An AlgaSORB Column for the Quantitative Sorption of Arsenic(III) from Water Samples

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This study examines a new Scytonema-based biosorbent (AlgaSORB-sc) using column chromatography for the biosorption of total inorganic arsenic [As(III) and As(V)] from aquatic samples. The AlgaSORB-sc was prepared by immobilizing a cyanobacterial biofilm (Scytonema-dimethyl-formamide slurry) over a polymer-modified silica gel and then characterized for stability and sorption/elution conditions under dynamic equilibrations followed by differential pulse polarographic detection. The sorbent exhibited a 100% affinity for As(III) in a multi-elemental solution [in the absence of As(V)] at pH 6.9 and a flow rate of 1 mL min⁻¹ giving rise to a preconcentration factor as high as 44-fold. The interference caused by As(V) in the sorption of As(III) on AlgaSORB-sc necessitated the pre-reduction of As(V) into As(III) by sodium sulfite. The biosorbent was found to be suitable for total arsenic enrichment in the form of As(III) species and demonstrated a better endurance with a recyclability of up to 59 cycles of sorption-elution. The polymeric spacer between the cyanobacterial biofilm and the silica gel enabled the biofilm monolayer to be held firmly onto a solid support and be accessible for quantitative arsenic uptake without encountering any problems of interfacial overlapping, re-adsorption, or matrix effects in the drinking water supplied.

Key words: Scytonema, AlgaSORB, polymer-modified silica gel, biosorption, polymeric spacer, cyanobacterial biofilm

Introduction

Arsenic is a ubiquitous trace element and its toxicity is strongly dependent on various chemical forms prevalent in certain ecosystems. Inorganic compounds of arsenic are much more toxic than their organic metabolites (Harrison et al. 1989). Trivalent inorganic forms [As(III), arsenite], such as arsenic trichloride, arsenic trioxide, and arsine, are highly toxic and sixty times more poisonous than the metal, its pentavalent salts or organoarsenic species (Cullen et al. 1989; Mabuchi et al. 1980; Morita 1991).

The largest outbreaks of arsenic poisoning in groundwater have been reported in the vast area of West Bengal, India; Tripura, India; and Bangladesh. The immediate source material for contamination was most likely ferric arsenate (with and without ferric arsenite) derived from an alteration product of the mineral arsenopyrite that had been geologically transported to the Bengal delta (Roy 1999). Groundwater contamination is predominantly affected by inorganic arsenic species [As(III) and As(V)] where chemical transformations lead to the formation of highly water-soluble poisonous arsenious acid (H₃AsO₃) from buried arsenate. Organoarsenic species are water-insoluble contaminants and thus unlikely to assume respective pathways to groundwater. The major problem of arsenic treatment and removal today is the removal of trace levels, i.e., from 50 µg L⁻¹ (the old permissible concentration limit), down to 10 µg L⁻¹ (the new legislated limit).

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Although a plethora of analytical methods are available for arsenic estimation, the best reported limit of detection with several sensors was 2 µg L⁻¹ (ppb). However, precision of results is equivocal owing to massive interferences and sensor fouling from coexisting species in natural waters (Hung et al. 2004). Therefore, to determine the total extent of inorganic arsenic species in water and to facilitate their effective preconcentration, the current study attempted to develop a robust, recyclable, selective and cost-effective sorbent involving the bioaccumulating characteristics of natural algae. To address the problem that algae, in a natural state or immobilized, can gradually clump together and/or incapacitate down to the frit of the column under the dynamic pressure of the medium resulting in an irregular flow, the present paper describes the utility of an algae biomass when immobilized as a biofilm with the help of a polymeric anchor on a silica gel. The use of a polymer electrolyte as a spacer between algae cells and silica has already proven to be advantageous (Prasad et al. 2000; Singh et al. 2000) in several respects against column clogging, rapid deterioration and metal percolation in the inner core of a macroporous silica gel. From the economic point of view, the proposed algae-silica preparation (AlgaSORB-sc) is deliberately made from the natural dead cells of the blue-green cyanobacterial alga, Scytonema, which provides a biofilm (in dimethylformamide) of excellent durability after immobilization over the polymer-modified silica gel. The system is not only suited for trace level removal and evaluation of trivalent arsenic selectively from real-world samples but could also be helpful in quantitative removal at pilot scale provided a large column is used.
for the purpose. This would necessitate the column optimi-
ization at pilot scale following optimization protocol as
described in the present investigation with a small solid-
phase extraction column.

Experimental

Chemicals

All reagents were of analytical grade. Triple-distilled
demineralized water was used for all experimental work
including the preparation of the test metal solutions.

Samples

Stock solutions of arsenic(III) and arsenic(V) were pre-
pared following standard methods of preparation (Scott
2000). For As(III) (1000 µg mL⁻¹), 0.1320 g of
arsenic(III) oxide (Fluka) was dissolved in 2 mL of 1 M
NaOH. After the addition of 25 mL of water, the solu-
tion was acidified with 4 mL of 1 M HCl, and then
diluted to 100 mL with water. For As(V) (1000 µg mL⁻¹),
0.4163 g of sodium arsenate (Fluka) was dissolved in
0.5 mL of concentrated H₂SO₄ and diluted to 100 mL
with water. The desired pH of the metal ion solution
was adjusted with the help of dilute HCl and NaOH.
Since As(V) is an electroinactive species, the reduction of
As(V) to As(III) is necessary prior to its determination
d through differential pulse polarography. The most suc-
cessful reduction procedure recommended is the use of
Na₂SO₃ as the reductant (Forsberg et al. 1975). Accord-
ingly, an equimolar solution mixture of As(V) and
Na₂SO₃ in 1 M HCl (1 L) was heated for 20 to 30 min
at 80 to 100°C. This procedure was also followed for a
solution containing both As(III) and As(V) in order to
estimate the total inorganic arsenic in the sample.
Diverse metal ions (Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺, Co²⁺, Fe²⁺,
Fe³⁺) in multi-elemental synthetic samples were intro-
duced from stock solutions of their respective nitrate,
chloride and sulphate salts.

The silica gel (Merck TLC grade, mesh 60–20), after
acid treatment and washing with water, was dried at
~120°C for 12 h, cooled, and then stored in a dessicator.
The polymer, [poly(N-xylylene-N,N'-dicyclohexyl-
ethylenediamine dibromide)] (abbreviated as C₂EXBr₂)
was prepared and characterized according to the estab-
lished recipe (Mukherjee et al. 1983).

The cyanobacterium Scytonema is a natural blue-
green alga, which contains significant amounts of lipids
(triglycerides/diglycerides) and non-reducing sugar tre-
halose which protect cells, membranes, proteins and
nucleic acids in dry conditions. This has highly pig-
mented sheaths of Scytonem located in the extracellular
polysaccharide layer with the structure based on indolic
and phenolic subunits (Singh et al. 2002). Scytonem
was collected from shady, moist and damp roadside soil
on the university campus. It was a dark bluish-green,
woolly and was growing in circular patches. It was iso-
lated from the crude material using forceps, washed
repeatedly with water, and finally treated with
0.1 M HCl. The isolated Scytonem was centrifuged, the
acid removed by washing with water, and then heat-
killed at ~80°C for 1 h in a water bath. It was finally air-
dried to obtain a dry powder. Dead algae are reportedly
more sorptive than live algae and are advantageous in
the determination of biosorption parameters (Volesky
et al. 1995; Abu Al-Rub et al. 2004). It is also reported
that certain genera of cyanobacteria produce potent
cyclic peptide hepatotoxins during the bloom period
(Carmichael 1992). Dead cells of the blue-green algea
produce toxic amines and phenolic compounds in
the water, during initial stages of decomposition, espe-
cially when temperatures are high (Sirenko et al. 1980).
There is apparently a negligible probability for an extra-
cellular release of any toxin in water when immobilized
in dead condition.

Immobilization Procedure

The preparation and characterization of the polymer-
modified silica gel (silica-C₂EXBr₂) used as the support
for the cyanobacterial immobilization, has been reported
elsewhere (Singh et al. 2000). For this, in a normal
batch, the silica gel (12 g) was simply treated with the
dimethylformamide (DMF) solution of C₂EXBr₂ poly-
electrolyte (0.12 g per 30 mL, DMF). The silica-C₂EXBr₂
(2.0 g), obtained after solvent evaporation, was vigor-
ously shaken with a DMF slurry of the Scytonem powder
(12.0 mg). The residual solvent was removed by
maintaining the mixture at ~40°C for 2 d. The exchangeable
counterions (Br⁻) of the polyelectrolyte, C₂EXBr₂, were exchanged with negatively charged
cyanobacterium cells (Christ et al. 1981). This was evi-
dent from a halogen test in the immediate water wash-
ings of the biosorbent (AlgaSORB-sc) so produced. The
cyanobacterial coating as a biofilm in the AlgaSORB-sc
was apparently a uniform monolayer with a restricted
amount (6.0 mg g⁻¹ silica-C₂EXBr₂); the subsequent
immobilization of biofilm was found to be non-adherent
owing to the electrostatic repulsion between two layers
of cyanobacterium anions.

The immobilization of the polymer onto the silica
gel provided an arm space whereby the total cyanobacte-
rial biomass could firmly hang for sorption over its outer
surface. This confirms the model (Fig. 1A) as proposed
and characterized through IR spectroscopy in an earlier
article (Singh et al. 2000). Pure cyanobacterial strains
and biosorbent AlgaSORB-sc in the form of KBr pellets
were studied through infrared spectroscopy. Typical
N-H stretching at 3483 cm⁻¹ (secondary amine group)
and 3135 cm⁻¹ (amine salts) as well as N-H bending
appearing at ~1573 cm⁻¹ for the polymer C₂EXBr₂ are
found absent in the silica-C2EXBr2 and AlgaSORB-scyc. The modification of silica surface imparts restrictions on N-H vibrations as a consequence of hydrogen bonding of the type >NH—O. However, the immobilization of polymer matrix onto silica gel is evident from the C-N and C-Br vibrations at 1385 and 670 cm⁻¹, respectively. The presence of a cyanobacterial functional amine acid group at ~3500 cm⁻¹ and a restricted carboxylate anion group with two key bonds, i.e., (i) 1650 to 1550 cm⁻¹ and (ii) 1400 cm⁻¹ and sulfhydryl group at 1060 cm⁻¹, is indicative of molecular electrostatic model (Fig. 1A) involving ion-exchange reaction between cyanobacterial anions and counter ions (Br⁻) of the polyelectrolyte. The microorganism distinctive peak for phosphate and sulfide groups [>P=O (~1100 cm⁻¹), -P-O-C (~760 cm⁻¹, ~1033 cm⁻¹) and -SO₂-O (~700 cm⁻¹, ~1200 cm⁻¹, ~1420 cm⁻¹)] were observed to be completely vanished after being doped onto the polymer-modified silica substrate. This indicates the presence of polycation-cyanobacterial anion interactions in a fashion similar to the Grahame’s modification of Stern-Gouy Chapman’s electrical double layer theory (Singh et al. 2000). Accordingly, the immobilization of the parent polycations onto silica gel proceeds through proton-transfer from silanol group to the medium (DMF) leading to the existence of an ion-pair interface through hydrogen bonding (>NH⁺—O –; Fig. 1A). The subsequent coating of the biofilm (cyanobacterial anions) occurred in the exterior at an arm space of the polymer-modified silica network following anion-exchange processes in the electrical double layer (Okada 1998). The polymeric thin layer did not have any sorption activity. It merely acts as a spacer which is held firmly on the solid support. The total Scytonema counterions are three-dimensionally exposed for arsenic sorption from all sides without any steric clogging of the matrix.

Analytical Method

The dynamic method was employed exclusively to study the metal sorption behaviour (optimum pH, flow rate, breakthrough volume, desorption conditions). The extent of the sorption of the metal ion was determined based on the complete stripping of the metal ion by 0.2 M HNO₃ + 15% H₂O₂ after a 20-min equilibration time.

The detection of the metal ion was performed at ~25°C using a PAR model 264A voltammetric analyzer in the conventional manner of the standard addition method in the differential pulse polarographic (DPP) mode (pulse height, 50 mV; scan rate, 10 mV s⁻¹; purge time, 4 min; sodium oxalate buffer, pH 4, 0.1 M).

A glass column (11.0 cm long and 1.4 cm in internal diameter) fitted with a G-1 sintered coarse glass frit as a bottom support was loosely packed (1.2 cm height) with 1.0 g of AlgaSORB-scyc. In the loading step, a 15.0-mL test solution with an appropriate pH containing a fixed amount of metal ion was passed through the biosorbent at a known rate via a peristaltic pump. During the loading step, the column effluent was directed as waste. Next, in the washing step, water was pumped through the column to rinse out the unreacted arsenic and interferents, if any, in the alkaline effluent from the column bed. Finally, in the elution step, the sorbed metal ion was directly stripped off the column using 9.0 mL of a 0.2 M HNO₃ + 15% H₂O₂ solution after a 20-min equilibration time, and then subjected to DPP measurements. The effect of pH on the sorption was studied at a flow rate of 0.5 mL.
The effect of the flow rate on the sorption was studied over the range of 0.5 to 1.5 mL min\(^{-1}\).

**Results and Discussion**

**Sorption Study and Column Characteristics**

The cationic polyelectrolyte, used as a spacer between the cyanobacteria and the silica gel, has interesting prospects related to its ability to hold the anionic functional groups of cyanobacteria through ion-exchange (Singh et al. 2000) and to provide a three-dimensional access for metal sorption. It is interesting to note that the routine methods of biosorption using alginate apparently involve interfacial overlapping resulting in one-dimensional sorption/desorption. Further, the severe metal percolation in the inner core of such adsorbate might give unreliable results in trace analysis. The polymeric layer in the present instance acts as an armor to macroporous silica gel resin, thereby avoiding any steric clogging, interfacial overlapping and metal percolation in the interior core of the silica gel. The firm adherence of the chemically complexed biofilm coating, is due to electrostatic interactions in the electrical double layer of the model (Fig. 1A) as well as \(\pi\)-electron overlappings between the aromatic xylene of the polymer and the Scytonema pigment of the biomass (Prasad et al. 2000; Singh et al. 2000). This was not found to be affected by common ions (Cl\(^{-}\), NO\(_3\), OH\(^{-}\), CH\(_3\)COO\(^{-}\), SO\(_4^{2-}\), PO\(_4^{3-}\)) had shown drastic interferences with arsenic biosorption as cyanobacterial cells of biofilm were found to be stripped off under reserve exchange process by the large concentration (>0.25 M) of ions.

The influence of flow rate on the sorption degree for As(III) and As(V) ions (60 µg per 15 mL) at the optimum pH of 6.9 revealed that the column attained a 100% sorption at flow rates of 0.5 to 1.0 mL min\(^{-1}\), whereas the metal retention started declining [As(III), 68.7% and As(V), 85.1%] at a higher flow rate of 1.5 mL min\(^{-1}\). Therefore, a flow rate of up to 1.0 mL min\(^{-1}\) was selected for the preconcentration of the arsenic metal. Unfortunately, neither As(III) nor As(V) could be separated in the mixture as they exhibited competitive sorption at pH 6.9 and a flow rate of 1.0 mL min\(^{-1}\). In a mixture of As(III) and As(V) (0.5 ppm each, 100 mL), the sorption of As(III) decreased by 30% owing to the co-sorption of As(V) [As(V) is an electro-inactive species]. After Na\(_2\)SO\(_3\) treatment of the mixture, an estimate of the total inorganic arsenic was obtained.

The maximum capacity for 100% As(III) ion sorption at pH 6.9 and a flow rate of 1.0 mL min\(^{-1}\) with AlgaSORB-scyc using the dynamic method was found to be 80 µg (1.07 µmol) per g of biosorbent (Fig. 3). The sorbent is quite effective towards trace levels of arsenic(III) in natural waters.

![Retention of metal ion on AlgaSORB-scyc column as a function of solution pH.](image)
The selection of a suitable eluent for the stripping of As(III) or As(V) from the biosorbent was based on a separate experiment. Only hydrochloric acid and nitric acid eluents (0.25 M) were found to be obdurate in the present case. In addition, higher concentrations of these acids had to be avoided to protect the column bed from any deterioration. The most suitable desorbing agent giving 100% recovery was found to be 15% H2O2 in 0.2 M nitric acid, owing to the formation of neutral H3AsO3 and H3AsO4 molecules (Palkholkov et al. 1980) (the hydrogen peroxide acts as an oxidizing agent which conveniently regenerates the biosorbent and retrieves arsenic species after oxidative cleavage [hydrolysis] of alga-arsenic complex [Fig. 1B] in dilute solution of the acid). The normalized elution curve for As(III) obtained with this reagent is shown in Fig. 4 which demonstrates that the quantitative recovery of As(III) was feasible when using 9.0 mL of the eluent for a 20-min equilibration time. The initial 0.5-mL volume of the eluent was determined as the dead volume.

The breakthrough volume, i.e., the volume that influenced the magnitude of sorption, is depicted in Table 1. The As(III) ion realized a breakthrough with the 0.4 L of sample (initial concentration, 1.8 µg L⁻¹) in the column. The reduction in the percentage sorption beyond this volume was due to the lack of metal retention by the excessive dilution of the solution. The preconcentration factor for a metal ion denotes the ratio of the maximum metal concentration recovered and the minimum metal concentration passed in the column. This is equivalent to the ratio of the maximum sample volume (breakthrough volume) passed and the minimum volume of the eluate collected from the column. In the present instance, the As(III) ion preconcentration factor was determined to be 44-fold with a minimum limit of detection (LOD = 3 × standard deviation of blank) of 1.8 µg L⁻¹ at ≥99% sorption. Although the actual preconcentration is dependent on the actual sample volume passed and collection volume, the recovery remained the same under the optimized conditions of the column operation. Insofar as trace arsenic removal and its subsequent evaluation employing the present AlgaSORB-scy column are concerned, for the maximum volume (0.4 L) of the sample recommended for the quantitative sorption, the LOD (1.8 µg L⁻¹) of the proposed method is less than the WHO arsenic guideline value of 10 µg L⁻¹.

The lifetime and recyclability of the column is evident from the plot (Fig. 5), which shows that the column maintained a 100% retention behaviour for 59 cycles. Beyond this there were ~5 to 20% losses in the sorption capacity in the ensuing cycles up to the hundredth run.

<table>
<thead>
<tr>
<th>Sample volume (L)</th>
<th>Sorption (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.050</td>
<td>100.0</td>
</tr>
<tr>
<td>0.100</td>
<td>99.9</td>
</tr>
<tr>
<td>0.150</td>
<td>99.7</td>
</tr>
<tr>
<td>0.200</td>
<td>99.8</td>
</tr>
<tr>
<td>0.250</td>
<td>100.0</td>
</tr>
<tr>
<td>0.300</td>
<td>99.6</td>
</tr>
<tr>
<td>0.350</td>
<td>99.7</td>
</tr>
<tr>
<td>0.400</td>
<td>99.2</td>
</tr>
<tr>
<td>0.450</td>
<td>90.0</td>
</tr>
<tr>
<td>0.500</td>
<td>84.0</td>
</tr>
</tbody>
</table>

aOptimum pH, 6.9; flow rate, 1.0 mL min⁻¹; sorbent bed, 1.0 g; loaded amount, 0.75 µg (0.01 µmol) of As(III) ion (concentration of samples ≤15 µg L⁻¹).
The reproducibility of the column was checked in terms of column to column, cyanobacterial batches and immobilization lots. Four columns (A₁α, A₁β, A₂γ, A₃δ) made from AlgaSORB-scycl were compared for their respective maximum sorption capacities after saturating each column with 15.0 mL of 0.080 µmol mL⁻¹ (5.92 mg L⁻¹) As(III) (the subscript indicates the cyanobacterial batch and the superscript represents the immobilization lot) (Table 2). The column performance was found to be reproducible with a relative standard deviation (RSD, n = 3) of as high as 3.5% (less than reported error limits ±8%) (Mahan and Holcombe 1992). The immobilization procedure was reproducible with different immobilization lots and various algae batches demonstrated consistent As(III) ion sorption capacities. This was due to the better homogeneity and identical mode of packing, which resulted in reproducible flow characteristics for all the columns studied.

Cost effectiveness is the main attraction of metal biosorption. Biosorbents derived from microbial biomass in simple processes should be the most low-priced for economical metal removal process applications (Vieira et al. 2000). On the basis of various factors such as natural abundance of Scytonema, the low cost of polymer and silica solid support, the number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the sites (i.e., availability), affinity between site and metal, and recyclability for further use, the new biosorbent (AlgaSORB-scycl) in the present study is well poised for analytical exploitation.

### Applications

Two synthetic water samples (30 mL) consisting of inorganic arsenic [As(III) and As(V)] ions (sample 1, 15.0 µg; sample 2, 20.0 µg; total metal content) were passed through the AlgaSORB-scycl column at pH 6.9 and a flow rate of 1.0 mL min⁻¹ after reducing the As(V) present in

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**TABLE 2.** Precision of experimentally determined arsenic capacity for AlgaSORB-scycl

<table>
<thead>
<tr>
<th>Name</th>
<th>µmol g⁻¹ of AlgaSORB</th>
<th>µmol g⁻¹ of AlgaSORB</th>
<th>µmol g⁻¹ of AlgaSORB</th>
<th>µmol g⁻¹ of AlgaSORB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column to column variability</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₁α</td>
<td>1.06</td>
<td>A₁β</td>
<td>1.12</td>
<td>A₂γ</td>
</tr>
<tr>
<td></td>
<td>1.04</td>
<td></td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.10</td>
<td></td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>Av.</td>
<td>1.06</td>
<td></td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>S.D.</td>
<td>0.03</td>
<td></td>
<td>0.04</td>
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</tr>
<tr>
<td>RSD%</td>
<td>2.8</td>
<td></td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Precision between immobilized lots</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₁α</td>
<td>1.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₁β</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Av.</td>
<td>1.11</td>
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<td></td>
</tr>
<tr>
<td>S.D.</td>
<td>0.07</td>
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</tr>
<tr>
<td>RSD%</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precision between harvested algae batches</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₁</td>
<td>1.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A₂</td>
<td>1.15</td>
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<td></td>
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<tr>
<td>A₃</td>
<td>1.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Av.</td>
<td>1.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S.D.</td>
<td>0.05</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>RSD%</td>
<td>4.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Av., average; S.D., standard deviation; RSD, relative standard deviation.*

Fig. 5. Percent As(III) capacity (normalized) of single column as a function of number of adsorption-elution cycles.
the mixture to As(III) using sodium sulfite. The retained metal ion was finally eluted and the corresponding DPP results are shown in Table 3.

To study the effect of diverse heavy metal ions on the As uptake, two synthetic water samples (30 mL) consisting of Cu2+, Pb2+, Zn2+, Cd2+, Fe2+, Fe3+, Co2+ and As3+ (sample 3, 15.0 µg; sample 4, 7.5 µg; each metal) were passed through the AlgaSORB-scym column at pH 6.9 and a flow rate of 1.0 mL min⁻¹. The retained As(III) ion was finally eluted with a 100% recovery without showing any interference of diverse ions (co-sorption not greater than 10%) and the corresponding DPP results are shown in Table 3.

Studies conducted using synthetic waters do not prove much insofar as the absence of usual complications viz. the matrix effect, readsorption and inter-metallic interferences found in real natural samples are concerned. To confirm the accuracy of the present method and investigate the application to polluted waters, the arsenic contents of two drinking water samples (from West Bengal region) were analyzed by solid phase extraction-DPP (SPE-DPP) hyphenated technique and also by graphite-furnace and hydride generation atomic absorption spectrometric methods (GF-AAS and HG-AAS). The results in Table 4 were found to be unaffected by matrix complications and show good correlations among these techniques.

### Conclusions

In view of the natural abundance of Scytonema, the prepared AlgaSORB-scym is a cost-effective column packing material and is highly selective for arsenic(III) at trace levels in real samples. Although various combinations of techniques, i.e., ICP-MS, GF-AAS and HG-AAS, have been described for accurate and reproducible analysis of inorganic arsenic in the laboratory environment, the reported SPE-DPP technique has proven to be able to give reliable results in an economic manner. AlgaSORB-scym has potential for a further development into a mobile, low-cost analytical device capable of fulfilling the requirement of a rapid and accurate sensor for on-site analy-

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**TABLE 3.** Analysis of total arsenic in synthetic water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optimum pH</th>
<th>Flow rate (mL min⁻¹)</th>
<th>Added (µg)</th>
<th>Found (µg)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>6.9</td>
<td>1.0</td>
<td>15.00</td>
<td>15.21 ± 0.91</td>
</tr>
<tr>
<td>2</td>
<td>6.9</td>
<td>1.0</td>
<td>20.00</td>
<td>20.12 ± 1.05</td>
</tr>
<tr>
<td>3</td>
<td>6.9</td>
<td>1.0</td>
<td>15.00</td>
<td>15.28 ± 0.11</td>
</tr>
<tr>
<td>4</td>
<td>6.9</td>
<td>1.0</td>
<td>7.50</td>
<td>7.57 ± 0.09</td>
</tr>
</tbody>
</table>

Ast samples 1 and 2 contain a mixture of arsenic(III) and arsenic(V), which were subjected to preconcentration in the AlgaSORB-scym column after Na₂SO₃ treatment. Initial concentration: sample 1, 0.25 µg mL⁻¹; sample 2, 0.33 µg mL⁻¹; each metal, 30 mL volume. Samples 3 and 4 contain As(III) with other diverse ions, viz., Pb²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Fe²⁺, Fe³⁺, Co²⁺ and As³⁺ (sample 3, 15.0 µg; sample 4, 7.5 µg; each metal) were directly subjected to preconcentration in the AlgaSORB-scym column. Initial concentration: sample 3, 0.5 µg mL⁻¹; sample 4, 0.25 µg mL⁻¹; each metal, 30 mL volume.

bStandard deviation for three determinations.

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**TABLE 4.** Determination of As(III) in drinking water samples (source: West Bengal, India) by DPP after preconcentration in AlgaSORB-scym column and standard methods (all concentrations in µg mL⁻¹)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added</th>
<th>Optimum pH</th>
<th>Flow rate (mL min⁻¹)</th>
<th>Found (µg)</th>
<th>Standardb GF-AA/HS-AAS methods</th>
<th>uc</th>
<th>td</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 1</td>
<td>0.4</td>
<td>6.9</td>
<td>1.0</td>
<td>0.398 ± 0.008</td>
<td>0.402 (0.315) t cal = 0.7, 1.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 2—sample 1 spiked by 3 µg of As(III)</td>
<td>0.5</td>
<td>6.9</td>
<td>1.0</td>
<td>0.496 ± 0.004</td>
<td>0.498 (0.500) 0.997, 0.982</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 3—sample 2 spiked by 3 µg of As(III)</td>
<td>0.6</td>
<td>6.9</td>
<td>1.0</td>
<td>0.623 ± 0.033</td>
<td>0.596 (0.620) t tab = 4.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

acStandard deviation for three determinations.

bValues obtained from the standard GF-AAS method (Leung et al. 1982), values in parentheses were based on anion-exchange chromatography coupled to HG-AAS method (Muñoz et al. 2000).

cCorrelation coefficient.

dStudent’s t-test for comparison of two methods at confidence level 95%, n = 3.
AlgaSORB Column for Sorption of Arsenic(III)

sis. The present work also merits special significance as AlgaSORB-scy can be utilized for the large-scale removal of arsenic(III) from water effluents.

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