Electronic Supplementary Information (ESI)

Speciation and determination of inorganic arsenic species in water and biological samples by ultrasound assisted-dispersive-micro-solid phase extraction on carboxylated nanoporous graphene coupled with flow injection-hydride generation atomic absorption spectrometry

Aisan Khaligh[a], Hamid Shirkhanloo[b,c], Hassan Zavvar Mousavi[a,1] , Alimorad Rashidi[c]

[a] *Department of Chemistry, Semnan University, Semnan 35131-1911, Iran.*

[b] *Occupational and Environmental Health Research Center (OEHRC), Iranian Petroleum Industry Health Research Institute (IPIHRI), Tehran 1485733111, Iran.*

[c] *Nanotechnology Research Center, Research Institute of Petroleum Industry, Tehran 1485733111, Iran.*

[1]Corresponding author at: Department of Chemistry, Semnan University, Semnan 35131-1911, Iran.
E-mail address: hzmousavi@semnan.ac.ir, Tel.: +98 23 3366194; Fax: +98 23 3354110

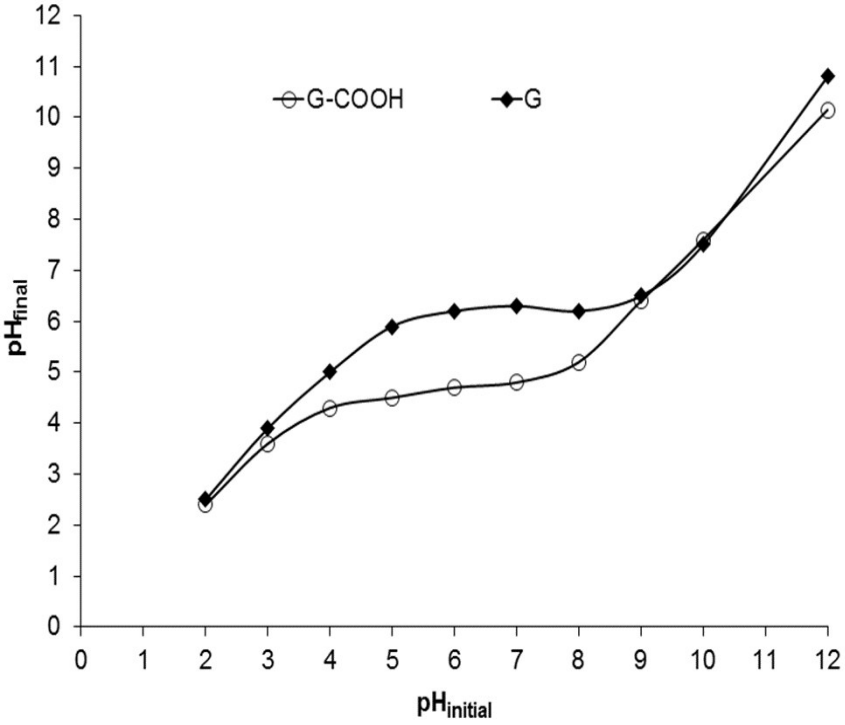

Fig. S1 Final pH versus initial pH plots for 0.15 g of pristine and carboxylated nanoporous graphene.

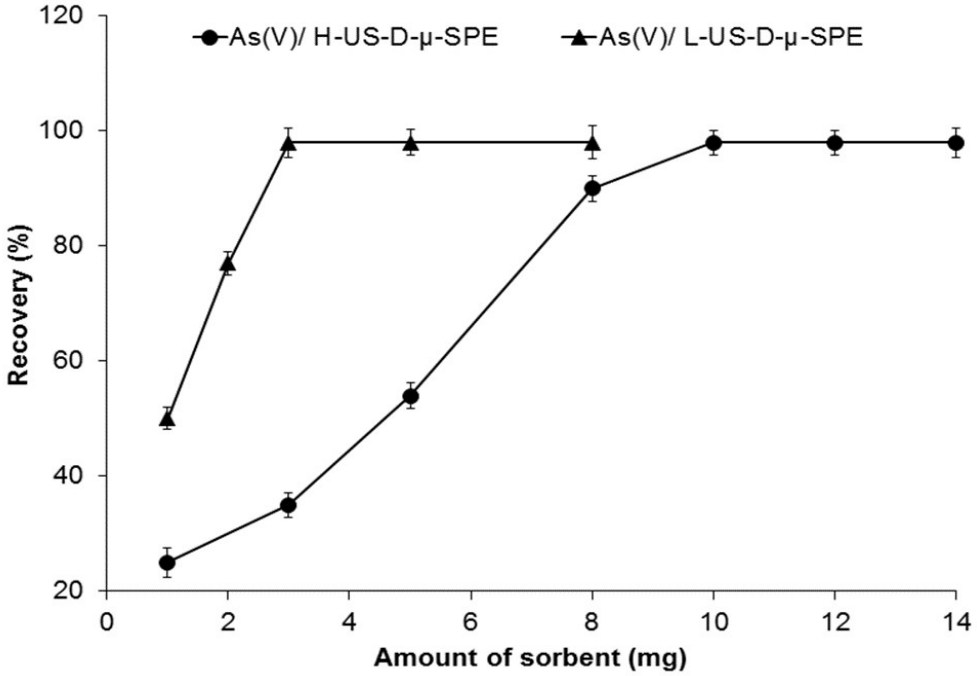

Fig. S2 Effect of amount of adsorbent on the recovery of 0.5 µg L^{-1} of As (V) ions. Conditions. solution pH 3.5; (a) H-US-D-µ-SPE: sample volume 50 mL; eluent 1000 µL of 0.5 mol L^{-1} NaOH; extraction time 3 min. (b) L-US-D-µ-SPE: sample volume 5 mL; eluent 1000 µL of 0.3 mol L^{-1} NaOH; extraction time 1 min.

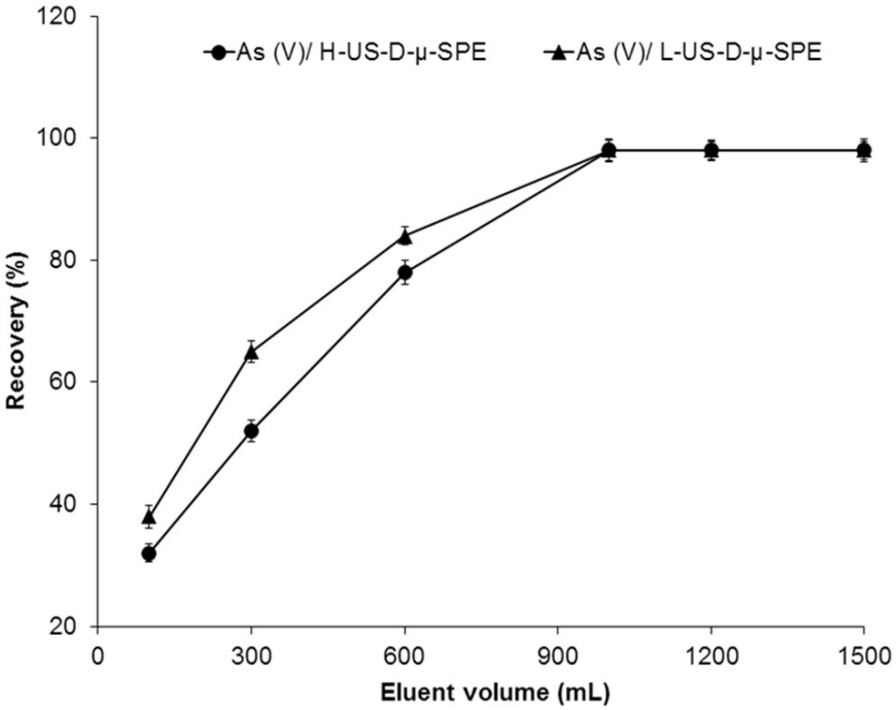

Fig. S3 Effect of eluent volume on the recovery of 0.5 µg L^{-1} of As (V) ions. Conditions. solution pH 3.5; (a) H-US-D-µ-SPE: sample volume 50 mL, sorbent 10 mg; eluent 0.5 mol L^{-1} NaOH; extraction time 3 min. (b) L-US-D-µ-SPE: sample volume 5 mL; sorbent 3 mg; eluent 0.3 mol L^{-1} NaOH; extraction time 1 min.

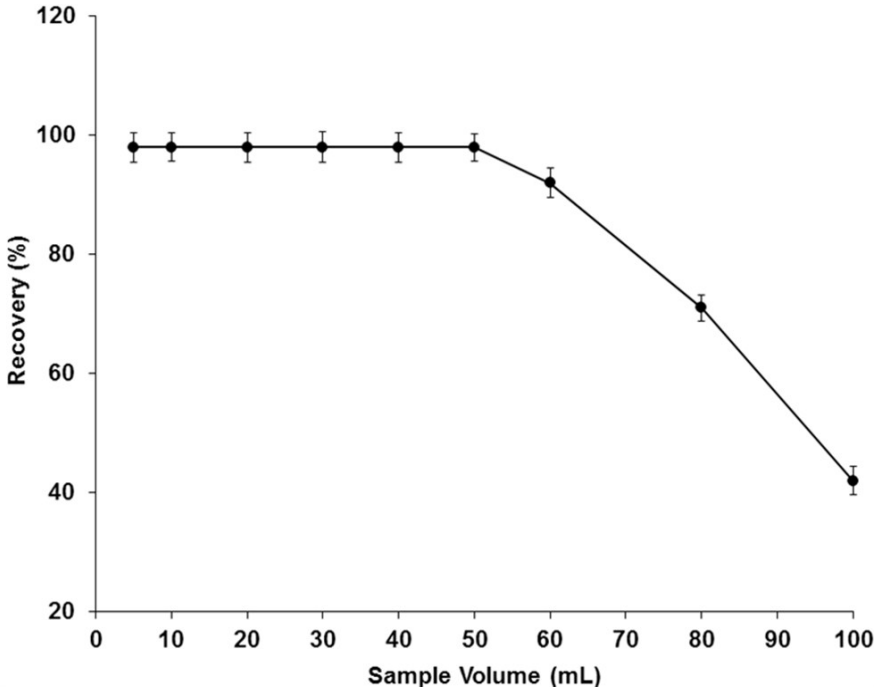

Fig. S4 Effect of sample volume on the recovery of 0.025 μg of As (V) ions. Conditions: solution pH 3.5; sorbent 10 mg; eluent 1000 μL of 0.5 mol L^{-1} NaOH; extraction time 3 min.

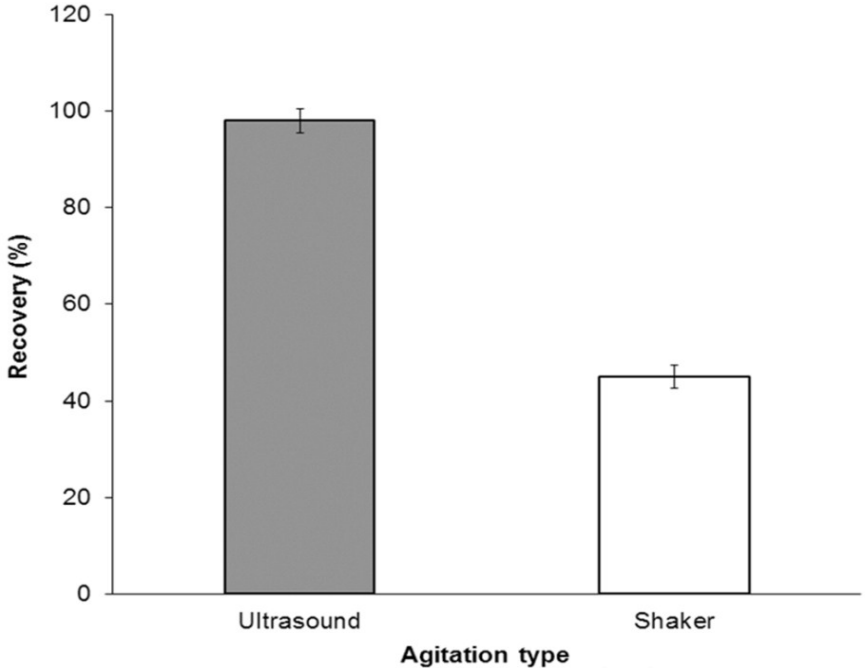

Fig. S5 Effect of agitation type on the recovery of 0.5 μg L^{-1} of As (V) ions. Conditions: sample volume 50 mL; solution pH 3.5; sorbent 10 mg; eluent 1000 μL of 0.5 mol L^{-1} NaOH; extraction time 3 min.

Table S1 The FI-HG-AAS conditions for arsenic determination.

Features	Value
Linear range, μg L^{-1}	0.5–30
Correlation coefficient	0.9988
Wavelength, nm	197.2
Lamp current, mA	8.0
Slit, nm	1.0
Mode	Peak Area
HCl carrier solution, % (v/v)	5.0
$NaBH_4$ reducing agent, % (m/v)	0.6 (in 0.5% w/v NaOH)
Argon flow rate, mL min^{-1}	10
Air flow rate, mL min^{-1}	4.7
Acetylene flow rate, mL min^{-1}	1.2

Table S2 Comparison of the adsorption capacities of various adsorbents for removal of As (V) ions from water samples by batch method.

Metal ions	Adsorbent	Adsorption capacity ($mg\ g^{-1}$)		Ref.
		As (III)	As (V)	
As (V)	GO[a] /ferric hydroxide	-----	23.78	[63]
As (V)	GO	-----	59.60	[64]
As (V)	Magnetic GO	-----	80.10	[64]
As (III), As (V)	GO–$ZrO(OH)_2$	95.15	84.89	[65]
As (III), As (V)	NZVI[b]–RGO[c] composite	35.83	29.04	[66]
As (III), As (V)	Fe_3O_4–RGO[c]–MnO_2 nanoparticles	14.04	12.22	[67]
As (III), As (V)	Cu doped Fe_3O_4	37.97	42.90	[68]
As (V)	Fe_3O_4-loaded activated carbon	-----	43.70	[69]
As (V)	Iron-treated clinoptilolite	-----	30.21	[70]
As (V)	Mn_3O_4 crystalline powder	-----	0.35	[71]
As (V)	surfactant-modified zeolite	-----	74.30	[72]
As (V)	Fe^{2+} oxide coated ethylenediamine-MWCNT[d]	-----	17.80	[73]
As (V)	Granular TiO_2	-----	41.40	[74]
As (V)	Carboxylated nanoporous graphene	-----	125.40	This work
As (V)	Nanoporous graphene	-----	35.00	This work

[a]Graphene oxide, [b]Nanoscale zero valent iron, [c] Reduced graphite oxide.

Table S2. Comparison of the developed US-D-μ-SPE methods with other reported procedures for determination of As ions in different matrixes.

Species	Method/ Detection	Sorbent	Matrix	PF [a]	LOD[b] (μg L^{-1})	R.S.D[c] (%)	Linear range (μg L^{-1})	Loading time (min)	Sample volume (mL)	Ref.
As(V), As(III) converted to As(V)	SPE[d]/ HG-AAS[e]	Nano ZrO_2/B_2O_3	Water	20	0.185	-----	0.03–40	33	100	9
As(V), As(III) converted to As(V)	SPE/ Molybdenum blue	CTAB@ACMNPs[f]	Water	175	0.028 mg L^{-1}	2.8	0.09–4.0	-----	350	19
As(V), As(III) converted to As(V)	Online-microcolumn SPE/ ICP-OES[g]	CTAB-alkyl silica	Water	27.6*	0.15	4	0.5-1000	106 s	3	75
As(V)	SPE/ HG-AFS[h]	Eggshell membrane	Water	33.3	0.001	2.1	-----	67	200	4
As(V), As(III)	SPE/ FI-ICP-OES	Anion exchange resin	Water	-----	As(V): 0.1 As(III): 0.1	5 3	0.5-2.0	15	20	76
As(III) As(V)	SPE/ ICP-MS[i]	APDC[j]-Carbon nanofibers	Water	33*	As(III):0.0045 As(V):0.24	1.9 2.6	-----	100	100	77
As(III), As(V) converted to As(III)	SPE/ HG-AAS	Alternaria solani coated HP-2MG resin	Water, Food, Human hair	35	0.011	< 7	-----	50	250	3
As(III), As(V) converted to As(III)	SPE/ HG-AAS	Streptococcus pyogenes immobilized on Sepabeads SP 70	Water and food	36	0.013	< 8	1-25	62.5	250	11

As (III, V), Sb (II, IV), As (V) converted to As (III)	SPE/ ET-AAS[k]	APDC-CNT[l]	Water	As (III):250	0.02	3.5	0.03–0.6	33	50	14
As (III, V), Sb (II, IV), Se (IV)	SPE/ ICP-MS	APDC-C18	water	50	As (V): 0.09 As (III): 0.0012	-----	-----	------	-----	78
As(III)	SPE/ GF-AAS[m]	Immobilized nanometer TiO_2	Water	50	0.024	4.8	Up to 200	50	50	79
As(III), As(V) converted to As(III)	On-line SPE/ FI-HG-AAS	SiO_2/ZrO_2	Water	20*	0.05	< 8	-----	31	100	80
As (III, V), Sb (III,V)	Online-micro column SPE/ ICP-OES	Modified mesoporous TiO_2	Water	10	As (III):0.49 As (V): 0.53	1.5 3.9	-----	----	----	81
As(III), As(V)	SPE/ ICP-MS	Thiol- and amine-bifunctionalized mesoporous silica	Water	----	As (III):0.025 As (V): 0.015	4.5 5.6	-----	-----	10	18
As(V), As(III) converted to As(V)	D-μ-SPE/FI-HG-AAS	Carboxalated nanoporous graphen	Water and Human serum and urine	50.3 5.1	0.0021 0.0248	3.1 2.6	0.01 – 0.65 0.11 – 6.60	3 1	50 5	This work

[a] Preconcentration factor, [b] Detection limit, [c] Relative standard deviation, [d] Solid phase extraction, [e] Hydride generation atomic absorption spectrometery, [f] Cetyltrimethyl ammonium bromide immobilized on alumina-coated magnetite nanoparticles, [g] Inductively coupled plasma optical emission spectrometry, [h] Hydride generation atomic fluorescence spectrometry, [i] Inductively coupled plasma mass spectrometry, [j]Ammonium pyrrolidine dithiocarbamate, [k] Electrothermal atomic absorption spectrometry, [l] Carbon nanotubes, [m] Graphite furnace atomic absorption spectrometry, * Enrichment factor

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