

Electronic Supplementary Information

Amino-functionalized zirconium-based metal-organic framework/graphene oxide nanocomposite for 2,4-dichlorophenoxyacetic acid determination by ion mobility spectrometry

Mohammad Saraji*, Mohammad Taghi Jafari and Vajihe Mohammadi

Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

*Corresponding author: Professor Mohammad Saraji, Department of Chemistry, Isfahan

University of Technology, Isfahan 84156-83111, Iran

E-mail address: saraji@cc.iut.ac.ir, msaraji@ymail.com

Fax: +98 31 33912350

ORCID: 0000-0002-1570-0718

Materials and methods

Instrumentation

The main parts of the SESI-IMS were IMS cell, injection port, syringe pump, electrospray needle, two high voltage power supplies, a pulse generator, and an analog to digital converter. The IMS cell consisted of three regions: an electrospray ionization region (3.0 cm), a desolvation and reaction region (4.0 cm) and a drift tube (11.0 cm in length). The electrospray solvent (methanol) was introduced through a stainless steel needle (P/N 7768-01, Hamilton, Reno, NV, USA) by a syringe pump at $6.0 \mu\text{L min}^{-1}$. The ionized solvent was entered to the desolvation and reaction region. To transfer analyte into the reaction region and perform SESI, the analyte solution was introduced into a heated GC injection port; and evaporated analytes moved to the reaction region using the stream of the carrier gas (N_2). The analyte molecules were ionized through a gas-phase reaction with the ionized solvent formed by the electrospray ionization source. The Bradbury–Nielsen shutter grid made from two series of parallel wires separate reaction and drift regions. To admit an ion pulse entering the drift region, shutter grid potential was removed for 300 μs . The drift tube was made of 16 aluminum rings insulated by thin PTFE rings. The ions were detected by a 21-mm diameter stainless-steel plate Faraday cup detector positioned ~ 1.0 mm behind the aperture grid. The schematic diagram of the secondary electrospray ionization-ion mobility spectrometer apparatus was shown in Fig. S1.

Real samples pretreatment

The water samples were filtered with $0.45 \mu\text{m}$ Nylon membrane filter (Millipore, Bedford, MA, USA) before extraction. For preparing rice sample, 0.5 g of grinded sample was drenched with 0.5 mL of water in a centrifuge tube for 10 min. Then, 1 mL of acetic acid/acetonitrile (1:9, v/v) was

added and shook by hand until the contents were mixed. After that, 10 mg of NaCl and 40 mg of MgSO₄ were added to the mixture and shook for 2 min. The mixture was centrifuged at 4000 rpm for 5 min. The supernatant liquid was collected, and the extraction of solid residue was repeated two more times with acetic acid/acetonitrile. The supernatants were mixed and evaporated using a mild stream of nitrogen gas to near dryness.¹ The analytes were reconstituted in water and extracted by TFME.

Table S1 Instrumental setting of SESI-IMS

Operating parameters	Setting
Needle voltage	-2 kV
Counter electrode voltage	-8.5 kV
Drift field	567 V cm ⁻¹
Drift region length	11 cm
Desolvation region length	4 cm
Electrospray solvent	Methanol
Drift gas flow (N ₂)	1000 mL min ⁻¹
Carrier gas flow (N ₂)	800 mL min ⁻¹
Liquid flow rate	6 μL min ⁻¹
Drift tube temperature	150 °C
Injector temperature	180 °C

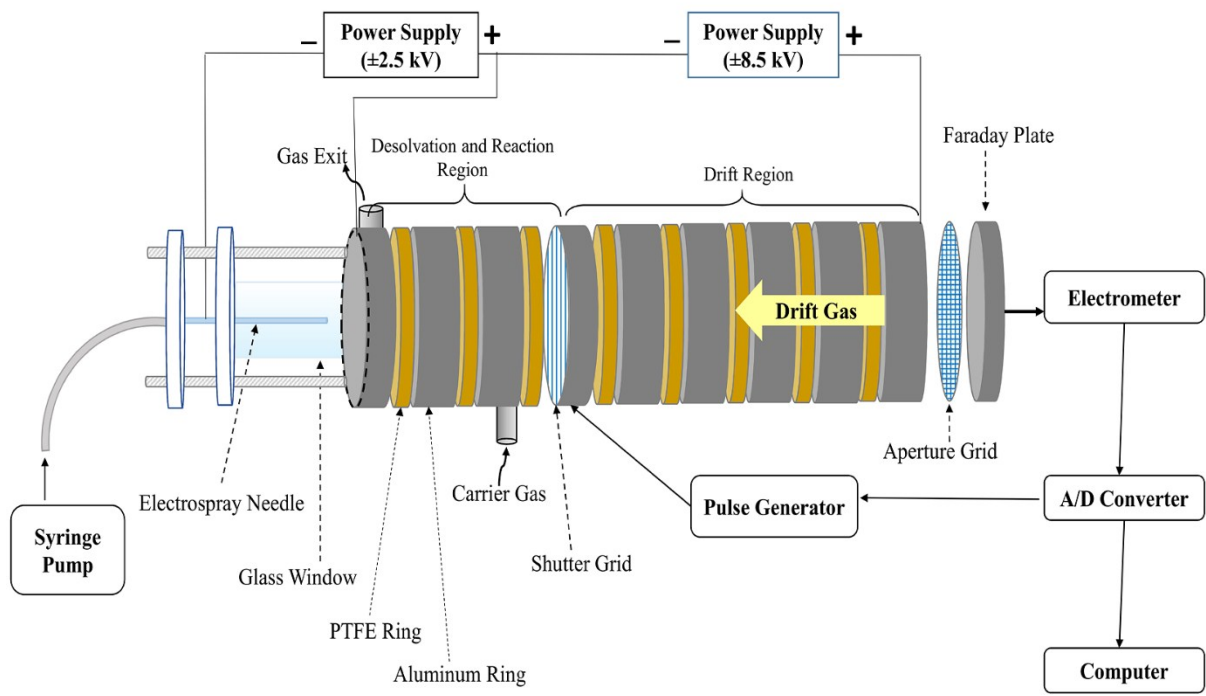


Fig. S1 The schematic diagram of the secondary electrospray ionization-ion mobility spectrometer apparatus

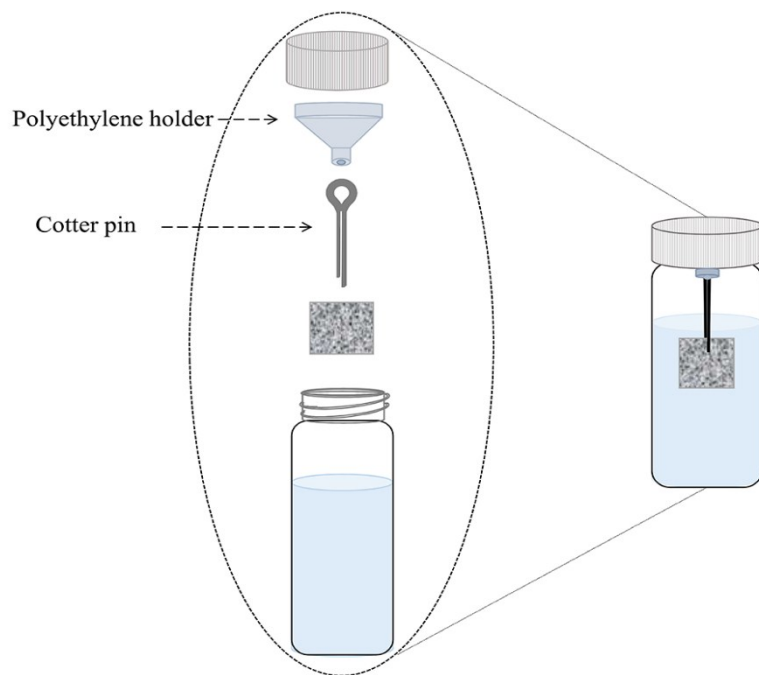


Fig. S2 Schematic illustration of TFME system

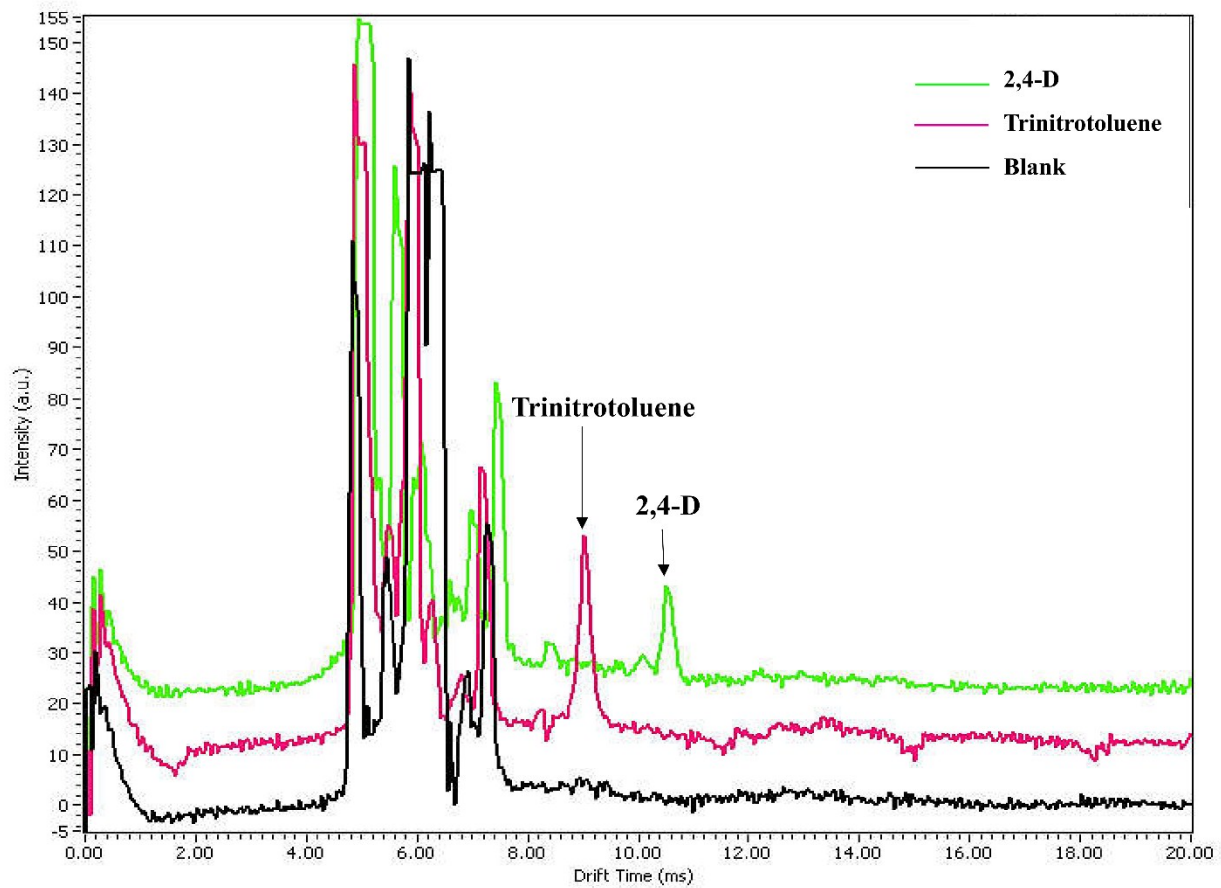


Fig. S3 The IMS spectra of 2,4-D, trinitrotoluene, and extracted blank sample

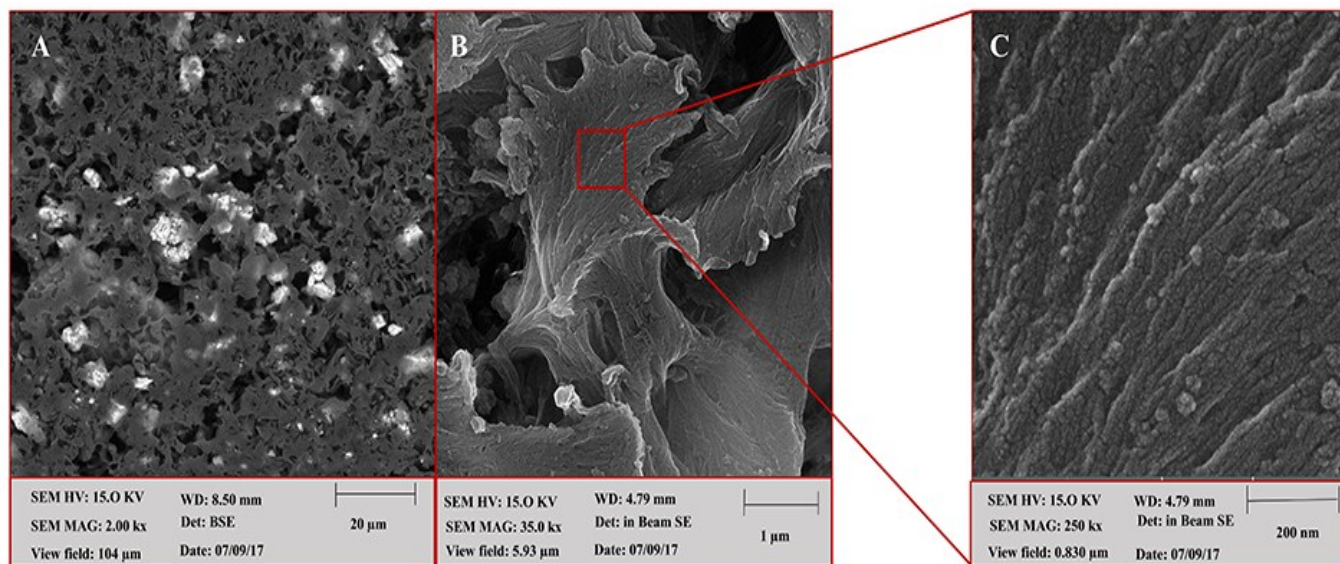


Fig. S4 FE-SEM images of UiO-66-NH₂/GO thin film at three different magnifications

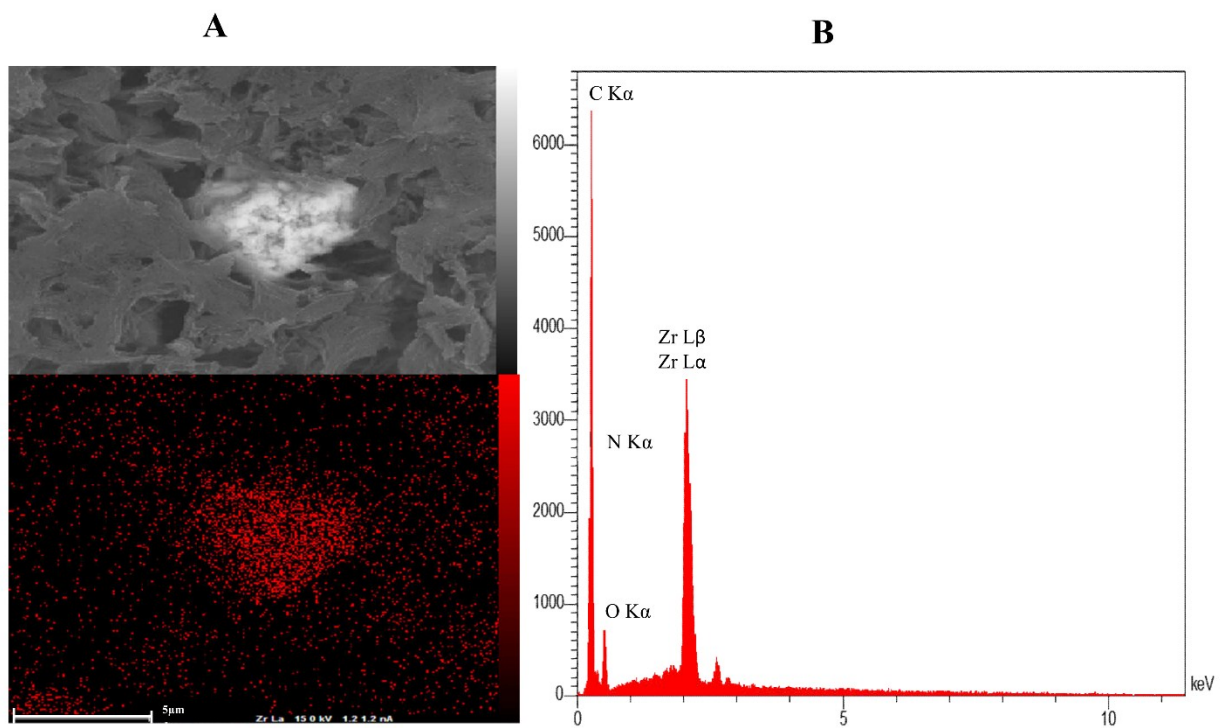


Fig. S5 (A) EDS elemental mapping of UiO-66-NH₂/GO thin-film, (B) EDS spectrum of UiO-66-NH₂/GO nanoparticles

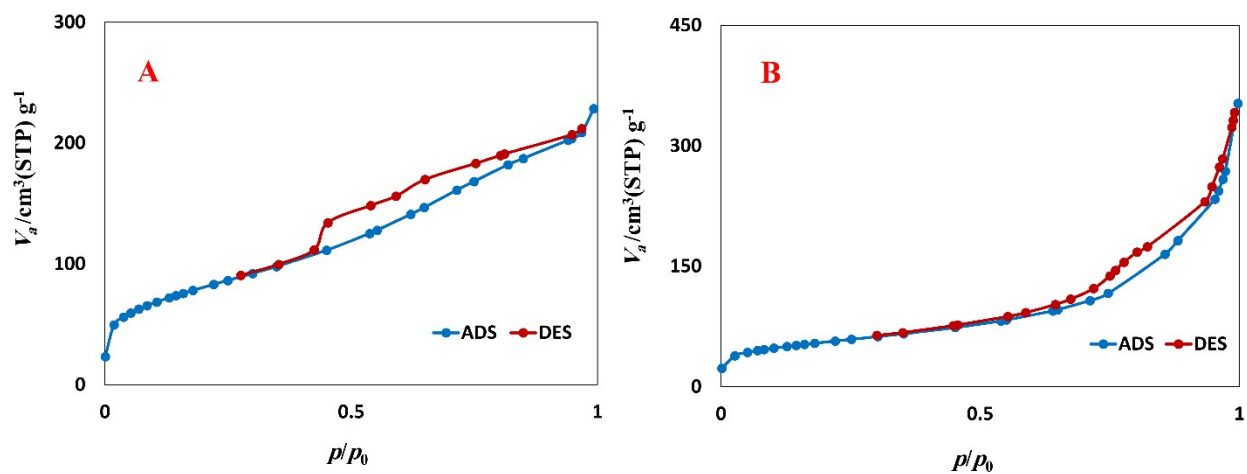


Fig. S6 N_2 adsorption-desorption isotherms at 77 K for (A) UiO-66-NH₂ and (B) UiO-66-NH₂/GO nanocomposite

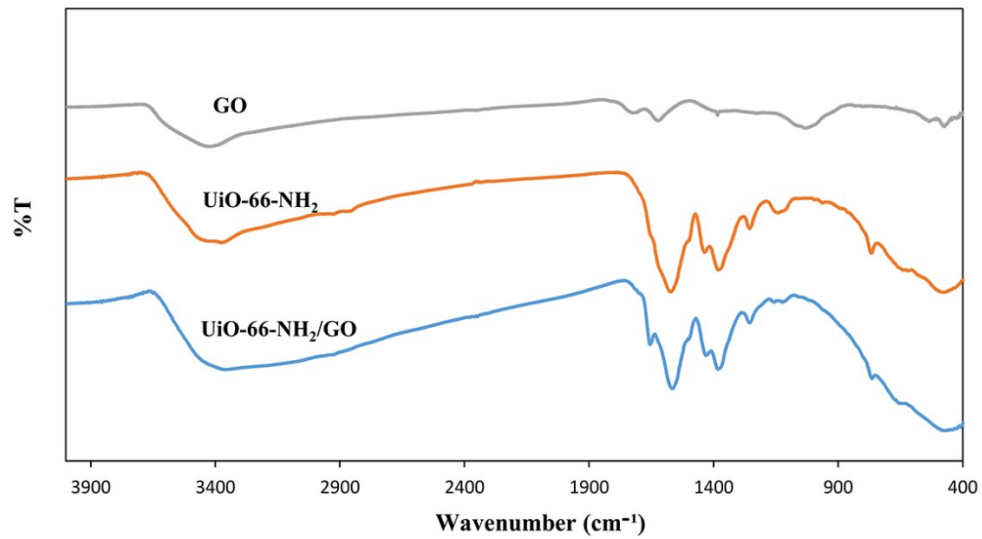


Fig. S7 FT-IR spectra of GO, UiO-66-NH₂ and UiO-66-NH₂/GO nanocomposite

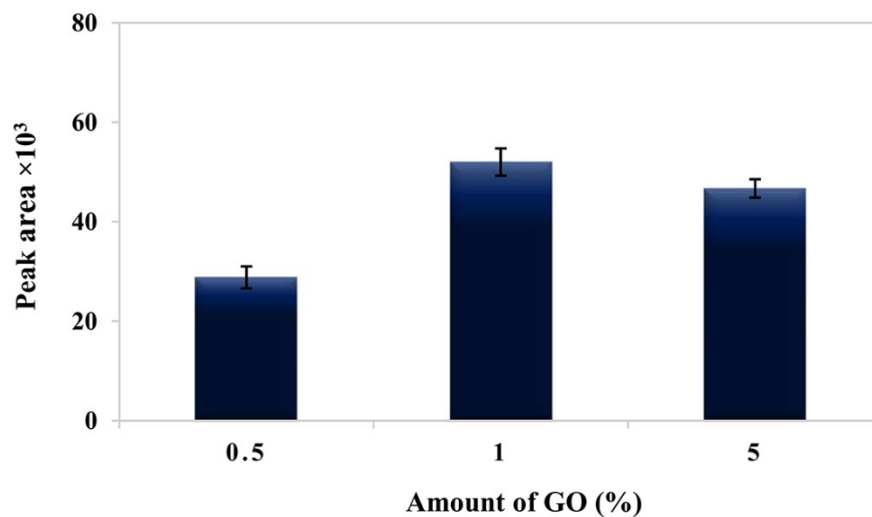


Fig. S8 Effect of amount of GO% (w/w) on the extraction efficiency of 2,4-D; (concentration of analyte: 200 $\mu\text{g L}^{-1}$; amount of UiO-66-NH₂/GO in thin-film: 20% (w/w); pH: 3; extraction time: 30 min; desorption solvent: methanol containing 1% (v/v) of TEA; desorption solvent volume: 200 μL ; desorption time: 8 min with using ultrasonication; number of replicates: 3)

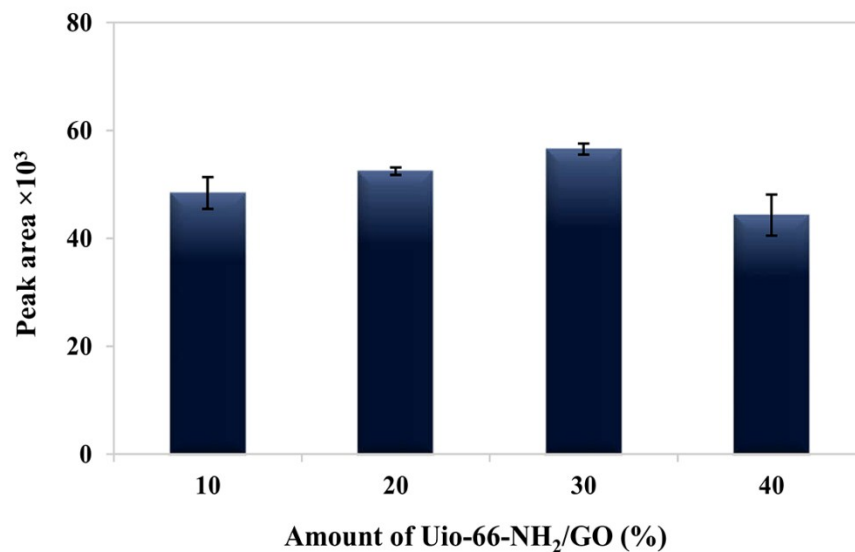


Fig. S9 Effect of the amount of UiO-66-NH₂/GO on the extraction efficiency of 2,4-D; (concentration of analyte: 200 µg L⁻¹; amount of GO: 1.0% (w/w); pH: 3; extraction time: 30 min; desorption solvent: methanol containing 1% (v/v) of TEA; desorption solvent volume: 200 µL; desorption time: 8 min with using ultrasonication; number of replicates: 3)

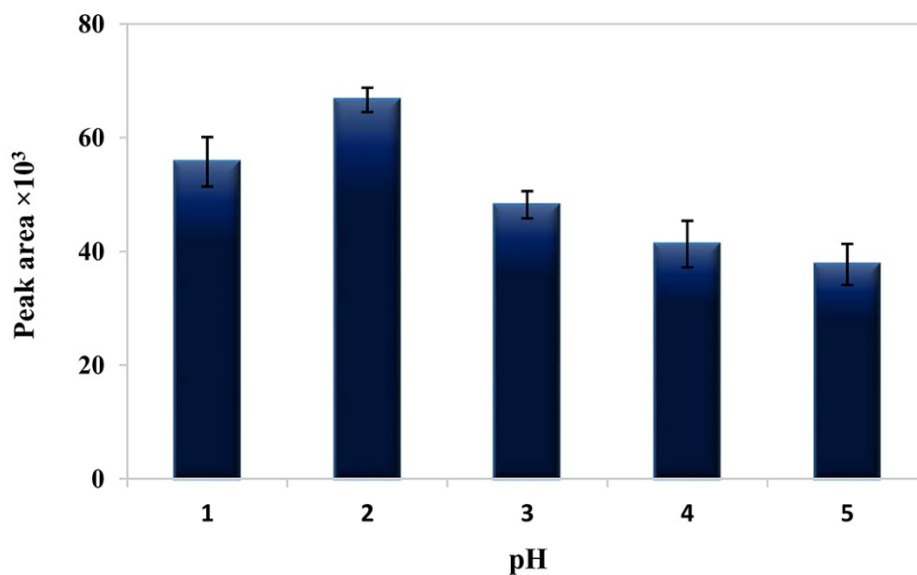


Fig. S10 Effect of the pH on the extraction efficiency of 2,4-D; (concentration of analyte: 200 $\mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); extraction time: 30 min; desorption solvent: methanol containing 1% (v/v) of TEA; desorption solvent volume: 200 μL ; desorption time: 8 min with using ultrasonication; number of replicates: 3)

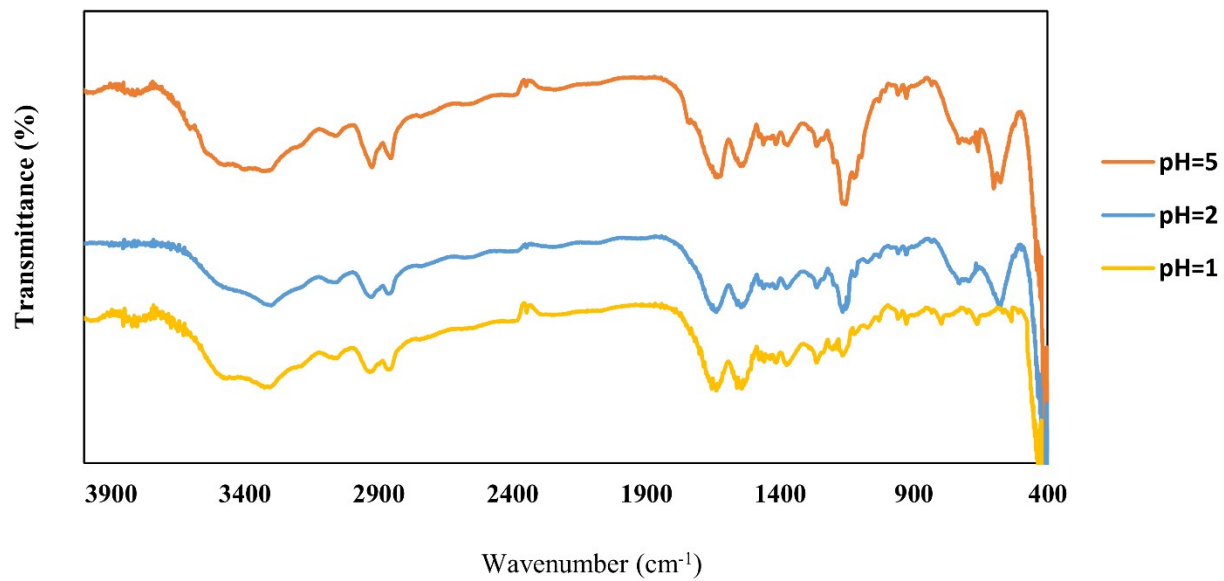


Fig. S11 FT-IR overlay of UiO66-NH₂/GO film after impregnation with HCl₂ solutions

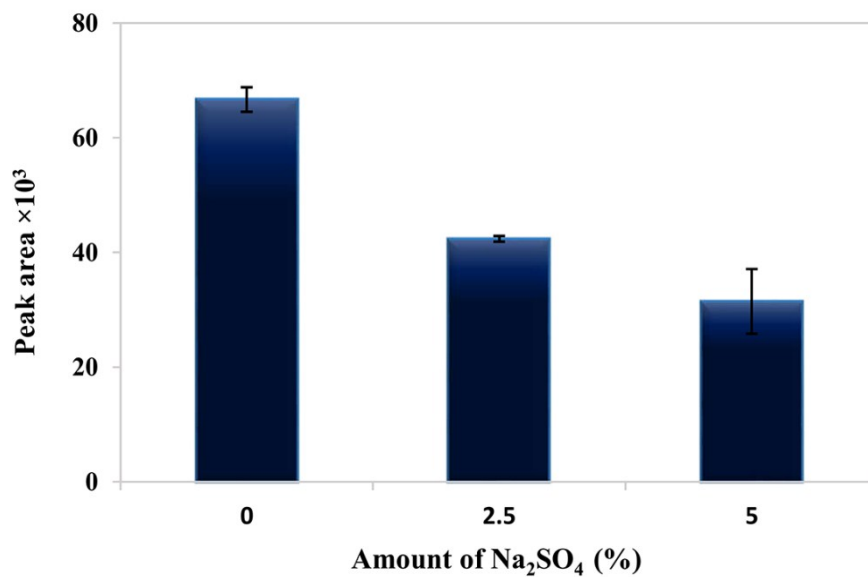


Fig. S12 Effect of the ionic strength on the extraction efficiency of 2,4-D; (concentration of analyte: 200 $\mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); pH: 2; extraction time: 30 min; desorption solvent: methanol containing 1% (v/v) of TEA; desorption solvent volume: 200 μL ; desorption time: 8 min with using ultrasonication; number of replicates: 3)

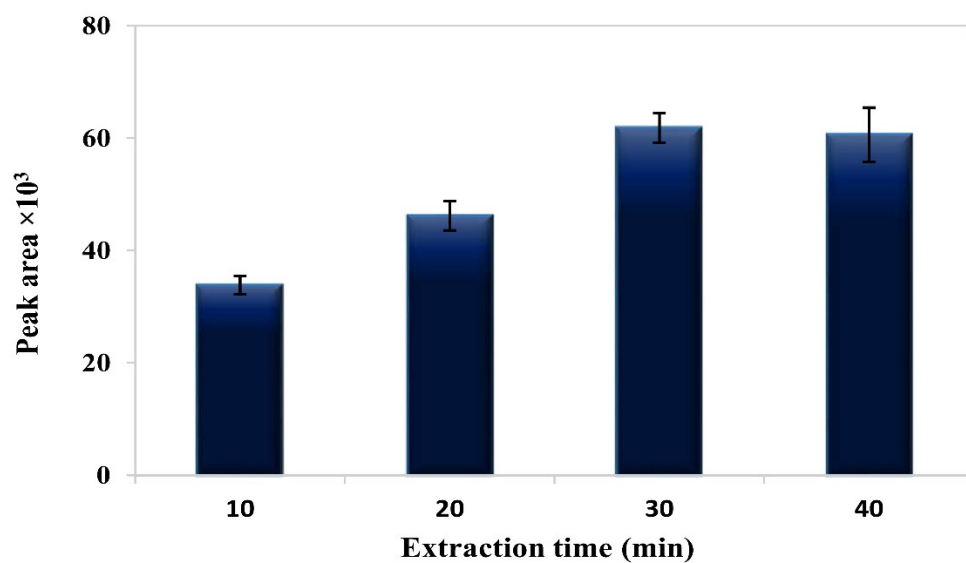


Fig. S13 Effect of the extraction time on the extraction efficiency of 2,4-D; (concentration of analyte: $200 \mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); pH: 2; desorption solvent: methanol containing 1% (v/v) of TEA; desorption solvent volume: $200 \mu\text{L}$; desorption time: 8 min with using ultrasonication; number of replicates: 3)

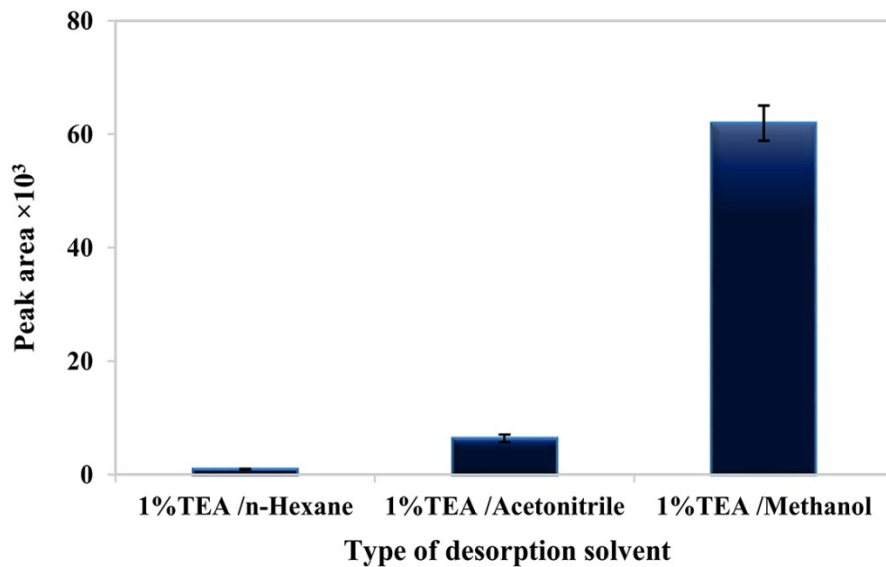


Fig. S14 Effect of the desorption solvent type on the desorption efficiency of 2,4-D; (concentration of analyte: $200 \mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); pH: 2; extraction time: 30 min; desorption solvent volume: $200 \mu\text{L}$; desorption time: 8 min with using ultrasonication; number of replicates: 3)

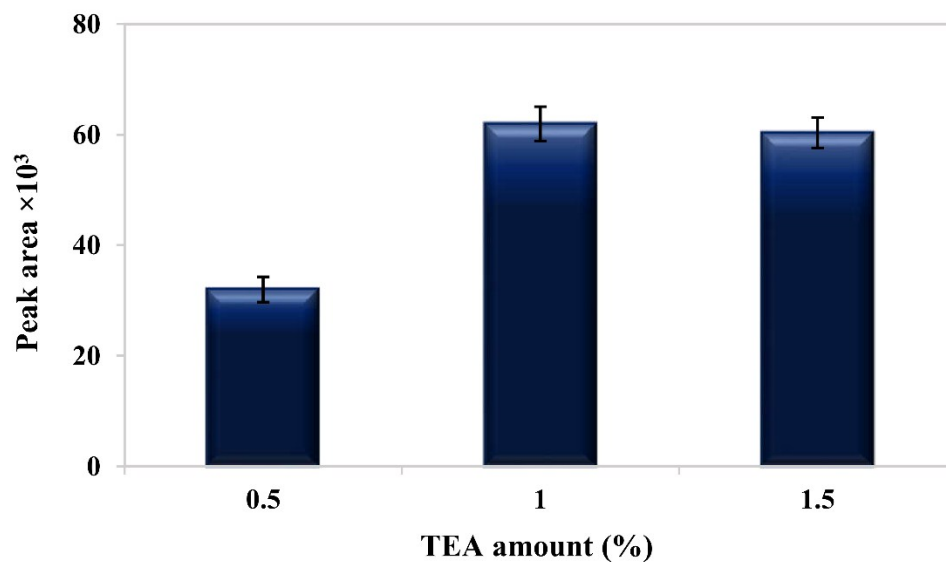


Fig. S15 Effect of the amount of TEA in methanol on the desorption efficiency of 2,4-D; (concentration of analyte: $200 \mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); pH: 2; extraction time: 30 min; desorption solvent volume: $200 \mu\text{L}$; desorption time: 8 min with using ultrasonication; number of replicates: 3)

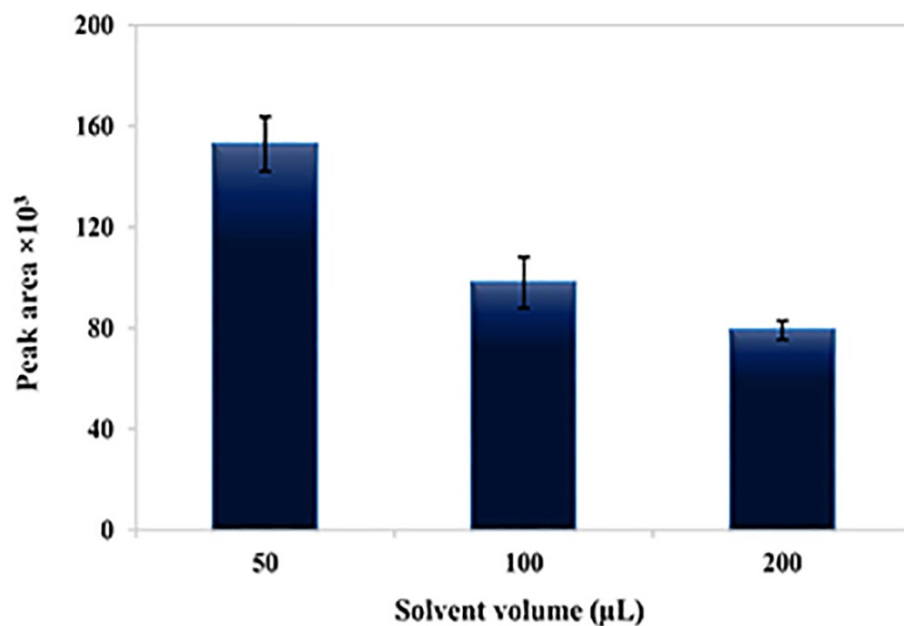


Fig. S16 Effect of the desorption solvent volume on the desorption efficiency of 2,4-D; (concentration of analyte: 200 $\mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); pH: 2; extraction time: 30 min; desorption solvent: methanol containing 1% (v/v) of TEA; desorption time: 8 min with using ultrasonication; number of replicates: 3)

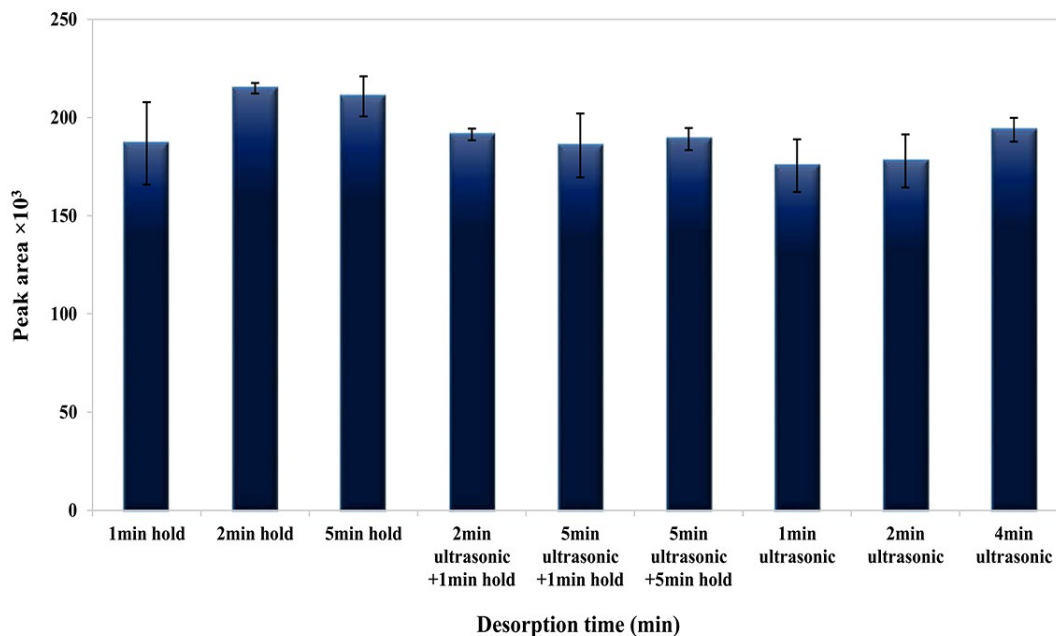


Fig. S17 Effect of the desorption condition on the desorption efficiency of 2,4-D; (concentration of analyte: $200 \mu\text{g L}^{-1}$; amount of GO: 1.0% (w/w); amount of UiO-66-NH₂/GO in the thin-film: 30% (w/w); pH: 2; extraction time: 30 min; desorption solvent: methanol containing 1% (v/v) of TEA; desorption solvent volume: $50 \mu\text{L}$; number of replicates: 3)

References

- 1 N. Li, J. Chen and Y. P. Shi, *Anal. Chim. Acta*, 2017, **949**, 23–34.