *N*-vinylpyrrolidone (PVP) and divinylbenzene (DVB) as monomers and Fe_2O_3 nanoparticles as magnetic material. These resins were successfully applied for the extraction of chemical warfare agents (CWAs) and their markers from water samples through magnetic dispersive solid-phase extraction (MDSPE). By varying the ratios of monomers, resin with desired hydrophilic–lipophilic balance was prepared for the extraction of CWAs and related esters of varying polarities. Amongst different composites Fe_2O_3 nanoparticles coated with 10% PVP + 90% DVB exhibited the best recoveries varying between 70.32 and 97.67%. Parameters affecting the extraction efficiencies, such as extraction time, desorption time, nature and volume of desorption solvent, amount of extraction sorbent and the effect of salts on extraction were investigated. Under the optimized conditions, linearity was obtained in the range of 0.5–500 ng mL^{-1} with correlation ranging from 0.9911–0.9980. Limits of detection and limits of quantification were 0.5–1.0 and 3.0–5.0 ng mL^{-1} respectively with RSDs varying from 4.88–11.32% for markers of CWAs. Finally, the developed MDSPE method was employed for extraction of analytes from water samples of various sources and the OPCW proficiency test samples.

1. Introduction

Chemical warfare agents (CWAs) are extremely toxic chemicals intended for use in war and terrorist activities [1–3]. CWAs include blister-, nerve-, blood-, choking- and behavioural- agents [3]. Amongst them, the nerve- and blister- agents are considered to be the most important from view point of toxicity, persistency and weaponization history [1,2]. Horrifying menace of CWAs persuaded the humanity to formulate a comprehensive treaty known as Chemical Weapons Convention (CWC) [4]. Organization for the Prohibition of Chemical Weapons (OPCW) administers this treaty through its verification regime [5]. To assist the verification program, OPCW maintains a global network of designated laboratories through international official proficiency tests (OPTs) [6–12]. Identification of CWAs and convention related chemicals (CRCs) in water samples is necessary to solve problems associated with the verification analysis of CWC [9,13]. Reliability of identifications depends on both sample preparation and instrumental analysis e.g. gas- and/or liquid-chromatography mass spectrometry (GC–MS/LC–MS) [7,8].

Sample clean-up methods for CRCs include liquid-liquid extraction (LLE) [11,12], solid-phase microextraction (SPME) [14,15], liquid-phase microextraction (LPME) [16–19], and solid-phase extraction [11,12]. Every method has its own advantages and limitations, and selection of a method depends upon the nature of analytes, characteristics of matrix & instrumental technique.

Some notable drawbacks of these methods are carryover effects (SPME) [7,11,14,15], cartridge choking (SPE) [20,21], emulsification (LLE) [21] and cumbersome operation (LPME) [8,11,12]. To overcome these limitations, a modern sample preparation method, namely magnetic dispersive solid-phase extraction (MDSPE) has been developed [22–24]. In this technique, micro- or nano-sized custom functionalized magnetic sorbents are dispersed in water, where analytes are efficiently adsorbed on sorbents due to large surface to volume ratio. After magnetic separation of the sorbent, analytes are desorbed in a suitable solvent. MDSPE, is operationally simple & eliminates several limitations associated with conventional methods e.g. it can dispense with centrifugation or filtration,

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handle turbid and large volume samples, and impart selectivity by custom functionalization of sorbents [23,24]. Silica-modified magnetic nanoparticles (MNPs) have been used to enrich heavy metals [25], polycyclic aromatic hydrocarbon (PAHs) [26], and drugs [27]. Octadecylsilane- modified MNPs were employed for sample preparation of phthalates [28], vitamins and pesticides [29]. Carbon nanotubes and graphene modified MNPs were used to extract estrogens [30], insecticides [31], herbicides and fungicides from water [32]. Recently, polymer coated MNPs were also used for sample preparation of PAHs, phthalates, pesticides and heavy metals [22]. However, MNPs and modified MNPs are rarely explored for CWAs. Composite of iron-oxide with carbon nano-tubes and graphene are studied to extract CWAs from water samples and their recoveries are monitored by GC- with specific detectors [33,34]. Carbon based sorbents are undiversified hence extract the analytes based on hydrophobic interactions only. This limits their application to hydrophobic analytes. Some of the CWAs (e.g. nerve agents) and their co-products (e.g. dialkyl methylphophonates) are quite polar and water soluble, hence their extraction from water requires blend of hydrophilic-hydrophobic sorbent. In last few years, polymer sorbents with enhanced hydrophilic surface are reported to extract analytes of varying polarities [35,36]. These sorbents are prepared by the copolymerization of hydrophilic monomers with hydrophobic styrene-divinylbenzene (St-DVB) [37]. By varying the ratios of hydrophobic/hydrophilic monomers, polymers with required surface polarities can be prepared for selective extraction of analytes. Coating of magnetic particles (iron oxide) with polymers of varying polarities endows the sorbent with diverse absorptivity and virtues of MDSPE. Thus Magnetic sorbents with required surface characteristics, especially hydrophilic–lipophilic balance can be prepared and evaluated for extraction of analytes of varying polarities. A widely used commercial hydrophilic–lipophilic sorbent is Oasis® HLB from Waters, whose sorption mechanism is well studied [38].

Commercial HLB cartridges have been evaluated towards pharmaceuticals [39,40], drugs [41], personal care products [42], sweeteners [43] and pesticides [44]. Few years' back we studied the extraction of CWAs using Oasis® HLB, and found that it out performs the conventional C_{18} sorbents [45]. Recently, combination of MDSPE with custom synthesized HLB sorbent is reported for efficient extraction of pesticides and herbicides [46]. Inspired by the excellence of MDSPE and diversity of sorption characteristics of hydrophilic–lipophilic balance polymers, here in we report the synthesis of HLB-magnetic sorbents and their evaluation as extractant for CWAs and CRCs from water.

To the best of our knowledge, this is the first study aimed to develop magnetic-HLB sorbents for extraction of CWAs and related di-esters (Fig. 1). Nerve agents (GB, GF, GA), sulphur mustard, *O, O′*-dialkyl alkylphosphonates (DEMP, DBMP, DEPP) and *O, O′*-diethyl *N, N*-diethylphosphoramidate (DEDEP) (Fig. 1) were selected for the study. Dialkyl alkylphosphonates are co-products of nerve agents; hence their presence in a sample is indicative of presence of nerve agents that is why these compounds are included in the schedule 2B4 category of the CWC. These non-toxic di-esters are considered as good models for development of an analytical method against toxic CWAs, as they are convenient to handle during an elaborate experimental protocol.

2. Experimental

2.1. Materials

The compounds, *O*-isopropyl methylphosphonofluoridate (sarin), *O*-cyclohexyl methylphosphonofluoridate (cyclosarin), *O*-ethyl-*N, N*-diethylphosphoramidocyanidate (tabun) and bis(2-chloroethyl) sulfide (sulfur mustard) were prepared in microgram quantities in our laboratory as per the reported procedures [47]. *O, O′*-diethyl methylphosphonate (DEMP), *O,O′*-diethyl propylphosphonate (DEPP), *O,O'*-dibutylmethylphosphonate (DBMP), *O,O'*-diethyl *N,N*-diethylphosphoramidate (DEDEPA) were also synthesized as per the reported procedures [48]. Tri-*n*-butyl phosphate (TBP) (chromatographic standard), polyethylene glycol (PEG-300), *N*-vinylpyrrolidone, divinylbenzene, azobisisobutyronitrile (AIBN), Fe_2O_3 nanoparticles (<50 nm) were purchased from Sigma–Aldrich Chemicals Pvt., Ltd. (Bangalore, India). *N*-vinylpyrrolidone and divinylbenzene were purified by passing through inhibitor remover column (Aldrich, USA) followed by distillation under high vacuum. AIBN was recrystallized from methanol. The analytical grade solvents and sodium sulphate (Na_2SO_4) were obtained from Merck Specialties Pvt., Ltd. (Mumbai, India). All the solutions were prepared in Milli-Q water (Millipore, Billerica, MA, USA). Tap water (supplied from local Municipal Corporation), muddy water (pooled rain water), pond water (from a nearby pond of the laboratory) and distilled water were used for the validation study.

2.2. Caution

Chemical warfare agents are extremely toxic chemicals. They should be prepared and handled by trained professionals in an efficient fume hood equipped with alkali scrubber. Individuals handling them must wear appropriate protective gears. Decontamination solution (approximately 15% w/v solution of bleach and alkali) must be kept at the workplace and the solvent waste must be properly decontaminated

2.3. Preparation of magnetic hydrophilic–lipophilic balance resin (MHLB)

Magnetic hydrophilic–lipophilic balance resin was prepared by precipitation polymerization [49]. The polymerization ingredients consist of medium CH_3CN, *N*-vinylpyrrolidone and DVB as monomer and AIBN as initiator. The total amount of monomers was set at 3.5 wt% of the medium (150 mL) and AIBN 0.6 wt% with respect to the total amount of the monomers (5 mL) used.

In a three neck round bottom flask equipped with a mechanical stirrer, condenser and nitrogen gas inlet, 150 mL CH_3CN was taken (deoxygenated by nitrogen bubbling for 30 min). Separately in a 100 mL beaker, pre-polymerization mixture was prepared by mixing 250 mg Fe_2O_3 nanoparticles, 0.5 mL *N*-vinylpyrrolidone and 4.5 mL divinylbenzene for 15 min. Afterwards, the pre-polymerization mixture was transferred to the three necked round bottom flask by dispersing it in CH_3CN. To this mixture, 30 mg AIBN was added and reaction was initiated thermally. Polymerization was carried out at stirring speed of 100 rpm at 70 °C for 24 h. After the completion of polymerization, the resultant particles were collected over an external magnet and washed with ethanol (3 × 100 mL) followed by acetone till supernatant became clear. The product obtained in the form of fine powder was dried under vacuum at 80 °C for 8 h.

2.4. Characterization

Infrared spectroscopy data were collected on Thermo FT-IR Nicolet 6700 (Madison, WI USA) spectroscope equipped with deuterated triglycinesulfate (DTGS) detector between 4000 and 450 cm^{-1} as KBr pellets. The shape and size of MHLB resin was visualized by the Environmental Scanning Electron Microscopy (ESEM) (FEI-Quanta 400 ESEM FEG, FEI, Hillsboro, OR) operated at 10 kV. Images were recorded at 50000 × magnification.