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A green sorbent of esterified egg-shell membrane for highly selective uptake of arsenate and speciation of inorganic arsenic

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ABSTRACT

Egg-shell membrane (ESM) is a promising adsorbent for heavy metal uptake. However, carboxylic groups on ESM surface barrier arsenic adsorption. Herein, ESM is modified by esterification and the methyl esterified egg-shell membrane (MESM) possesses positive charge within pH 1–9. As a novel green sorbent material, MESM exhibits 200-fold improvement on sorption capacity of arsenate with respect to bare ESM. It presents an ultra-high selectivity of 256:1 toward arsenate against arsenite. At pH 6, 100% sorption efficiency is achieved for 2 μg L^{-1} As(V) by 10 mg MESM, while virtually no adsorption of As(III) is observed. This provides great potential for selective sorption of arsenate in the presence of arsenite. By loading 4.0 mL sample within 0.05–5.00 μg L^{-1} As(V) followed by elution with 300 μL HCl (1.5 mol L^{-1}), a detection limit of 15 ng L^{-1} is obtained along with a RSD of 3.5% at 0.5 μg L^{-1}. Total inorganic arsenic is achieved by converting As(III) to As(V) and following the same sorption process. This procedure is applied for arsenate determination and inorganic arsenic speciation in Hijiki and water samples. The results are confirmed by graphite furnace atomic absorption spectrometry and spiking recovery.

1. Introduction

Arsenic is among the most toxic element for human beings even at very low exposure levels. Arsenic accumulation in food chains, i.e., water, vegetables, milk and rice, remains inevitable because of the introduction of arsenic pollutant into the environment through various pathways [1], including geochemical reactions, industrial waste discharges, use of arsenic pesticides and ceramic industries. Arsenic pollution has been recognized as one of the most serious environmental problems [2,3]. In order to control the emission of arsenic, many environmental regulations have been launched. In 1993, the World Health Organization had recommended maximum contaminant level (MCL) of arsenic in drinking water as 10 μg L^{-1} [4]. In 2003, European Commission recommended a reduction of arsenic MCL in drinking water from 50 μg L^{-1} to 10 μg L^{-1} [5,6]. In Directive 2000/60/EC, the European Community has defined more restrictive limits of 1.6 and 1.4 μg L^{-1} for arsenic in superficial waters to be achieved within 2008 and 2015, respectively [7,8]. From this point of view, effective and reliable techniques for the analysis of ultra-trace arsenic are highly appreciated. On the other hand, the determination of solely total amount of arsenic is no longer sufficient for providing comprehensive information about their toxicity or ease of removal among the various arsenic oxidation states, as both properties depend strongly on the chemical forms of a specific arsenic species. Thus, the accurate identification of arsenic species has become one of the most important issues when evaluating the toxic effects of arsenic [9–11].

Generally, there are many analytical techniques available for the detection of arsenic. These include hydride generation atomic absorption spectrometry (HG-AAS) [9], inductively coupled plasma mass spectrometry (ICP-MS) [12], hydride generation atomic fluorescence spectrometry (HG-AFS) [13–15] and inductively coupled plasma optical emission spectroscopy (ICP-OES) [16]. Among these approaches, ICP-MS and HG-AFS are most widely employed as they both possess undoubtedly high sensitivity and wide linear dynamic range [12,17]. On the other hand, HG-AFS is achieving increasing interests in the quantification of arsenic because of its considerably low running cost with respect to ICP-MS. In addition, the operation of HG-AFS is much simple which makes it favorable for routine analysis, especially when performing single element analysis.

In the analysis of environmental and biological samples, suitable separation and preconcentration procedures are generally necessary prior to the detection process when considering very low analyte concentration and complex sample matrix components. Nowadays, many new materials have been exploited as novel sorbent media for solid phase extraction (SPE) of target analytes. Some of the most widely used materials include nanoparticles [18,19], carbon nanotubes

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and their derivatives [20], carbon nanofibers [21], surfactant modified silica [22,23] and various kinds of bio-sorbent materials [24–27]. It is worth mentioning that recently pertinent attentions have been devoted to the application of biomaterials as sorbent media for performing sample pretreatment. Biological cells and natural biomass have been reported for the separation and preconcentration of arsenic, selenium and chromium [25–27]. As a cheap and green biomass, egg-shell membrane (ESM) is readily available. ESM is mainly composed of interwoven and coalescing fibers, containing abundant functional groups, e.g., carboxyl, hydroxyl, amino, amide, phosphoryl and thiol [28], which facilitates binding of various metal species at certain experimental conditions. The batch removal of anionic selenium and arsenic from aqueous media has been evaluated by using egg-shell membrane as adsorbing material [29], and it indicated that carboxylic groups on the surface of ESM is a barrier for the adsorption of arsenic. In addition, similar results are shown by using ESM as sorbent for the direct extraction of trace arsenic from water samples [30], where a very limited adsorption capacity of less than 4 $\mu g\ g^{-1}$ is recorded. The use of this material is largely limited when treating arsenic containing samples with high concentration or large concentration discrepancy. From the view point of practical applications, the sorption capacity of ESM toward arsenic species requires significant improvement.

In the present work, we report the esterification of carboxylic groups on egg-shell membrane with methanol. The obtained methyl esterified egg-shell membrane (MESM) exhibits a 200-fold improvement on the sorption capacity toward arsenate with respect to that achieved by bare ESM. Furthermore, the MESM provides ultra-high selectively for the uptake of As(V) against As(III). On this basis, a speciation procedure for arsenate and arsenite is developed with detection by hydride generation atomic fluorescence spectrometry.

2. Experimental

2.1. Instrumentation

An AFS-9130 atomic fluorescence spectrometer (Titan Instruments Co., Beijing, China) is employed for arsenic determination. The AFS instrument is equipped with two 2.5-mL syringe pumps for fluidic delivering. An arsenic hollow cathode lamp (197.2 nm, Beijing General Research Institute for Nonferrous Metals, China) is used as radiation source. The operating parameters of the AFS instrument, including atomizer height, negative high voltage of the photomultiplier, lamp current, carrier and shield argon flow are investigated in terms of detection sensitivity and reproducibility. The optimized AFS parameters are summarized in Table S1.

For evaluating whether reduction of arsenate is involved during the adsorption of arsenate by the MESM, a L-2130 pump and a L-2300 column oven (Hitachi High-Technologies Corporation, Japan) with C30 Phase Develosil RPAQUEOUS-AR-5 columns ($Ø6 \times 250\ mm^2$ and $Ø6 \times 150\ mm^2$) (Nomura Chemical Co., Ltd., Japan) are employed for chromatographic separation of the arsenic species after recovered from the MESM surface. A HITACHI Z-2000 atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) integrating a graphite furnace atomizer and a quartz flame atomizer is used for the detection of arsenic, the parameters for GFAAS determination are summarized in Table S2.

pH measurement is performed with an Orion Model 868 pH meter (Thermo Electron, USA). VORTEX Genius2 vortex generator (Ika-Werk Instruments, Germany) is used for facilitating the adsorption of arsenate by ESM/MESM.

Surface charge analysis is investigated by measuring zeta potential with a Nano Zetasizer (Malvern, England). SSX-550 scanning electron microscopy (SEM) with an EDS spectrometer (Shimadzu, Japan) is used for surface imaging and elemental analysis. FT-IR spectra are recorded on a Nicolet-6700 FT-IR spectrophotometer (Thermo Instruments Inc, USA) from 500 cm^{-1} to 4000 cm^{-1}.

2.2. Reagents and solutions

All the reagents used are at least of analytical reagent grade, and de-ionized (DI) water of 18 $M\Omega\ cm^{-1}$ is used throughout.

Working standard solutions of As(III) and As(V) are prepared by stepwise dilution of stock solutions of 1000 $mg\ L^{-1}$. A 1.0% (m/v) $NaBH_4$ solution is prepared by dissolving appropriate amount of $NaBH_4$ (Sinopharm Chemical Reagent Co., Shanghai, China) in 0.5% (m/v) NaOH. This solution is prepared daily.

Other chemicals used include hydrochloric acid, methanol, nitric acid, ammonium nitrate and hydrogen peroxide (Sinopharm Chemical Reagent Co., Shanghai, China),

2.3. Methyl esterification of egg-shell membrane and arsenate sorption

The fresh egg-shell is first pretreated with 15% (v/v) HCl for overnight to dissolve the outer layer of the shell and leave the egg-shell membrane (ESM). Afterwards, the ESM is cleaned thoroughly using de-ionized water and dried overnight at room temperature [25]. 100 mg of the pretreated ESM is taken and immersed into 50 mL methanol containing 2% (v/v) HCl for 10 h at 80 °C, during which process the carboxylic groups on the ESM structure is esterified [29]. The product of the methyl esterification, i.e., MESM, is rinsed thoroughly by using de-ionized water and dried overnight at 50 °C in an oven. The MESM is then ground and sieved to 20–40 mesh for future use.

The adsorption of arsenate is performed in a 5-mL centrifugal tube, in which 10 mg of the esterified ESM is immersed in 4.0 mL of arsenate solution of different concentrations. The centrifugal tube is shaken in a vortex generator for 10 min to facilitate the adsorption process. After removal of the supernatant, 4 mL de-ionized water is introduced to rinse the MESM surface. The retained arsenate by the MESM is then eluted by 300 μL hydrochloric acid of 1.5 $mol\ L^{-1}$ and the eluate is collected for the ensuing hydride generation process. 100 μL of the eluate is aspirated by syringe pump SP1 of the AFS 9130 system, while 600 μL of $NaBH_4$ solution is aspirated by syringe pump SP2. The two fluidic zones are dispensed simultaneously by SP1 and SP2 at same flow rate of 250 $\mu L\ s^{-1}$ to mix downstream and facilitate the hydride generation process. After phase separation, the isolated hydride is transported into the AFS instrument for quantification. For GFAAS confirmation and HPLC separation-quartz flame AAS speciation of arsenic experiments, 300 μL of 0.5 $mol\ L^{-1}$ NH_4NO_3 is used as eluent.

2.4. Sample pretreatment

Hijiki sample is treated by following a similar procedure as detailed in a previous study [9]. A short description of the procedure: 0.2 g of the homogenized sample is transferred into a 15-mL centrifugal tube with 10 mL de-ionized water. The mixture is then sonicated for 30 min. After centrifugation, 7 mL of the supernatant is filtered through a 0.22 μm mixed cellulose ester membrane, and then diluted to 50 mL for further processing and analysis.

Fresh snow is collected from the campus of Northeastern University and stored in an air-tight flask at 4 °C after melting. Before starting the adsorption and preconcentration process, it is filtered through a 0.22 μm mixed cellulose ester membrane and diluted one-fold with de-ionized water. For total arsenic quantification, 2 mL snow water is oxidized with hydrogen peroxide (0.5 mL, 30%) under 8 W UV light irradiation for 30 min [31] and then diluted to 4 mL for undergoing the determination process.

The processing and analysis of other water samples, e.g., spring water and river water, follows a same procedure as described herein for snow water.

3. Results and discussion

3.1. Characterization of the methyl esterification egg-shell membrane

Surface charge analysis results for ESM and MESM are showed in Fig. 1. It is seen that the bare EMS is positively charged within a range of pH 1–6, and it turns to negatively charged at pH 6–9. On the other hand, the methyl esterified product, i.e., MESM, is positively charged within the whole pH range studied, i.e., pH 1–9. This observation is obviously attributed to the esterification of carboxylic groups. The positively charged surface of MESM offers a potential for the adsorption of anionic arsenic species.

FT-IR spectra of the bare egg-shell membrane and its esterified derivative are illustrated in Fig. 2. It illustrated that after the esterification process, two new absorption bands are recorded at 1731 cm^{-1} and 1187 cm^{-1} respectively. These are clear indications for the presence of ester, i.e. –C=O and –C–O–C [32], and further demonstrated that the esterification of egg-shell membrane is successful. On the other hand, the major absorption bands for the bare ESM are still clearly observed after esterification, e.g., the absorption at 3315 cm^{-1} assigned to the stretching vibration of hydroxyl groups, and the absorptions at 1660 cm^{-1} and 1542 cm^{-1} attributed to the –C=O stretching and –NH deformation mode of the amide group [32]. These observations indicated that the structure of the egg-shell membrane is maintained during the esterification process.

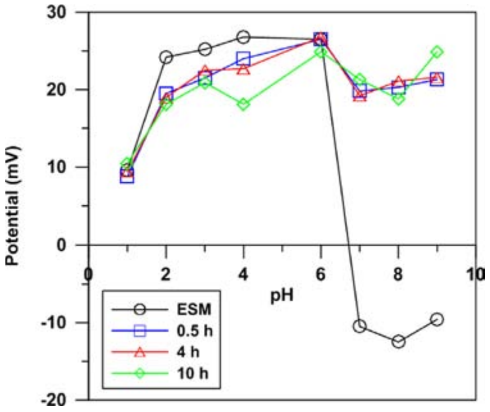

Fig. 1. Surface potential analysis of the bare egg-shell membrane (ESM) and the methyl esterified product (MESM) at different esterification times.

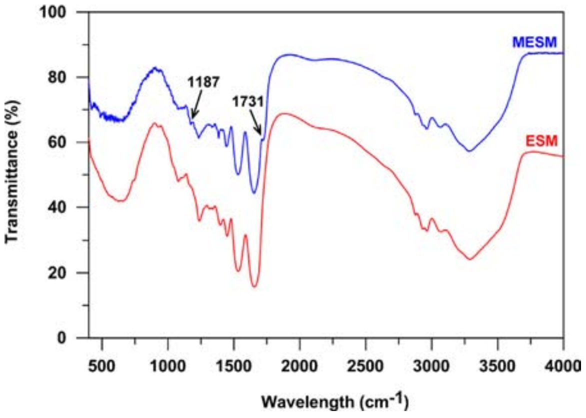

Fig. 2. FT-IR spectra of the bare egg-shell membrane (ESM) and the methyl esterified product (MESM) at an esterification time of 10 h.

Scanning electron microscopic (SEM) images revealed that after the esterification process, similar interwoven and coalescing nature as that of the bare egg-shell membrane is observed (Fig. 3) [29], which is obviously in accordance with that demonstrated by FT-IR spectra. The energy dispersive spectroscopic (EDS) studies showed that weight percentages of C, N and S in the bare ESM are 41.5%, 32.0% and 10.3% respectively. After methyl esterification, the weight percentages of these elements are derived to be 52.3%, 20.1% and 8.4%. The increase of carbon content and the decrease of nitrogen/sulfur percentage further demonstrated the esterification of carboxylic group on the bare egg-shell membrane.

3.2. The improvement of arsenate adsorption by esterification

It is known that egg-shell membrane is composed of approximately 95% of protein, which contains amines and carboxylic groups, as well as fiber with a small amount of polysaccharide [25,33]. The surface property of the egg-shell membrane dominates its sorption behaviors toward various species. In the bare ESM, the negatively charged carboxylic groups should obviously play an inhibitory role for the adsorption of anionic species [29]. Surface charge property of ESM is changed after esterification of the carboxylic group, which is the main driving force for the improvement of sorption capacity toward arsenate. The adsorption efficiencies of arsenate by the bare ESM and the MESM obtained at different esterification times are carefully investigated as illustrated in Fig. 4. It indicated that the esterification of carboxylic groups results in a significant improvement on the adsorption efficiency of arsenate. For the bare ESM, 25–38% arsenate is adsorbed within the range of pH 3–6, while virtually no adsorption is observed beyond this pH range. This is well in accordance with the result of surface Zeta potential analysis, e.g., positive charge of the ESM surface within this pH range facilitates arsenate adsorption through electrostatic interactions. For the case of MESM, the adsorption efficiency of arsenate is gradually improved with the increase of esterification time. Within pH 3–9 the adsorption efficiency falls into a plateau with an esterification time of more than 2 h. At a longer esterification time of 10 h, the adsorption efficiency is improved to reach ca. 94% within pH 6–9. This indicated that after methyl esterification of the egg-shell membrane, the surface chemistry on ESM is directed to be more favorable to the adsorption of arsenate.

The adsorption capacity of MESM for As(V) is investigated according to the method in a previous work [34]. Shortly, 1 mL of As(V) solution of various concentration within a range of 0.5–30 mg L^{-1} at room temperature and pH 6 is mixed with 10 mg MESM. The mixture is allowed to stand for 10 min to facilitate adsorption and reach equilibrium. The adsorbed amount of As(V) in each portion is derived by quantifying the content of As(V) in the supernatant. The retention capacity of As(V) on the MESM is derived by the following equation [35]:

$$\frac{C_e}{Q_e}=\frac{1}{Q_mK}+\frac{C_e}{Q_m}$$

The dynamic adsorption curve for As(V) is illustrated in Fig. S1 (A) by plotting the retained mass of arsenate on per gram MESM (Q_e) in equilibrium versus the original arsenate concentration (C_0). Fig. S1(B) is obtained by plotting the ratio of As(V) concentration at equilibrium/retained mass of As(V) on per gram MESM (C_e/Q_e) versus C_e. It is seen that the adsorption behavior to arsenate by the MESM well fit *Langmuir* adsorption model, and from which a maximum adsorption capacity of 790 μg g^{-1} is derived, which is ca. 200-fold higher than that achieved by the bare ESM in

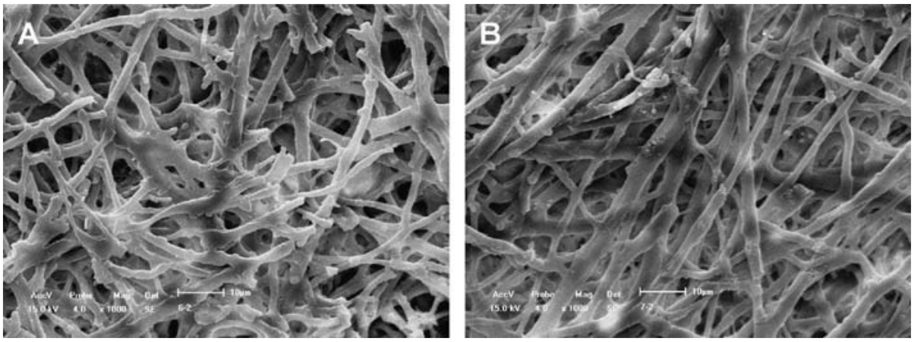

Fig. 3. SEM images of (A) the bare egg-shell membrane (ESM) and (B) the methyl esterified product (MESM).

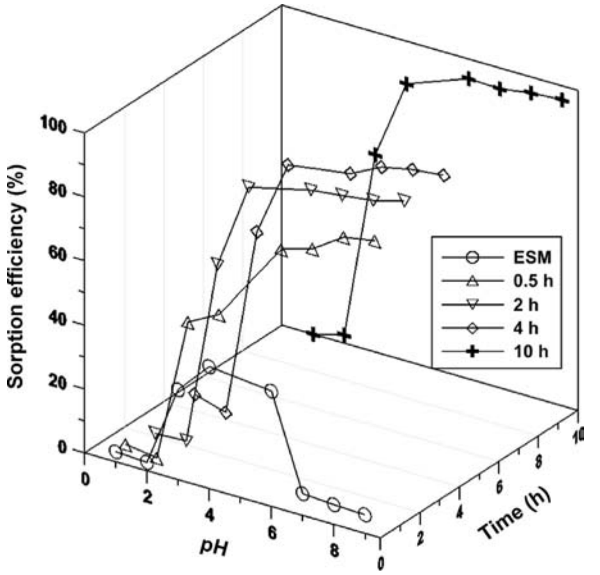

Fig. 4. The dependence of arsenate adsorption efficiency on pH value and esterification time. The amount of MESM: 5 mg; sample volume: 2 mL; As(V) concentration: 20 μg L^{-1}; adsorption time: 10 min.

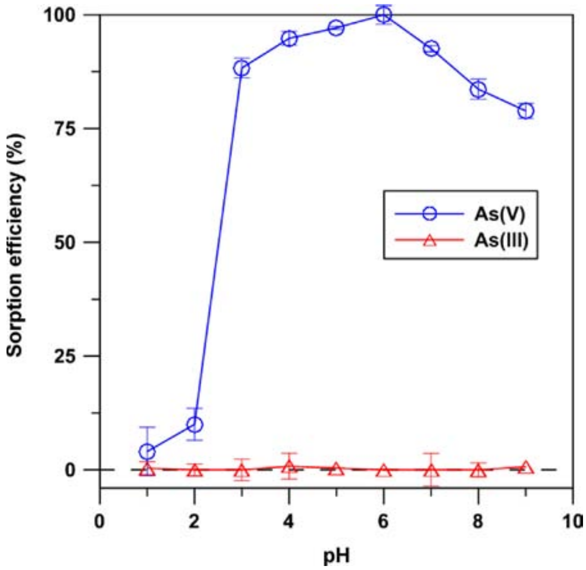

Fig. 5. pH dependence of the adsorption efficiencies for arsenate and arsenite by the MESM surface. Sample volume: 4 mL; MESM: 10 mg; concentration of arsenic: 2 μg L^{-1}; adsorption time: 10 min.

a previously reported work [30]. This indicated that esterification of ESM provides a more favorable medium for the adsorption and preconcentration of arsenate.

3.3. The pH-dependent adsorption behavior of arsenate and arsenite

The charge properties of the MESM surface and the inorganic arsenic species are closely related to pH value of the sample solution, and the electrostatic interactions between them are the driving force for the adsorption of arsenic species. The dissociation constants (pK_a) of H_3AsO_4 are 2.2, 6.9 and 12.2 [29], this means that within a wide range of pH 2–9, arsenate exists in the forms of $H_2AsO_4^{-}$, $HAsO_4^{2-}$ and AsO_4^{3-}. On the other hand, the pK_a values for H_3AsO_3 are 9.2, 12.1 and 13.4 [29], this indicates that at $pH < 9$ arsenite exists mainly in the form of neutral molecules, with a small fraction as anionic species at a higher pH value. We have investigated the effect of pH value on the adsorption of both As(V) and As(III) within pH 1–9 as shown in Fig. 5. The adsorption efficiencies are derived by monitoring the residual concentration of arsenic species in the supernatant after adsorption by the MESM. It is clearly seen that very limited adsorption of arsenate, i.e., ca. 10%, is observed at $pH < 2$. The increase of pH value results in significant improvement on the adsorption of arsenate at pH 2–9, and a maximum adsorption of 100% is recorded at pH 6. For the case of arsenite, the adsorption efficiency is negligible within the whole pH range studied, i.e., pH 1–9. These results are well consistent with the electrostatic interactions between the arsenic species and the MESM surface. Within the range of pH 2–9, the MESM surface is positively charged, while arsenate exists in the form of anionic species. The electrostatic interaction facilitates the adsorption of arsenate by the MESM surface. On the other hand, arsenite exists as neutral molecular form within the same pH range, and its retention on the positively charged MESM surface is not favorable. This observation demonstrates high selectivity toward arsenate, i.e., a selectivity of 256:1 is achieved for arsenate over arsenite. This makes it feasible for the speciation of inorganic arsenic by selective capture and quantification of arsenate followed by a second determination step in which total inorganic arsenic is determined by first oxidizing all inorganic arsenic to arsenate, with detection by hydride generation atomic fluorescence spectrometry.

3.4. The recovery of arsenate and its quantification by HG-AFS

The above investigations have demonstrated that at $pH < 2$ the methyl esterified egg-shell membrane uptake virtually no arsenate. This indicates that an acidic medium might be favorable for stripping the retained arsenate from the MESM surface. Our investigations have showed that favorable recovery efficiency of $> 90\%$ could be achieved with HCl, NH_4NO_3 and HNO_3 as stripping reagents. For LC separation and HG-quartz flame AAS speciation, 0.5 mol L^{-1} NH_4NO_3 is used as eluent. While for GFAAS detection, 0.1 mol L^{-1} HNO_3 is used. When considering the ensuing hydride generation process for atomic fluorescence spectrometric detection, hydrochloric acid should be the most suitable choice as an eluent for arsenate recovery. For this purpose, the recovery of the retained arsenate is evaluated with 300 μL of hydrochloric acid of 0.5–2.5 mol L^{-1} in terms of achieving reasonable elution efficiency and at the same time a favorable precision and limit of detection. For the latter case, a minimum and stable blank signal is preferential. The experimental results indicated that an obvious improvement of the recovery for arsenate is obtained with the increase of hydrochloric acid concentration up to 1.5 mol L^{-1}, and afterwards a decline of the elution efficiency is observed when further increase the HCl concentration to 2.5 mol L^{-1}. For the ensuing experiments, the concentration of HCl is fixed at 1.5 mol L^{-1}. The volume of hydrochloric acid is further evaluated within the range of 150–400 μL, and it indicated that an eluent volume of 300 μL is sufficient for the effective recovery of the retained arsenate from the MESM surface, i.e., a recovery of $>95\%$ is achieved.

It has been previously reported that metal species could be retained by ESM through reductive bio-sorption interaction [25,27], in which process the reduction of cationic metal species is involved. In the present case, it is crucial to understand whether such a reduction process is involved during the adsorption of arsenate on the MESM surface, especially when pursuing arsenic speciation. For this purpose, after recovering arsenate from the MESM surface, the collected stripping reagent or the eluate is directed to undergo HPLC separation followed by hydride generation quartz flame atomic absorption spectrometric detection. The recorded chromatogram is illustrated in Fig. 6. The results clearly show that the chemical form of arsenate is strictly maintained after the adsorption and de-sorption process from the MESM surface. There is no reduction of arsenate involved during the adsorption and elution process. This observation clearly provides solid basis for the speciation of arsenate and arsenite.

The arsenic species in the collected eluate is quantified by atomic fluorescence spectrometry with de-ionized water as carrier for delivering the eluate to meet a $NaBH_4$ solution zone to facilitate the hydride generation process. Our results have demonstrated that 1.5 mol L^{-1} HCl in the eluate is appropriate for the ensuing hydride generation of arsenate in the 300 μL eluate. Further studies indicated that 1.0% (m/v) of $NaBH_4$ in a 0.5% (m/v) NaOH solution is sufficient for the complete reduction of arsenic species in the eluate within the concentration range studied to ensure high efficiency hydride generation. At this juncture, the volume of $NaBH_4$ solution in addition to the flow rates of reducing reagent and HCl are the most critical parameters for the hydride generation process and the ensuing atomic fluorescence spectrometric detection. The results indicated that 600 μL $NaBH_4$ solution ensures a complete reduction of arsenate in the eluate. A same flow rate for the eluate and the $NaBH_4$ solution, i.e., 250 μL s^{-1}, results in maximum fluorescence intensity with better peak shapes. These parameters are thus used for the ensuing experiments.

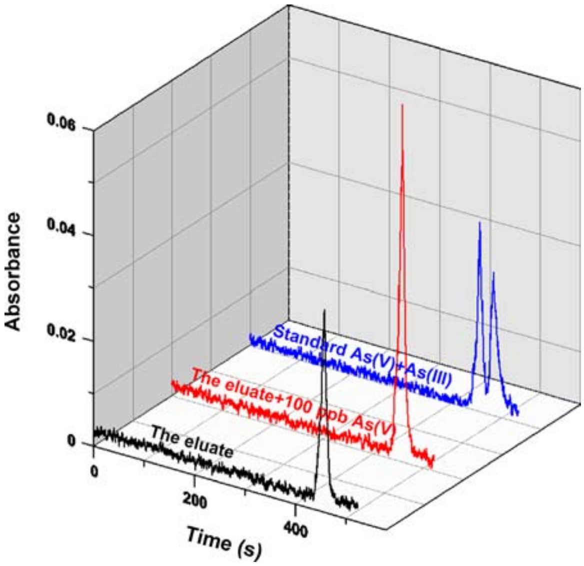

Fig. 6. The recorded chromatograms for the collected eluate/stripping reagent after recovering arsenate from the MESM surface, in comparison with 100 μg L^{-1} standard arsenate and arsenite solutions. The conditions for LC separation and HG-quartz flame AAS detection are illustrated in Table S3. The eluate is obtained by stripping arsenic species from MESM surface with 0.5 M NH_4NO_3 as eluent, 4 mL of sample (30 μg L^{-1} As(V)), 300 μL eluent.

3.5. *Interferences*

For the practical environmental analysis, especially for surface water samples, chloride is generally among the most serious interfering species. In this respect, the potential interference of chloride is carefully studied. The result indicated that when pre-treating 0.5 μg L^{-1} arsenate within an error range of $\leq \pm 5\%$, 45,000-fold of chloride causes no interfering effect. In addition, the potential interfering effects of some commonly encountered foreign ionic species in environmental and biological sample matrixes are investigated in the presence of 0.5 μg L^{-1} arsenate. By controlling within a same error range, the following concentrations of the various coexisting species are tolerated, i.e., 30,000-fold of Na^+, 7000-fold of Mg^{2+}, 5000-fold of NO_3^-, 400-fold of Cu^{2+} and Al^{3+}, 100-fold of Fe^{3+}, Se(IV), Pb^{2+}, 80-fold of Cd^{2+}, 60-fold of Ag^+, 40-fold of Co^{2+} and Cr^{3+}, 30-fold Zn^{2+}.

3.6. *Analytical performance of the procedure and its validation*

At the above mentioned experimental conditions, the characteristic performance data are presented in Table 1 for the sorption of arsenate by using esterified egg-shell membrane as the sorption medium and with detection by hydride generation atomic fluorescence spectrometry. With a sampling volume of 4.0 mL and 300 μL HCl (1.5 mol L^{-1}) as stripping reagent, a detection limit of 15 ng L^{-1} is obtained. A linear range within 0.05–5.00 μg L^{-1} is achieved, along with a RSD of 3.5% at the level of 0.5 μg L^{-1} ($n=7$). A comparison of the characteristic performance data of the present system with some of the reported procedures based on solid phase extraction or adsorption/preconcentration with detection by various spectrometric procedures, e.g., ICPOES, HG-AFS, GF-AAS and HG-ICPMS, are summarized in Table 2. It is seen that the sensitivity of the present method is comparable with those of the procedures with detection by HG-AFS and ICP-MS. In addition, the sensitivity of this procedure is much improved with respect to those achieved by GF-AAS and ICP-OES based approaches. It is also worth mentioning that high selectivity for arsenate adsorption is facilitated by using the methyl esterified egg-shell membrane.

Table 1
The performance data for separation and preconcentration of As (V) with MESM as adsorbent and detection by hydride generation-atomic fluorescence spectrometry.

Items	Values
Sample volume	4000 μL
Eluent volume	300 μL
Detection limit (3σ, $n=9$)	15 ng L^{-1}
RSD (0.5 μg L^{-1}, $n=7$)	3.5%
Linear range	0.05–5.0 μg L^{-1}

Table 2
A comparison of the detection limit and precision of the present procedure by using MESM as adsorbent for arsenate preconcentration with some of the reported approaches based on separation and preconcentration protocols with detection by atomic spectrometry and ICP-MS.

Sorbent/sample	Sample volume (mL)	LOD (ng L^{-1})	RSD (%)	Ref.
Cell-sorption/GFAAS/river water	0.45	50/As(V)	1.7% at 1.25 μg L^{-1}	[26]
Knotted reactor/ICPMS/river water and pore water	5	29/Total As 21/As(III)	2.8% for As(III) at 1 μg L^{-1}	[12]
Mesoporous TiO_2 sorption/ICPOES/surface water	40	110/As(III) 100/As(V)	$<6.7\%$ at 20 μg L^{-1}	[16]
Octadecyl modified silica for As(III), anion exchange resin for As(V)/HGAFS/water	1	30/As(V) 20/As(III)	2.8% for As(III), 2.9% for As(V) at 1 μg L^{-1}	[13]
Esterified ESM sorption/HG-AFS/Hijiki and water	4	15/As(V)	3.5% at 0.5 μg L^{-1}	This method

Table 3
Analytical results of arsenic in Hijiki and water samples as well as inorganic arsenic speciation ($n=3$, 95% confidence level).

Sample	Found As(V) (μg L^{-1})	Found As(III) (μg L^{-1})	GFAAS As(V) (μg L^{-1})	Spiked As(V) (μg L^{-1})	Recovery (%)
Hijiki	38.9 ± 4.1[a]		40.5 ± 4.4[a]		
River water	0.85 ± 0.08	0.11 ± 0.08	1.05 ± 0.37	1.0	101
Snow water	0.83 ± 0.03	0.13 ± 0.13		0.7	102
Spring water	1.13 ± 0.09	0.11 ± 0.13		1.0	95

[a] μg g^{-1}.

The present procedure is applied for the determination and speciation of inorganic arsenic in Hijiki and various surface water samples. The amount of As(V) is obtained by following the present procedure as described in the previous sections. For the quantification of total inorganic arsenic, pre-oxidation of As(III) is required to achieve a complete conversion to As(V). In the present study, this is achieved by oxidation of 2 mL sample solution with 0.5 mL of hydrogen peroxide (30%, v/v) under 8 W UV light irradiation for 30 min [31]. Afterwards, the same procedure is followed as detailed for the quantification of As(V) by adopting the herein developed adsorption procedure for arsenate with MESM. The analytical results obtained for total arsenic in Hijiki and river water samples are further confirmed by determination with graphite furnace atomic absorption spectrometry (GFAAS). The analytical results in Table 3 illustrate a fair agreement between the results achieved by the present procedure and those by GFAAS, which demonstrate the reliability of the present procedure. In addition, acceptable spiking recoveries for As(V) have been observed for all the water samples.

4. Conclusions

A novel green adsorbent, methyl esterified egg-shell membrane (MESM), is reported with a 200-fold improvement on the adsorption capacity toward arsenate with respect to the bare egg-shell membrane. In addition, the MESM exhibits ultra-high selectivity to arsenate over arsenite which provides a practical approach for the speciation of inorganic arsenic species. The observations in the present study demonstrate a new approach for the development of bio- or green-adsorbent through modification of the surface of biomaterials focusing on certain functional groups.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.07.061.

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