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40	Abstract	<p>We describe a hybrid nanoadsorbent prepared by depositing graphene on the zeolite clinoptilolite by chemical vapor deposition. The resulting sorbent is well suited for the preconcentration of lead(II) and cadmium(II) by ultrasound-assisted dispersive micro solid phase extraction. An extraction unit has been designed and manufactured that facilitates handling of small sample volumes. The effects of sample pH, amount of sorbent, concentration and volume of elution and time of ultrasonic bath were investigated. The nanoadsorbent was characterized by scanning electron microscopy, X-ray diffraction and energy dispersive X-ray microanalysis, all of which revealed the high surface area of the graphene sheets on the clinoptilolite. The extraction recoveries when using the new nanoadsorbent were 97 % (as opposed to a mere 10 % in case of clinoptilolite only). It is assumed that the graphene sheets located around the porous structure of clinoptilolite was acting as a barrier against macromolecules potentially existing in the sample matrices. The method was applied to the determination of lead and cadmium in water and human serum samples by electrothermal atomic absorption spectrometry. The detection limits were as low as 70 and 4 ng L⁻¹ for Pb(II) and Cd(II), respectively. The accuracy of the method was underpinned by correct analysis of a standard reference material (SRM: 203105 Seronorm Trace Elements Serum L-2).</p> <p>Graphical Abstract: New nanoadsorbent, graphene/ clinoptilolite hybrid, was prepared which is suitable for separating and preconcentrating the metal ions from biological samples. In the propose method, the synthesized G/CL nanoadsorbent was used in ultrasound- assisted dispersive micro solid phase extraction method with applying the new designed extraction unit.</p>
41	Keywords	Lead - Cadmium - Graphene-clinoptilolite hybrid - Ultrasound-assisted dispersive micro solid phase extraction

42 Foot note
information

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Electronic supplementary material

ESM 1
(DOC 217 kb)

Ultrasound-assisted dispersive solid phase extraction of cadmium(II) and lead(II) using a hybrid nanoadsorbent composed of graphene and the zeolite clinoptilolite

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Hassan Zavvar Mousavi · Ali Morad Rashidi

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Abstract

We describe a hybrid nanoadsorbent prepared by depositing graphene on the zeolite clinoptilolite by chemical vapor deposition. The resulting sorbent is well suited for the preconcentration of lead(II) and cadmium(II) by ultrasound-assisted dispersive micro solid phase extraction. An extraction unit has been designed and manufactured that facilitates handling of small sample volumes. The effects of sample pH, amount of sorbent, concentration and volume of elution and time of ultrasonic bath were investigated. The nanoadsorbent was characterized by scanning electron microscopy, X-ray diffraction and energy dispersive X-ray microanalysis, all of which revealed the high surface area of the graphene sheets on the clinoptilolite. The extraction recoveries when using the new nanoadsorbent were 97 % (as opposed to a mere 10 % in case of clinoptilolite only). It is assumed that the graphene sheets located around the porous structure of clinoptilolite was acting as a barrier against macromolecules potentially existing in the sample matrices. The method was applied to the determination of lead and cadmium in water and human serum samples by electrothermal atomic absorption spectrometry.

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The detection limits were as low as 70 and 4 ng L⁻¹ for Pb(II) and Cd(II), respectively. The accuracy of the method was underpinned by correct analysis of a standard reference material (SRM: 203105 Seronorm Trace Elements Serum L-2).

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Keywords Lead · Cadmium · Graphene-clinoptilolite hybrid · Ultrasound-assisted dispersive micro solid phase extraction

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Introduction

42

Cadmium (Cd) and lead (Pb) have been renowned as toxic elements for human and environment. Heavy metals are stable in the environment [1]. Pb(II) has most hazardous effects to human health. Lead inhibits biosynthesis and reduces the functions of kidneys, brain cells, bone formation and liver membrane. It can be accumulated in the body and can promote disturbances such as nausea, vomiting, diarrhea, coma and death [2]. Cadmium may cause dysfunction and reproductive deficiencies by accumulation in bodies [3]. As a result, the quantification of trace level of heavy metal ions in human body fluids is important [4]. Therefore, the development of sensitive, precise and reproducible method for the determination of heavy metal is important and necessary.

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Several detection techniques including inductively coupled plasma mass spectrometry (ICP-MS) [5], inductively coupled plasma optical emission spectrometry (ICP-OES) [6], electrothermal atomic absorption spectrometry (ETAAS) [7] and flame atomic absorption spectrometry (FAAS) [8] have been introduced for the determination of heavy metals. Although all these detection techniques has earned robust recognition in trace heavy metals and have many advantages such as,

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Q3

64 multi-elemental analysis capability; large dynamic linear
65 range; low detection limits; high productivity, but direct deter-
66 mination of heavy metal ions in biological fluids is limited
67 because of their low level of concentration and matrix inter-
68 ference. Thus for detection and elimination interfering matrix
69 component, the extraction and clean-up steps are required for
70 the pre-concentration of analyte.

71 Micro scale based sample preparation techniques are
72 being developed rapidly in chemical and biological as-
73 says owing to the compatible advantages of biological
74 fluids and micro-scale assay with low sample/reagent
75 consumption [9]. Micro-extraction methods overcome
76 some of the limitations of traditional techniques such as
77 liquid-liquid extraction (LLE) and solid phase extraction
78 (SPE). Both of these methods are multi-steps extraction
79 and clean-up procedure that's become tedious, time con-
80 suming, high level of dilution and consuming high
81 amounts of hazardous organic solvent. Nowadays, devel-
82 oping simple and fast sampling techniques that require
83 less amount of solvent and allows widespread monitoring
84 of trace level contaminations is the subject of great im-
85 portance. In this Thread, solid phase microextraction
86 (SPME) has been developed to overcome some of the
87 limitations of conventional methods [10]. It incorporates
88 extraction, concentration and extract introduction of an
89 analytical system into a single step and it is a solvent-
90 free sample preparation method. The drawbacks of
91 SPME method are carryover problems, fiber fragility
92 and comparatively high cost of fibers [11, 12]. Recently,
93 μ SPE as a miniaturizing format of SPE has been devel-
94 oped to reduce consuming of solvent, sorbent usage and
95 sample handling [13, 14]. In this method, sorbent is
96 dwelled in a sealed porous membrane envelope and
97 protected from the sample matrix [15]. Sample clean-up
98 and the extraction step are carried out simultaneously in
99 μ -SPE and so, it is suitable for the extraction in complex
100 matrices. The μ -SPE method overcomes on many disad-
101 vantages of SPME such as; the sorbent is being unpro-
102 tected from matrix effects, limited range of commercial
103 sorbent types, Since μ -SPE has been applied to a wide
104 range of compounds [13, 16, 14]. In D- μ SPE procedure,
105 the extraction is carried out in the bulk solution [17, 18]
106 and adsorbent enables to interact rapidly and uniformly
107 with the all the target analytes. Recently, dispersive mi-
108 cro solid phase extraction (D- μ SPE) has been introduced
109 to reduce the extraction time and avoid channeling and
110 blocking of the cartridge or disk-SPE. Nanoparticles of
111 different absorbents can be applied in D- μ SPE to absorb
112 target analyte in various matrixes. The D- μ SPE method
113 were used to extract and enrichment of analytes in vari-
114 ous samples such as; pesticides, tetracyclines, organic
115 UV-filters, N-nitrosodimethyl-amine, polycyclic aromatic
116 hydrocarbons and various ions [18].

Graphene, a novel and attractive nanomaterial of carbon,
was discovered in 2004 [19]. Graphene has interested in-
creasing attention because of its two-dimensional structure
consisting of a single-layer of sp^2 networks of carbon atoms
[19]. This structure possesses unique electronic, thermal,
and mechanical properties such as high specific surface
area, good thermal conductivity, fast mobility of charge
carriers, and high values of Young's modulus and fracture
strength [20]. Graphene with high adsorption capacity ow-
ing to a large surface area (theoretical value is $2360 \text{ m}^2 \text{ g}^{-1}$)
use as a sorbent in SPE [21], solid phase microextraction
(SPME)[22] and magnetic solid-phase extraction (MSPE)
[23]. Graphene has been generated by chemical vapor de-
position (CVD) growth on metal substrate [24], radio-
frequency plasma-enhanced CVD [25], aerosol pyrolysis
[26] and solvothermal synthesis [27].

Natural zeolites are three-dimensional structures consisted
of hydrated aluminosilicates of group I and group II metals.
In structural standpoint, these aluminosilicates structures are
based on an infinitely extending three-dimensional network of
 AlO_4 and SiO_4 tetrahedral linked to each other with oxygen
bridges. Zeolitic materials skeleton contains channels and inter-
connected cavities which are occupied by the mobile cation and
water molecules. The non-framework cations such as: sodium,
calcium, titanium, cobalt, magnesium, aluminum, and zinc are
quite mobile which easily exchange to varying degrees by other
cations in the surrounding environment [28]. Clinoptilolite
(CL) is one of the most common natural zeolites, easily obtain-
ed from mines, suitable as a sorbent due to its natural charac-
teristics [29]. The CL contains about; 1.25 % Fe_2O_3 [30], and
can be used as a catalyst for growth of carbon nanotube [31].

In the present study, ultrasound assisted dispersive mi-
cro solid phase extraction (US-assisted-D μ SPE) method
based on G-CL as a nanoadsorbent was used for separation
and preconcentration of Pb(II) and Cd(II) in water and
human blood serum. By using of G-CL, the clean-up and
pre-concentration of analytes occur simultaneously. In US-
assisted-D μ SPE method, a small volume of sample was
used that is suitable for a limited amount of biological
samples. This method has enough sensitively and simplic-
ity for determination of analytes in biological samples by
ET-AAS.

Experimental

Reagent and material

The analytical grade of the chemical solvents such as;
nitric acid 65 % (w/v), hydrochloric acid 37 % (w/v),
glacial acetic acid, sodium hydroxide, lead nitrate (Pb
 $(\text{NO}_3)_2$), cadmium nitrate ($\text{Cd} (\text{NO}_3)_2$) were purchased
from Merck (Darmstadt, Germany). Clinoptilolite (natural

166	zeolite) was prepared from Rashm region (Semnan, Iran).	213
167	Zeolitic rock was pulverized and sieved to give a particle	214
168	size smaller than 105 μm . More information was provided	215
169	in Electronic Supplementary Material (ESM) .	216
170	Apparatus	217
171	The evaluation and determination of cadmium and lead	218
172	ions were performed using spectra GBC electro-thermal	219
173	atomic absorption spectrometer (Plus 932, Australia) with	220
174	a graphite furnace module (GF3000) equipped with a hol-	221
175	low cathode lamp and a deuterium background correction.	222
176	More details are provided in Electronic Supplementary	223
177	Material . Instrumental condition and the graphite furnace	224
178	temperature program for Pb(II) and Cd(II) are summarized	
179	in Table S1 (ESM). The catalytic chemical vapor deposi-	
180	tion (CCVD) technique was carried out in a horizontal	
181	furnace consisting of a quartz tube with 45 mm in diameter	
182	and 150 cm in length. The X-ray diffraction (XRD) of	
183	samples was carried out with an INEL EQUINOX 3000 X-	
184	ray diffractometer (INEL, France). The morphology of the	
185	graphene-clinoptilolite hybrid was analyzed via scanning	
186	electron microscopy (SEM) (VEGA\crTESCAN) and the	
187	chemical characterization was tested by energy dispersive	
188	X-ray microanalyser (EDX, Rontec, Quantax) which was	
189	attached to SEM. Raman spectra of synthesized sample	
190	was performed by Alpha Thermo Nicolet Dispersive Ra-	
191	man Spectrometer, 100 mW, Nd:YLF laser with excitation	
192	wavelength 532 nm.	
193	Synthesis of graphene-clinoptilolite hybrid	
194	Graphene-clinoptilolite hybrid (G-CL) was prepared through	
195	a special CCVD method. Here clinoptilolite was used as a	
196	catalyst and support for production of graphene. The	
197	clinoptilolite powder was placed in a quartz boat and then	
198	placed in a quartz tube. The clinoptilolite was purged in the	
199	hydrogen stream at the flow rate of 300 mL min ⁻¹ for 180 min	
200	in order to reduce the metal oxides existing in the clinoptilolite	
201	structure while temperature was reached from ambient tem-	
202	perature to reaction temperature during this time. The reaction	
203	was carried out using methane as the carbon source with a	
204	flow rate of 50 mL min ⁻¹ , and hydrogen was used as carrier	
205	gas with a flow rate of 250 mL min ⁻¹ at 900 °C for 120 min.	
206	The furnace was then cooled to room temperature under a	
207	nitrogen atmosphere and the final black product was formed	
208	after the completion of the reaction.	
209	Purification of synthesized graphene-clinoptilolite hybrid	
210	In general, the pristine sample synthesized by the CCVD	
211	method contains the carbonaceous impurities such as amor-	
212	phous carbon and carbon nanoparticles, which need to be	
	eliminated before the experiments. In this work, we used a	213
	two-step purification method for removing such impurities.	214
	The purification procedure was done as follows: first, 10 g	215
	of the synthesized hybrid was added to 150 mL of an 18 %	216
	HCl solution and mixed for about 16 h at ambient tempera-	217
	ture. The resulting mixture was filtered and washed several	218
	times with distilled water until the pH of the filtrate was neu-	219
	tral. In second purification step, the prepared materials were	220
	dissolved in 6 mol L ⁻¹ nitric acid for 3 h at 70 °C. After that,	221
	the washing step was repeated as mentioned above for the	222
	treatment process with HNO ₃ solution. The resulting cake	223
	was dried at 120 °C for 8 h.	224
	Sampling	225
	Working solutions were prepared by dilution of 1 mL of the	226
	serum samples (with deionized water) in a 2 mL volume flask.	227
	The resulting solutions were applied in US-assisted-D μ SPE	228
	method. The human blood serum was maintained at -20 °C in	229
	a cleaned glass tube. River water has been collected from Kan	230
	River, Tehran, Iran. Fresh serum samples were taken from	231
	petroleum worker, Tehran, Iran.	232
	Extraction unit and ultrasound-assisted dispersive micro solid	233
	phase extraction procedure	234
	An extraction unit was designed to apply G-CL hybrid in	235
	US-assisted-D μ SPE method. The extraction unit was	236
	consisted of a PTFE filter which was kept by PTFE O-	237
	ring inside the 2-mL conventional syringe and was pre-	238
	pared by putting the filter into the syringe and tightening	239
	by PTFE O-ring. Using this device, the sorbent can be dis-	240
	persed into the sample which is desirable for increasing the	241
	contact surface and it can be separated from the sample	242
	easily. Laboratory glassware and vessels were cleaned by	243
	soaking in 10 % (v/v) nitric acid for at least 24 h and then	244
	rinsed with deionized water prior to use.	245
	The US-assisted-D μ SPE extraction was performed as	246
	follows, 2 mL of water samples containing 0.2 $\mu\text{g L}^{-1}$ of	247
	Cd and 0.5 $\mu\text{g L}^{-1}$ of Pb(II) and dilution of serum sample	248
	with deionized water (1:1) (v/v) was transferred into the	249
	extraction unit, before that the pH was adjusted to the value	250
	of 5. Then 5 mg of G-CL was introduced into the extraction	251
	unit and ends of the syringe were closed with its plunger.	252
	The extraction unit was immersed in an ultrasonic water	253
	bath (60 s) at room temperature to disperse the G-CL in	254
	the sample solution. After sonication, the solution was sep-	255
	arated from solid phase easily with pushing the plunger.	256
	Then sorbent was rinsed with deionized water to remove	257
	interference and not absorbed analytes on solid phase.	258
	Then, 100 μL of nitric acid (0.5 mol L ⁻¹) was added to	259
	the extraction unit and allowed to perform elution of the	260

261 analytes by sonication for 30 s then pushed the plunger and
 262 injected to GFAAS by autosampler.
 263

264 **Result and discussion**

265 **Choice of Materials**

266 Zeolites have been used extensively as adsorbents for the re-
 267 moval of metal ions from water and wastewater due to their
 268 high exchange capacities and environmental compatibility.
 269 Clinoptilolite is one of the most commonly used natural zeo-
 270 lites because of its availability, cost-effectiveness, and its high
 271 selectivity towards metal ions such as Pb(II) and Cd(II). But in
 272 preconcentration procedure and recovering metal ions there are
 273 some interfering species. Besides, parts of metal ions in biolog-
 274 ical samples are bonded to proteins and large biomolecules,
 275 which make these parts of metal ions not easily be adsorbed.
 276 So, for extraction of metal ions from biological samples, zeo-
 277 lites are not suitable singly and need some hydrophobic struc-
 278 ture such as graphene or carbon nanotubes. In this method,
 279 clinoptilolite was used without any treatment and modification
 280 for synthesis of graphene. Therefore combination of
 281 clinoptilolite and graphene was produced well adsorbent for
 282 extraction of free and bounded metal ions from biological ma-
 283 trices. Clinoptilolites from other sources may also work.

284 **Graphene-clinoptilolite hybrid characterization**

285 The surface morphology of the G-CL was characterized by
 286 SEM, which is presented in Fig. 1. It shows the presence of
 287 porous clinoptilolite structure and graphene sheets around it.

288 The phase structure of the G-CL was characterized by
 289 XRD measurements as shown in Fig. 2. The peak observed

at diffraction angle (2θ) of 24.42° is highly specific for the
 crystalline nature of graphene. However, the XRD pattern
 shows three peaks at 2θ value of 24.42 , 43.15 , 44.56 and
 51.85° for the planes (002), (100), (101) and (004). Three
 peaks at 2θ value of 22.03 , 28.19 and 28.48 are related to
 SiO_2 structure and the peak at 38.59 is corresponded to
 Al_2O_3 in clinoptilolite structure.

The EDX spectrum confirms that the G-CL hybrid consists
 of Si, C, Al, O and Ca elements (Fig. 3). The strong Si signal
 originates from the SiO_2 in clinoptilolite structure, while the
 Carbon signal comes from the graphene sheets. The oxygen
 peak comes from the SiO_2 .

Raman spectroscopy is a sensitive method for graphene
 characterization. The Raman spectrum of the G-CL hybrid
 is shown in Fig. 4. As shown, G-CL hybrid has three bands,
 the D band, G band and 2D band at 1360 , 1600 and
 2676 cm^{-1} , respectively. The G-band originates from the
 in-phase vibration of the graphite lattice, while the D-
 band mainly comes from the structure defects in the
 graphene lattice, as holes and edges. G band is usually
 assigned to the E_{2g} phonon of C sp^2 atoms, while D band
 is a breathing mode of k-point phonons of A_{1g} symmetry
 [32]. The position and shape of the G peak shown in Fig. 4
 provided further evidence that graphene was synthesized.
 Raman spectrum of the pristine graphite displays a strong G
 band at 1579 cm^{-1} , a weak D band at 1360 cm^{-1} , and a
 middle 2D band at 2700 cm^{-1} . In the Raman spectra of
 the exfoliated graphene, the G band is broadened and
 shifted upward to 1595 cm^{-1} , which was mainly caused
 by stress [33]. The most prominent feature in the Raman
 spectrum of graphene is the 2D peak and the intensity ratios
 of G and 2D peaks (I_{2D}/I_G) that is dependent on the layer
 number of graphene [34]. The ratio I_{2D}/I_G of these bands for
 G-CL hybrid was equal to 0.45, it can be deduced that the
 G-CL hybrid is consisted of about 6 layers.

Fig. 1 FE-SEM image of G-CL hybrid

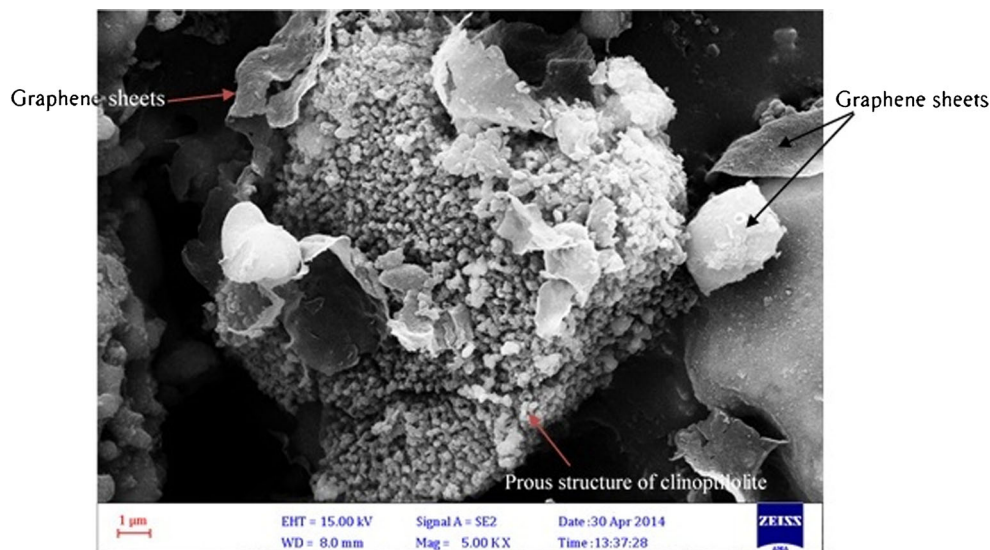
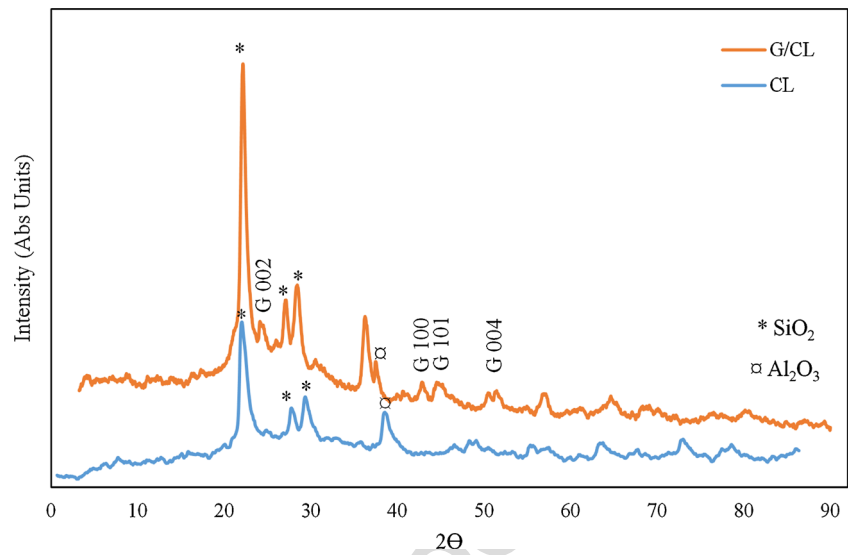


Fig. 2 XRD patterns of G-CL hybrid



325 Optimization of the ultrasound-assisted dispersive micro solid
326 phase extraction conditions

327 Dispersive solid phase extraction allows direct contact
328 between the analytes/interferents with the sorbent. This
329 method is presented to increase the selectivity and it can
330 be used to increase the sensitivity by holding the target
331 analytes on the appropriate sorbent material [35]. This
332 technique could be easily miniaturized and it is another
333 advantage of this method because it permits the reduction
334 of the sample volume (a few mL) and the amount of
335 sorbent (several mg or less). Meanwhile, in this work,
336 effective parameters for quantitative adsorption of
337 analytes on the surface of solid phase were investigated.
338 These parameters are listed below.

Effect of pH

339

340 The acidity of a solution is one of the most important factors
341 affecting the adsorption process. The influence of pH on the
342 retention of Pb(II) and Cd(II) on the sorbent was studied by
343 applying the presented procedure to the sample solutions at
344 the different pH values from 2 to 9. The pH of each solution
345 was adjusted with HNO₃ and NaOH solutions. It could be
346 seen from Fig. 5 that lead can be quantitatively recovered
347 (>90 %) by the G-CL at pH values ranging from 5 to 7. While,
348 complete recovery of cadmium was obtained in the pH range
349 of 4 to 5. The mechanism of adsorption of metal ions on the
350 G-CL may be based on electrostatic forces, and it was found to
351 be highly dependent on the solution pH value. At lower pH
352 values, the recovery was lessened due to the competition

Fig. 3 Energy dispersive X-ray microanalysis of G-CL

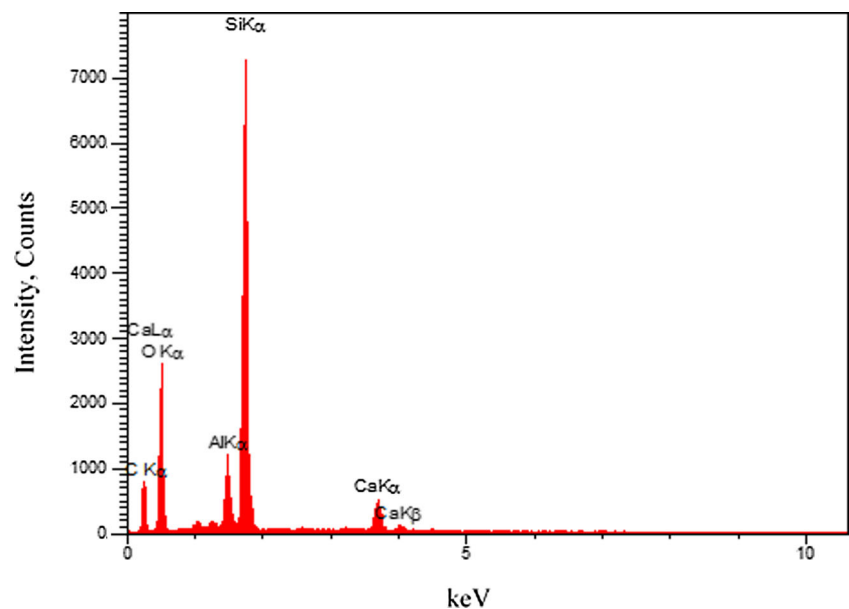
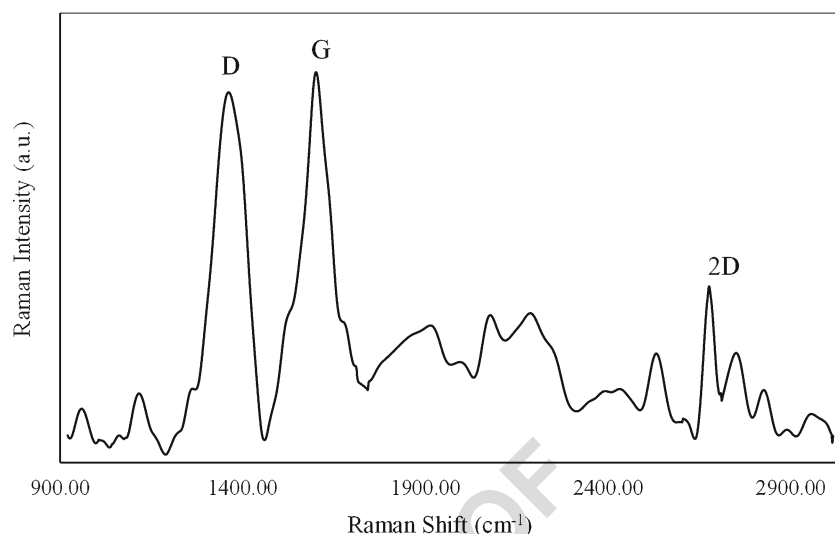


Fig. 4 Raman spectrum of graphene-clinoptilolite hybrid



353 between protons and the analytes for occupying the active
 354 sites. At middle pH values, the surface charge of the adsorbent
 355 will be negative, which is responsible for enhanced recovery
 356 of analytes. However, at higher pH values, lead and cadmium
 357 ions form precipitates with OH⁻ and their retention is changed
 358 and the recovery of the method is decreased.

359 Amount of sorbent material

360 The sorbent amount is crucial in any extraction. For this reason,
 361 different amounts of G-CL in D-μ-SPE devices in the range of 1.0 to 10.0 mg
 362 were evaluated for extracting 2 mL of sample solutions. The results indicated
 363 (Fig. S1, ESM) that 5 mg of G-CL seemed to be sufficient to extract the analytes
 364 effectively.
 365

Effect of concentration and volume of elution solution

366

In order to recover the retained analyte on the G-CL hybrid
 367 quantitatively, diluted HNO₃ was used for elution of the
 368 retained analytes from the sorbent. Therefore, several concentra-
 369 tions of HNO₃ were investigated for this purpose, and the
 370 result was shown in Fig. S2 (ESM). It was found that
 371 0.5 mol L⁻¹ was sufficient for simultaneous desorption Pb(II)
 372 and Cd(II). Therefore, a 0.5 mol L⁻¹ HNO₃ eluent was select-
 373 ed for the rest of this work.
 374

The influence of HNO₃ eluent volume on the recoveries of
 375 Pb(II) and Cd(II) was studied in the range from 50 to 300 μL.
 376 As shown in Fig. S3 (ESM), the minimum volume of eluting
 377 solution could quantitatively desorb the analytes from the sorbent
 378 by rinsing the nanoadsorbent with 100 μL of 0.5 mol L⁻¹
 379 HNO₃. Volumes higher than 100 μL (Fig. S3) indicated the
 380 unnecessary dilution. Consequently, 100 μL of 0.5 mol L⁻¹
 381 HNO₃ was chosen as optimum value.
 382

Effect of ultrasonic

383

The agitation of the sample during the extraction usually im-
 384 proves the extraction efficiency as it increases the contact be-
 385 tween the sample and the sorbent; on the other hand, dispersion
 386 is one of the most important factors in the performance of the
 387 US-assisted-DμSPE method. For these reasons, the effect of
 388 type of agitation (shaker or ultrasound assisted) was evaluated.
 389 The results showed (Fig. 6) that ultrasound was propitious to
 390 the enhancement of extraction yields and the reduction of op-
 391 erating time. So ultrasound was chosen as an agitation method
 392 for dispersing the G-CL in the sample solution.
 393

Time of ultrasonic bath

394

Sonication process is a useful way to increase the reactivity of
 395 chemicals and also enhance the rate of mass transfer [36].
 396

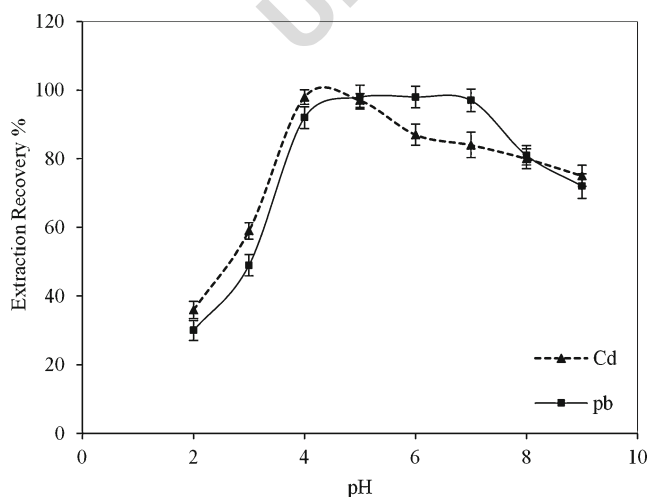


Fig. 5 Effect of pH on the recovery of 0.5 μg L⁻¹ of lead and 0.2 μg L⁻¹ of cadmium. Conditions: volume 2.0 mL; amount of adsorbent 5.0 mg; volume of eluent 100 μL

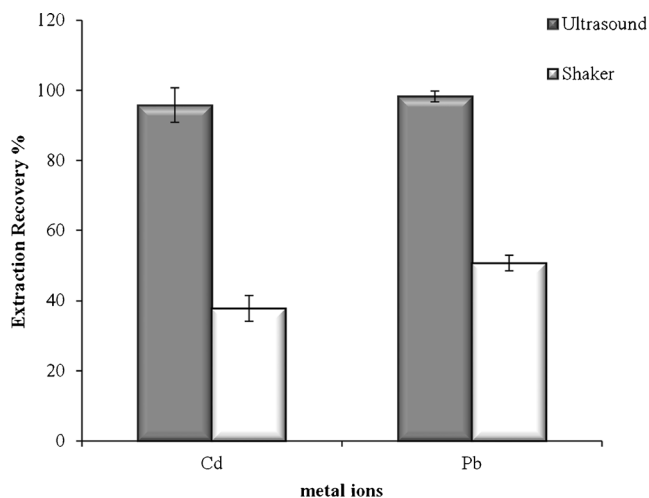


Fig. 6 Effect of ultrasound on the recovery of 0.5 $\mu\text{g L}^{-1}$ of lead and 0.2 $\mu\text{g L}^{-1}$ of cadmium. Conditions: pH 5.0; volume 2.0 mL; amount of adsorbent 5.0 mg; concentration of acid 0.5 mol L^{-1} ; extraction time 5 min

397 Therefore, the sonication time for the sorption and desorption
 398 of Pb(II) and Cd(II) by US-assisted-D μ SPE was investigated
 399 from 10 to 1200 s. Fig. S4 (ESM) shows the extraction time
 400 profiles; so an extraction time of 60 s was adopted for the
 401 presented method; Moreover, the optimum sonication time
 402 for desorption of Pb(II) and Cd(II) from G-CL was found to
 403 be 30 s.

404 Effect of diverse ions

405 The effect of potential interference encountered in natural
 406 samples on the recovery using the presented US-assisted-
 407 D μ SPE method was investigated with the optimized proce-
 408 dure. The tolerance limit was defined as the amount of poten-
 409 tially interfering ion, causing a change of less than $\pm 5\%$ in the
 410 absorbance reading. The results have shown that, Al (III), Hg
 411 (II), Cr (III), Cr (IV), Fe (III) and Mn (II) are tolerated up to 10
 412 mgL^{-1} while Cu (II), Co (II) and Zn (II) are tolerated up to
 413 1 mg L^{-1} . Also, the effect of common potentially interfering
 414 cations such as Ca (II), Mg (II), Ba (II), Na (I) and K(I) were
 415 also investigated and showed that no significant variation in
 416 the absorbance was observed at concentrations up to
 417 1000 mg L^{-1} .

t1.1 **Table 1** Analytical performance
 t1.2 characteristics of the USA-
 t1.3 D μ SPE method for lead and
 t1.4 cadmium determination (2 mL
 t1.5 sample volume, pH 5, adsorbent
 t1.6 5 mg of G-CL, ultrasonication
 t1.7 60 s, elution volume 100 μL , $n=$
 t1.8 3)
 t1.9

Parameter	Lead	Cadmium
Preconcentration factor	20	20
Detection limit (3 s, $\mu\text{g L}^{-1}$)	0.07	0.004
Intra-day precision (RSD %, $n=10$)	3.4 (2 $\mu\text{g L}^{-1}$)	3.9 (0.2 $\mu\text{g L}^{-1}$)
Inter-day precision (RSD %, $n=6$)	7.6 (2 $\mu\text{g L}^{-1}$)	6.8 (0.2 $\mu\text{g L}^{-1}$)
Linear range ($\mu\text{g L}^{-1}$)	0.24–10.3	0.011–0.48
Correlation coefficient	0.998	0.997
Regression equation ($\mu\text{g L}^{-1}$)	$A=0.1497 [\text{Pb}]+0.0032$	$A=1.3781 [\text{Cd}]+0.0024$

Figures of merit

418

419 The analytical figures of merit of the presented method were
 420 determined by using 2 mL aqueous standard solutions of the
 421 interested analytes over a concentration range of 0.24–
 422 10.3 ng mL^{-1} for Pb(II) and 0.011–0.48 ng mL^{-1} for Cd(II).
 423 Analytical data obtained are summarized in Table 1. The
 424 preconcentration factor calculated as the ratio of the concen-
 425 tration of analyte after preconcentration to that prior
 426 preconcentration.

Application of presented method in real sample

427

428 The accuracy of the presented method was tested by determin-
 429 ing the trace level of Pb(II) and Cd(II) in a certified reference
 430 material, that is, 203105 Seronorm Trace Elements L2 (trace
 431 elements in serum). The presented method was applied also to
 432 the analysis of tap water, river water and human serum. Aque-
 433 ous standard solutions as a calibration were used for the con-
 434 centration determination, without further matrix specific opti-
 435 mization for the samples. The results are collected in Table 2.
 436 The recovery ranged between 92.3 and 99.0 % showing better
 437 performance of the method not only in all types of natural
 438 waters samples, but also in complex matrixes such as serum.

Comparison graphene-clinoptilolite hybrid and clinoptilolite
 as an adsorbent

439
 440

441 In order to evaluate the performance of the graphene-
 442 clinoptilolite hybrid in US-assisted-D μ SPE method against
 443 the clinoptilolite, without Manipulation, these two mate-
 444 rials were used as a sorbent in presented method. The re-
 445 sults showed (Table 3) that clinoptilolite had a relatively
 446 good ability for preconcentration of Pb(II) and Cd(II) from
 447 water samples, nevertheless desorption solution possess
 448 numerous interfering peak in ETAAS. But, efficiency of
 449 clinoptilolite in a serum sample was very low, while the
 450 graphene-clinoptilolite hybrid quantitatively extracted the
 451 interest analytists. These results showed that synthesized
 452 graphene-clinoptilolite hybrid had a good ability to extract
 453 the analytes from complex matrixes which was probably
 454 due to the presence of the graphene sheets. Graphene sheets

t2.1 **Table 2** Analytical results of lead and cadmium determination in spiked natural water samples, spiked human serum and certified reference material with the USA-D μ SPE method (sample volume 2 mL, pH 5, adsorbent 5 mg of G-CL, ultrasonication 60 s, elution volume 100 μ L, $n=3$)

t2.2	Sample	Certified ($\mu\text{g L}^{-1}$)		Add ($\mu\text{g L}^{-1}$)		Found ^a ($\mu\text{g L}^{-1}$)		Recovery	
		Pb	Cd	Pb	Cd	Pb	Cd	Pb	Cd
t2.4	Tap water	–	–	–	–	0.83 \pm 0.13	0.052 \pm 0.007	–	–
t2.5				2	0.2	2.79 \pm 0.14	0.248 \pm 0.015	98	98
t2.6				4	0.4	4.73 \pm 0.22	0.448 \pm 0.025	97.5	99
t2.7	Kan water	–	–	–	–	5.36 \pm 0.19	0.182 \pm 0.013	–	–
t2.8				2	0.2	7.31 \pm 0.32	0.376 \pm 0.020	97.5	97
t2.9				4	0.4	9.30 \pm 0.43	0.578 \pm 0.05	98.5	99
t2.10	Human serum 1	–	–	–	–	9.15 \pm 0.51	0.271 \pm 0.02	–	–
t2.11				1	0.2	10.09 \pm 0.61	0.459 \pm 0.04	94	94
t2.12	Human serum 2	–	–	–	–	8.57 \pm 0.48	0.164 \pm 0.013	–	–
t2.13				0.5	0.1	9.04 \pm 0.61	0.257 \pm 0.023	94	93
t2.14				1	0.2	9.50 \pm 0.65	0.355 \pm 0.031	93	95.5
t2.15	CRM level 2 203105	1.11	0.13	–	–	1.05 \pm 0.06 ^b	0.12 \pm 0.01 ^b	95.5	92.3

^a Mean value \pm standard deviation based on three replicate measurements

^b Not significantly different from the certified value, at the 95 % level

455 was a barrier against the macromolecules, so metal ions can
 456 be penetrated through the porous structure of clinoptilolite,
 457 while part of the metal ions that bond with the proteins of
 458 plasma, can be adsorbed on the surface of the graphene, so
 459 whole the metal ions (free and bonded) can be extracted.

460 **Comparison with other reported method**

461 A comparison of the US-assisted-D μ SPE method and some of
 462 the published sorbent based methods for preconcentration of
 463 Pb(II) and Cd(II) ions are summarized in Table S2 (ESM). As
 464 it can be seen, the presented method with using only small
 465 amount of sample volume compared to other methods pos-
 466 sesses the applicable linear range. Meanwhile, the limit of
 467 detection and precision are comparable to those in the reported
 468 sorbent based methods. These characteristics can be of key
 469 interest in applying in biochemical and clinical studies.

470 Ghaedi et al. used Amberlite XAD-16 modified with
 471 DCPIMI (as a chelating agent) for extraction of Cu²⁺, Zn²⁺ and
 472 Mn²⁺ [37]. They used chelating agent for adsorbing the metal

ions on the packed adsorbent into column which makes this
 procedure complicated and time consuming and creates
 channeling phenomenon. But in the present study,
 nanoadsorbent was dispersed in sample, so that reduce extrac-
 tion time, avoid channeling and enhance contact surface with-
 in analytes and adsorbent. Also in the present work, metal ions
 can be maintained on the sorbent without any chelating agent.
 Also he used SDS coated alumina for determination of metal
 ions and adsorbent was dispersed into the sample, but extrac-
 tion time was very long [38]. Sample volume and amount of
 adsorbent in both of these works were high, but in present
 work sample volume and amount of adsorbent were low and
 applicable for biological approaches.

Conclusions

In the present study, a graphene-clinoptilolite hybrid (G-CL)
 has been synthesized using clinoptilolite as a support and cat-
 alyst. The synthesis of G-CL was performed by CVD method
 and methane was used as the carbon source. The G-CL hybrid
 was characterized using different techniques and the results
 showed that graphene sheets were placed around the porous
 structure of zeolite. This nanomaterial was used as an adsor-
 bent to separate and pre-concentrate trace Pb(II) and Cd(II)
 from biological samples prior to their determination by
 ETAAS. An extraction unit was designed to apply to the syn-
 thesized nanoadsorbent under the ultrasound-assisted disper-
 sive micro-solid phase extraction method. This unit is simple
 and adopted to treat a low sample volume which is of interest

t3.1 **Table 3** Comparison of synthesized G-CL with Clinoptilolite in water and human serum samples (sample volume 2 mL, pH 5, adsorbent 5 mg of G-CL, ultrasonication 60 s, elution volume 100 μ L, $n=3$)

t3.2	Sorbent	Recovery in water sample		Recovery in serum sample	
		Pb	Cd	Pb	Cd
t3.4	Clinoptilolite	63 \pm 1.5	58 \pm 2.2	9 \pm 2.7	6 \pm 2.9
t3.5	Graphene/CL hybrid	99 \pm 1.8	98 \pm 2.1	98.5 \pm 2.1	97 \pm 2.8

Mean of three determinations \pm standard deviation

501 in bio-analysis and it may integrate the extraction and final
502 elution of the analytes. Also, the unit provides the possibility
503 to wash the adsorbent with low volume of eluent, which in
504 turn increases the pre-concentration factor. The designed ex-
505 traction device with G-CL applied to the analysis of serum
506 samples, with satisfactory results. Recovery values ranged
507 from 92 to 96 % in serum, which illustrates the applicability
508 of the presented nanomaterial and device in bio-analysis. Fi-
509 nally, G-CL hybrid was compared to CL for extraction of the
510 metal ions and the results showed that the synthesized
511 nanoadsorbent has better ability for extraction from complex
512 matrixes. Production of the nanoadsorbent was based on nat-
513 ural catalyst and simple CVD method that is economically
514 cost effective.

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