Área: ANA

Synthesis, characterization, and evaluation of the extracting capacity of ionic liquids supported on graphene oxide for determining pesticides by LC-MS/MS.

Alessandra Timóteo Cardoso (PG),[1*] Fernando Mauro Lanças (PQ)[1].

alessandracardoso@usp.br.

[1]*Instituto de Química de São Carlos, IQSC-USP.*

Palavras Chave: *Graphene oxide (GO), Ionic Liquids (ILs), Sorbents, Sample Preparation, Pesticides, LC-MS/MS.*

Highlights

Synthesis of new selective extractor phases for determination of selected pesticides by LC-MS/MS. Good extractability of carbamates and triazines compared to commercial phases.

Abstract

One of the main advantages of using ionic liquids in sorbents for sample preparation is the various combination possibilities between the ions to favor pronounced interactions with the compound of interest, improving the cleaning and pre-concentration of the analytes.[1] Thus, this work aimed to develop and characterize two phases based on ionic liquids supported on graphene oxide, with subsequent evaluation of their extraction capacity for selected pesticides, with determination by LC-MS/MS. Two ionic liquids with imidazole cation were developed: a zwitterionic[2] – ILz (1-vinyl-3-(butyl-4-sulfonate)imidazolium), and a hydrophilic[3] – [VHiM]Br (1-vinyl-3-hexylimidazolium bromide), and anchored in GO according to the methodology of Zhang et al. [4] Characterization analyzes were carried out to confirm the deposition of ILs on the surface of GO nanosheets. As it is possible to observe in Figure 1A, there are differences between the GO spectra after the anchoring of the ionic liquids (b and c) referring to the appearance of bands of the 1-vinylimidazolium cation bonds (1585 cm^{-1} and 2927 cm^{-1}) and decrease of some bands concerning pure GO (a) (1053 cm^{-1} and 3600 cm^{-1}). After this stage, experiments were carried out to evaluate the selectivity and adsorption capacity of the sorbents for the pesticides: 5 mg of each sorbent were weighed in triplicate and placed in Eppendorf (2 mL), and separately 1 mL of the standard solution of triazines and carbamates to 100 ng mL^{-1} were added and stirred for 1 h. Then, the supernatant was collected and filtered through a 0.22 µm membrane and injected into UPLC-MS/MS (Waters, Milford) under the following conditions: Column C18 (ACQUITY UPLC® HSS T3, 1.8 µm - 300 µm X 150 mm); oven temperature: 35 °C; injection volume 0.5 µL; mobile phase constant flow rate: 10 µL min-1 in gradient elution mode composed of: (A) water / 0.1% formic acid (B): ACN / 0.1% formic acid v:v; total running time 10 min; ESI+ ionization mode with MRM acquisition mode monitoring the following *m/z* transitions for carbamates (carbofuran: 165.1>123, carbaryl 145>127, methomyl 88>106) and for triazines (amethrin: 95>90, atrazine: 95>103, simazine: 131>123). It was possible to observe (figure 1B) that, in general, for the extraction of triazines, the best sorbent was ILz@GO. For carbamates, the best sorbent was [VHiM]Br@GO, presenting a greater extraction capacity than the C18 phase in both cases. This occurs because ILs anchored to GO have multiple adsorption mechanisms, such as π-π and electrostatic interactions promoted by GO, in addition to hydrogen bonds between the imino groups and the electronegative atoms of the analytes and ion exchange between the imidazole ring of the cation and ionized analytes. Thus, the extractive phases developed proved to be selective for the extraction of selected pesticides, as they showed high extraction capacity, which makes them suitable for later application in sample preparation techniques involving sorption mechanisms.

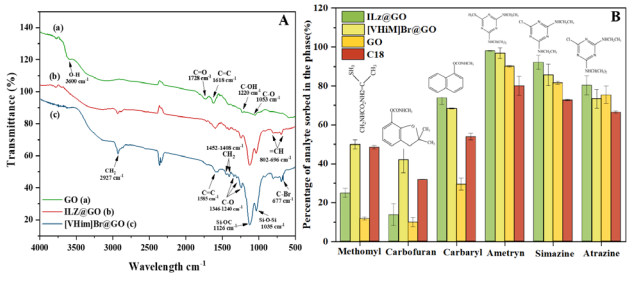

Figure 1. (A) IR spectra (a) GO, (b) ILz@GO, and (c) [VHim]Br@GO; **(B)** adsorptive capacity of synthesized phases(%).

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Acknowledgments

CNPq (Grant 308843/ 2019-3), FAPESP (Grant 2017/02147-0; 2017/21984-0 – EMU; 2017/21985-6 – EMU), and CAPES (Finance Code 001) for financial support. IQSC and CROMA for the provided framework.