Journal of Chromatography A, 1459 (2016) 38–46

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Planar graphene oxide-based magnetic ionic liquid nanomaterial for extraction of chlorophenols from environmental water samples coupled with liquid chromatography–tandem mass spectrometry☆

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ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form 30 June 2016
Accepted 30 June 2016
Available online 1 July 2016

Keywords:
Planar graphene oxide-based magnetic ionic liquid
Magnetic solid-phase extraction
Chlorophenols
Environmental water
Liquid chromatography–tandem mass spectrometry

ABSTRACT

A planar graphene oxide-based magnetic ionic liquid nanomaterial (PGO-MILN) was synthesized. The prepared PGO-MILN was characterized by transmission electronmicroscopy (TEM) and Fourier-transform infrared spectrometry (FTIR). The results of adsorption experiments showed that the PGO-MILN had great adsorption capacity for 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and pentachlorophenol (PCP). Based on the adsorption experimental data, a sensitive magnetic method for determination of the five CPs in environmental water samples was developed by an effective magnetic solid-phase extraction (MSPE) procedure coupled with high-performance liquid chromatography–tandem mass spectrometry (LC–MS/MS). The effects of main MSPE parameters including the solution pH, extraction time, desorption time, and volume of desorption solution on the extraction efficiencies had been investigated in detail. The recoveries ranged from 85.3 to 99.3% with correlation coefficients (r) higher than 0.9994 and the linear ranges were between 10 and 500 ng L^{-1}. The limits of detection (LODs) and limits of quantification (LOQs) of the five CPs ranged from 0.2 to 2.6 ng L^{-1} and 0.6 to 8.7 ng L^{-1}, respectively. The intra- and inter- day relative standard deviations (RSDs) were in the range from 0.6% to 7.4% and from 0.7% to 8.4%, respectively. It was confirmed that the PGO-MILN was a kind of highly effective MSPE materials used for enrichment of trace CPs in the environmental water.

1. Introduction

Chlorophenols (CPs) including 2-chlorophenol(2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), and pentachlorophenol (PCP), which are widely used in industrial processes, have been classified as one of priority pollutants by the European Union and US Environmental Protection Agency (EPA) [1–4]. The US EPA established a maximum allowable concentration of 1 μg L^{-1} for PCP in drinking water, while the European Union set a maximum allowable concentration of 0.5 μg L^{-1}, 0.1 μg L^{-1} and 1 μg L^{-1} for total phenols in drinking water, for the individual compounds, and for PCP in inland and other surface waters, respectively. Therefore, it is necessary to develop a rapid, sensitive, and accurate analytical method for the determination of CPs in environmental samples. High-performance liquid chromatography (HPLC) is one of the most widely used methods for the separation and determination of CPs. Various detectors including fluorescence [5], ultraviolet (UV) [6], diode array detector (DAD) [7], mass spectroscopy (MS) [8], and tandem mass spectroscopy (MS/MS) in conjunction with HPLC [9] were used for the determination of CPs.

Due to the low concentration of CPs and the complex nature of matrices of the environmental samples, sample preparation steps including extraction and pre-concentration are usually needed prior to the analysis. Several methods have been developed for the pre-concentration of CPs in environmental water samples, such

☆ Selected paper from the 43rd International Symposium on High Performance Liquid Phase Separations and Related Techniques, 21–25 September 2015, Beijing, China.

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http://dx.doi.org/10.1016/j.chroma.2016.06.086
0021-9673/

Table 1
The reproducibility of the extraction using six different batches of PGO-MILN.

Compound	Added ($ng L^{-1}$)	Recovery (%)						
		Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6	RSD%
2-CP	10	89.2	89.1	88.9	88.8	88.7	87.6	0.65
	50	88.3	87.3	88.1	86.2	86.7	86.2	1.06
	400	88.6	88.7	87.6	86.2	86.8	86.4	1.25
2,4-DCP	5.0	92.0	91.4	91.2	90.8	90.7	89.7	0.85
	50	90.9	91.2	90.7	89.8	89.6	89.2	0.89
	400	91.2	91.5	89.6	89.8	89.6	88.9	1.13
2,4,6-TCP	2.0	91.6	92.0	89.2	89.1	89.1	88.9	1.57
	50.0	92.3	91.8	91.5	91.9	91.2	89.9	0.92
	400	91.8	92.9	91.8	91.2	90.2	90.1	1.17
2,3,4,6-TeCP	1	96.1	96.7	95.9	95.3	95.2	94.7	0.75
	20.0	95.3	95.8	94.3	93.8	93.1	93.0	1.22
	400	93.2	94.3	92.1	91.7	91.3	91.0	1.36
PCP	1	97.8	98.4	96.5	96.1	95.7	95.3	1.26
	20.0	99.1	98.5	98.4	97.5	97.3	97.1	0.81
	400	99.1	99.1	98.5	98.1	96.2	96.9	1.22

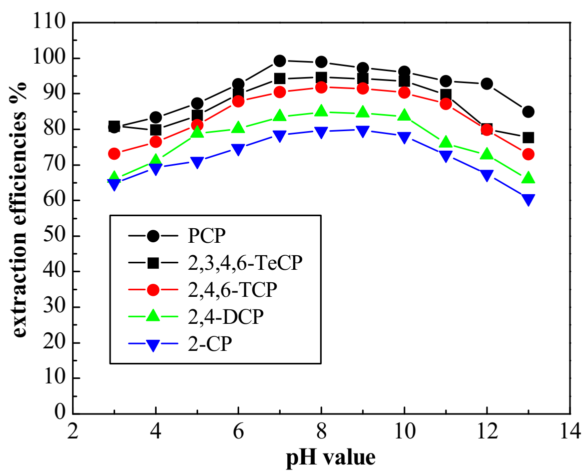

Fig. 1. Effect of pH on the extraction efficiencies of CPs at 2.0 $\mu g L^{-1}$.

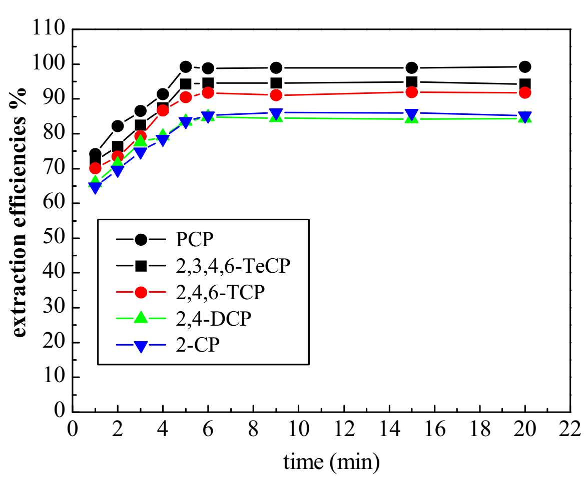

Fig. 2. Effect of extraction time on the extraction efficiencies of CPs at pH 10.0.

as liquid–liquid extraction (LLE) [10], solid–phase extraction (SPE) [11,12], solid-phase micro-extraction (SPME) [13], molecularly imprinted polymers (MIP) [14], and microextraction by packed sorbents (MEPS) [15]. However, these methods are usually tedious, time consuming, non-environment-friendly, and lead to analyte loss.

Graphene, a new class of carbon nanomaterial with 2-dimensional properties, has attracted a mass of attentions as an adsorbent for SPE and SPME due to its large surface area of theoretical value 2630 $m^2 g^{-1}$, high dispersibility and hydrophilicity [16,17]. Graphene oxide (GO) is a chemically modified graphene sheet containing a wide range of reactive oxygen functional groups such as —COOH and —OH, so GO is much more hydrophilic than G and is expected to promote interfacial interactions with organic compounds. In addition, its very large delocalized π-electron system also provides strong π-π stacking interaction with the aromatic rings of organic compounds [18–20]. However, difficulties for rapid separation after treatment from solution restrict their applications for conventional SPE adsorbents. An efficient method to solve the problem is to introduce magnetic nano-particles (MNPs), such as Fe_3O_4 or a-Fe_2O_3, into GO. Unfortunately, the common MNPs do not have significant adsorption efficiency. To overcome this limitation, modification of the surface of MNPs with specific chemical functional group has been used.

Ionic liquids (ILs) and polymeric ionic liquids (PILs) characterized by melting points lower than 100 °C, have emerged as possible "green" solvents because they have unique physicochemical properties, such as negligible vapor pressure, significant thermal stability, variable viscosity and multiple solvation interactions with analytes [21,22]. These physical properties can be easily tuned and modulated by altering the structural vectors of the ILs or PILs, allowing them to be used in analysis. There are a couple of reports using ILs and PIL_S in SPME for extraction of non-polar or medium-polar analytes [23–25]. ILs coated MNPs have also been successfully used as adsorbent for the extraction of polycyclic aromatic hydrocarbons (PAHs) [26], linuron [27], organophosphorus pesticides [28] and anthraquinones [29]. The introduction of ILs into magnetic GO is expected to increase the water-solubility of magnetic GO and improve the extraction efficiency of CPs. However, there are only few reports on the pre-concentration of analytes using magnetic graphene oxide-based ionic liquid as a solid-phase extraction adsorbent [30,31]. For example, a guanidinium ionic liquid magnetic chitosan graphene oxide-functional composite can be successfully applied in magnetic solid-phase extraction of trypsin, lysozyme, ovalbumin and bovine serum albumin, showing potential application value in extraction of other biomolecules [30]. However, the reusability and regeneration of this material may be limited in their applications because IL was grafted on magnetic graphene oxide via adsorption, which might cause the loss of IL [30,31].