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Portable and rapid arsenic speciation in synthetic and natural waters by an As(V)-selective chemisorbent, validated against anodic stripping voltammetry

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ABSTRACT

Inorganic arsenic speciation, i.e. the differentiation between arsenite and arsenate, is an important step for any program aiming to address the global issue of arsenic contaminated groundwater, whether for monitoring purposes or the development of new water treatment regimes. Reliable speciation by easy-to-use, portable and cost-effective analytical techniques is still challenging for both synthetic and natural waters. Here we demonstrate the first application of an As(V)-selective chemisorbent material for simple and portable speciation of arsenic using handheld syringes, enabling high sample throughput with minimal set-up costs. We first show that ImpAs efficiently removes As(V) from a variety of synthetic groundwaters with a single treatment, whilst As(III) is not retained. We then exemplify the potential of ImpAs for simple and fast speciation by determining rate constants for the photooxidation of As(III) in the presence of a TiO_2 photocatalyst. Finally, we successfully speciate natural waters spiked with a mix of As(III) and As(V) in both Indian and UK groundwaters with less than 5 mg L^{-1} dissolved iron. Experimental results using ImpAs agreed with anodic stripping voltammetry (ASV), a benchmark portable technique, with analysis conditions optimised here for the groundwaters of South Asia. This new analytical tool is simple, portable and fast, and should find applications within the overall multi-disciplinary remediation effort that is taking place to tackle this worldwide arsenic problem.

1. Introduction

Up to 200 million people worldwide are at risk from arsenic contaminated groundwater (Naujokas et al., 2013). These waters are distributed globally with a variety of sources such as reducing aquifers in the sediment basins of South Asia, oxidising aquifers in arid regions of Mexico and Chile, mining activity in Burkina Faso, the USA and the UK, and geothermal waters (USA, New Zealand) (Smedley, 2008). Arsenic contaminated waters thus display a wide range of properties, differing in pH, redox conditions, presence of organic matter/bacteria, and the concentration of inorganic anions (bicarbonate, phosphate, sulphate) and cations such as Fe(II) and Mn(II) which precipitate once exposed to air. It is, therefore, not surprising that environmental arsenic presents itself as a range of species, differing in redox state, protonation state, and incorporation of organic groups (Cullen and Reimer, 1989).

Knowledge of arsenic speciation in groundwater systems is important for many reasons. Firstly, at pH 5–8, typical for most groundwaters, arsenic is present as inorganic H_3AsO_3 ("arsenite" or As(III)) and $H_2AsO_4^-/HAsO_4^{2-}$ ("arsenate" or As(V)). Since As(III) is up to 60 times more toxic than As(V) in humans, knowing the speciation is important when assessing public health risk (Shahid et al., 2018) (Markley and Herbert, 2009). Secondly, since H_3AsO_3 is neutral, its removal is not efficiently achieved through typical water treatment processes such as coagulation-flocculation or adsorption. Instead, addition of a pre-oxidation step is needed (Hering et al., 2017). Thirdly, knowledge of the speciation can help

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understand the cycling of arsenic within the environment (Shankar et al., 2014).

Speciation of inorganic arsenic in groundwater is thus needed but rarely achieved. For example, large scale surveys of groundwater contamination, including the 5 million tube wells tested in Bangladesh in 2000–2003 (Johnston and Sarker, 2007), have been limited to determination of total As. While arsenic speciation is now routinely achieved using hyphenated techniques such as high-performance liquid chromatography mass spectrometry (HPLC-ICP-MS), these remain expensive, time consuming, and limited to specialist laboratories. On-site speciation is preferable for field samples, in order to avoid problems of sample storage, primarily the progressive oxidation of As(III) on an hours-to-days timescale (Gibbon-Walsh et al., 2011), however field speciation continues to be a specialist pursuit and surveys of arsenic groundwater contamination around the world remain mostly limited to determination of total arsenic (McGrory et al., 2017) (Rabbani et al., 2017) (Liang et al., 2018).

Reliable, low-cost and easy-to-use analytical techniques are also needed for the speciation of arsenic in synthetic media. Research groups in industry and academia continue to investigate the chemistry of arsenic including (i) chemical oxidation (e.g. Fenton's reagent) (Wang et al., 2013), (ii) photooxidation (Chai et al., 2017), (iii) competitive adsorption between As(III) and As(V) (Qi and Pichler, 2017), and (iv) oxidation over naturally occurring mineral surfaces (Ding et al., 2015), all requiring reliable speciation techniques. Whilst previous studies often employ costly techniques requiring specialist knowledge and time to set-up, such as hydride generation atomic fluorescence spectrometry (HG-AFS) and HPLC-ICP-MS, many laboratories lack access to this specialised analytical instrumentation.

Portable and low-cost arsenic speciation has been achieved by various techniques, including colorimetric and electrochemical methods. The preferred molybdenum blue method for colorimetric determination of arsenic, wherein a blue colour-complex is formed between molybdate and As(V), suffers from a well-known phosphate interference. This is a major problem, particularly since contaminated groundwaters in the Bengal Basin contain ten times more phosphate than arsenic (McArthur et al., 2004) (Hug et al., 2008). Colorimetric speciation therefore necessitates a number of chemical pre-treatments to remove phosphate and interconvert As(III) and As(V), complicating field analysis (Okazaki et al., 2013). Speciation of arsenic by electrochemical means does not suffer from phosphate interference and is best achieved using gold electrodes (Huang and Dasgupta, 1999), but historically the perceived lack of "reliability, selectivity and sensitivity" has prevented wider use (Brainina et al., 2000). More recently, several systems have been developed and successfully deployed in environments including reducing groundwaters (Gibbon-Walsh et al., 2011), however commercial uptake has been limited (Borrill and Reily, 2019).

An alternative method is to separate arsenite and arsenate immediately at the time of sampling for later detection under laboratory conditions (Chen et al., 2019) (O'Reilly et al., 2010) (Watts et al., 2010). This can be achieved by passing the solution through a sorbent that is selective to As(V) but leaves As(III) unaffected, for which chloride and acetate anion exchange resins have been used (solid phase extraction, SPE) (Mihucz et al., 2017) (Bednar et al., 2004). By measuring total As before and after treatment the inorganic speciation can be determined. There are two potential drawbacks to ion-exchange resins. Firstly, these resins are selective to a wide range of anions beside As(V). In groundwaters such as the Bengal Basin, phosphate, sulphate and carbonate are 1, 2, and 4 orders of magnitude more prevalent than arsenic (McArthur et al., 2004) (Ayers et al., 2016) and much adsorption capacity may be lost to competing anions (particularly sulphate) (Pakzadeh and Batista, 2011), with resins reaching saturation more quickly than intended (Voice et al., 2011). Second is the leaching of exchanged ions into the effluent, particularly chloride, where the polyatomic $^{40}Ar^{35}Cl^{+}$ ion has historically been an interference with the ^{75}As peak during ICP-MS analysis (Benramdane et al., 1999), although modern instruments with collision cells now counter this problem (An et al., 2015). Finally, SPE often requires additional elution steps to remove sorbed As(III) (Zhao et al., 2019) (Montoro Leal et al., 2018) (Chen et al., 2016).

To date, no study has considered the application of arsenic-selective chemisorbent materials towards the analytical speciation of arsenic. We recently reported an As(V)-selective receptor immobilised onto polymeric beads yielding a chemisorbent material (ImpAs) with a very high affinity for arsenate (patent number US, 2017/0113949 A1) (Moffat et al., 2014). The active component of ImpAs is a metal-organic complex containing two Zn(II) centres to which As(V) oxyanions coordinate. ImpAs shows the greatest affinity towards As(V) at pH 6–8 and is thus suitable for most global groundwaters (Moffat et al., 2014). Chemisorbent resins offer an interesting new route towards arsenic speciation, as their high selectivity reduces interference from other anions, which may enable easy application in challenging waters.

This work aims to assess the performance of ImpAs for the analytical speciation of arsenic in synthetic and natural waters. We first tested the ability of ImpAs to separate As(V) from As(III) for laboratory applications using simple buffer solutions and complex synthetic groundwaters. We considered both Challenge Water (NSF Standard 53), a standard used to certify arsenic remediation products in the USA, and a second synthetic groundwater, representative of arsenic-contaminated groundwaters in West Bengal, India. We then applied ImpAs for the determination of As(III) photooxidation rates (catalysed by TiO_2). Finally, we tested the ability of ImpAs to separate As(V) from As(III) in natural waters, using samples from oxic waters in Cornwall, UK, and from anoxic waters in West Bengal, India - regions both known for arsenic contamination. All experiments were conducted in conjunction with anodic stripping voltammetry (ASV), used as the benchmark technique for portable arsenic speciation, to validate the results of speciation by ImpAs (Fig. 1).

2. Experimental

2.1. Materials and reagents

All chemicals used were reagent or analytical grade (SI Table S1). Stock solutions (1000 mg L^{-1}, 13.3 mM) of As(V) and As(III) were prepared from $Na_2HAsO_4 \cdot 7H_2O$ and As_2O_3 respectively. Stock solutions were calibrated against a standard solution of arsenic (Fluka, 1000 ± 4 mg L^{-1}, traceCERT) and kept refrigerated. As(III) solutions were contained within opaque containers to prevent photooxidation. Stock solutions of 24 mM aqueous hydrazine were prepared from hydrazine hydrate or hydrazinium sulphate salt. Stock solutions of 0.5 M ethylenediaminetetraacetic acid (EDTA) were prepared from EDTA tetrasodium salt, acidified to pH 8. A stock solution of 60 mM Fe(II) (pH 2.1) was prepared from $FeSO_4 \cdot 7H_2O$. A stock solution of 10 mM Mn(II) was prepared from $MnCl_2.4H_2O$. A solution of 10 mM 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was prepared from HEPES free acid and adjusted to pH 7.44 with small volumes of 1 M NaOH.

Synthetic groundwaters CW (pH 7.42), SGW-1 (pH 7.09) and SGW-2 (pH 8.32) were prepared to the concentrations given in Table 1, following the procedure given in the Supplementary Information. ImpAs was prepared as previously reported (Moffat et al., 2014), however improvements in the synthesis increased the As(V) capacity to at least 16.0 ± 1.3 mg g^{-1} (SI Fig. S1).

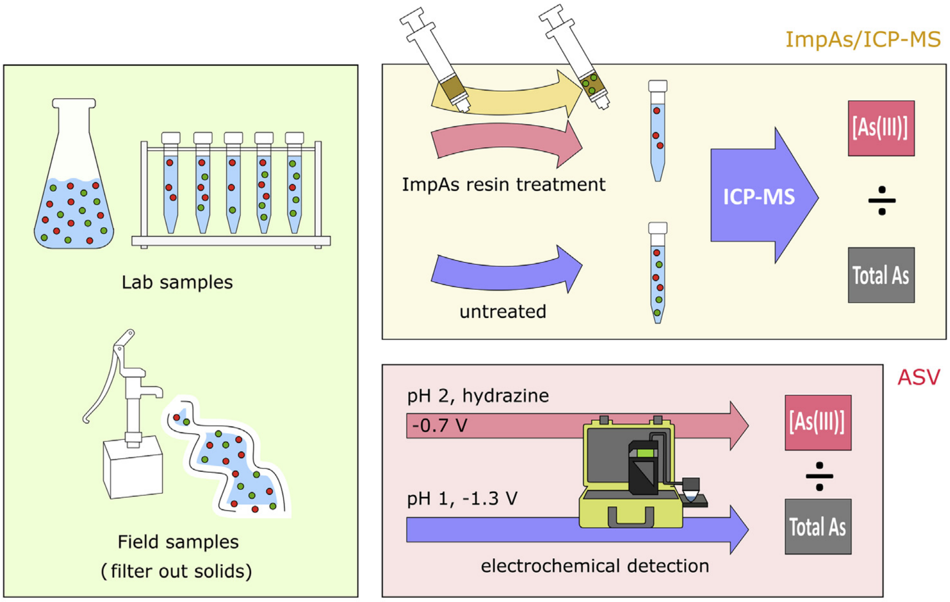

Fig. 1. Concept schematic for arsenic speciation as performed by the two methods used in this study. As(III) is represented in red, and As(V) in green. Blue arrows denote determination of total As, whilst red arrows denote determination of As(III). Speciation is reported as the percentage of total As which is As(III).

Table 1
Composition of waters used in this study. Synthetic groundwater compositions were determined from the mass of the reagents used. The composition of natural waters was determined by ICP-MS using a multi-element standard. Blank cells indicate where a species was not added to solution or detected. '<LoD' refers to species that were under the detection limit.

Ion	Concentration (mg L^{-1})									
	Synthetic media			Natural media						
	SGW-1 (ImpAs experiments)[a]	SGW-2 (ASV experiments)[a]	CW	bottled mineral water	Cornish groundwater	Cornish surface water	well 3 (West Bengal deep well)	well 4 (West Bengal shallow well)	STN13 (West Bengal shallow well)	STN5 (West Bengal deep well)
HCO_3^-	590	650	180	–	–	–	–	–	–	–
Ca^{2+}	34	1.5	47	2.5	2.5	2.1	16	14	18	19
Na^+	250	250	88	9.8	9.8	11	990	860	139	68
Mg^{2+}	37	39	13	9.0	3.9	3.1	29	19	17	16
Cl^-	160	160	82	–	–	–	–	–	–	–
NH_4^+	–	27	–	–	–	–	–	–	–	–
H_4SiO_4	63	–	31	–	–	–	–	–	–	–
SO_4^{2-}	14	12	50	–	–	–	–	–	–	–
K^+	2.7	0.57	–	6.7	3.0	2.7	4.1	2.1	9.0	9.1
Fe^{2+}	–	0 or 3.4 added	–	<LoD	<LoD	<LoD	1.8	5.0	4.3	13
Mn^{2+}	0.97	–	–	0.0002	0.021	0.0002	0.13	0.14	0.3	0.3
HPO_4^{2-}	1.1	1.4	0.13	–	–	–	–	–	–	–
NO_3^-	0.62	4.5	8.8	–	–	–	–	–	–	–
Sr	–	–	–	0.057	0.060	0.047	0.49	0.27	0.37	0.35
Ba	–	–	–	<LoD	0.007	0.006	0.12	0.17	0.23	0.20
F^-	–	–	1	–	–	–	–	–	–	–
pH	7.09 ± 0.02	8.32 ± 0.02[b]	7.42 ± 0.02	7.39 ± 0.02	6.52 ± 0.02	7.55 ± 0.02	7.3 ± 0.1	7.2 ± 0.1	8.2 ± 0.1	8.4 ± 0.1
absorbance at 254 nm (cm^{-1})	–	–	–	0.023	0.025	0.105	–	0.046	0.022	0.044

The uncertainty in pH is determined from the sensitivity of the two different pH meters used in the lab and in the field.
a: SGW-1 and SGW-2 were both based on data from McArthur et al. (2004). SGW-1 was used for ImpAs experiments in London, whilst SGW-2 was used for electrochemistry experiments in Liverpool.
b: Since SGW-2 was used for optimisation of ASV conditions, this sample was always acidified to pH 1 or 2 during analysis.

2.2. *ImpAs chemisorbent*

2.2.1. *Batch experiments*

To verify that ImpAs does not remove As(III) from solution, batch experiments under equilibrium conditions were carried out. Three background media were used: 10 mM HEPES, CW, and SGW-1. Solutions of 1 mg L^{-1} total As (13 μM) in ratios of 0:100, 25:75, 50:50, 75:25 and 100:0 As(III) to As(V) were prepared in each media using 100 mg L^{-1} (1.3 mM) As(III) and As(V) stock solutions. To each solution 0, 1 or 20 g L^{-1} ImpAs was added. Solutions were shaken overnight in an incubated shaker at 25 °C and filtered gravimetrically to remove ImpAs. Samples were kept wrapped in aluminium foil to prevent photooxidation of As(III). As(III) and total As were determined by ASV within 24 h, and total As was determined by ICP-MS.

2.2.2. Syringe experiments

As a prototype portable device for high sample throughput, disposable plastic syringes (5 mL volume) were loaded with ImpAs. To investigate the influence of mass loading, 0.2, 0.4 or 1.0 g of ImpAs were used, giving path lengths of 2.5, 5 and 12 mm respectively (Fig. 2). Solutions of 1 mg L^{-1} As(V) (13 μM) in 10 mM HEPES, CW or SGW-1 were prepared (total volume 50 mL). Each treatment consisted of loading 5 mL aliquots of solution into the top of the syringe by pipette, and passing through the syringe until the total 50 mL had been processed. Sequential treatments were performed, with 1 mL collected after each for determination of total As by ICP-MS. The flow rate was controlled by hand, with solutions passed through the syringes dropwise (1 drop per second, *ca.* 1 min per 5 mL aliquot). The effluent solution was collected directly, without discarding the first portion. Experiments were performed with and without prior conditioning of ImpAs. Without conditioning, ImpAs was used dry. When conditioned, the background media was passed through ImpAs several times and care was taken to ensure that air space in the top of the syringe did not re-aerate and thus dry out the resin. Conditioning took 30–60 s. A single syringe was prepared for each mass of ImpAs, and these three syringes reused for all synthetic groundwater experiments. A control experiment was performed in duplicate, with 1 mg L^{-1} As(III) (10 mM HEPES) replacing the 1 mg L^{-1} As(V) influent sample and [As(III) (aq)] determined by ASV to verify that As(III) was neither removed nor oxidised during ImpAs treatment.

2.3. Electrochemical speciation

As(III) and total As were determined by ASV using a portable PDV6000 Ultra potentiostat (Modern Water – UK) powered by 4 × 1.5 V AA batteries and equipped with the associated reference electrode (Ag/AgCl/KCl(3M)) and auxiliary platinum electrode. The working electrode was a 30 μm diameter, 5 mm long gold microwire. Operating parameters are summarised in SI Table S2. Detection was made by Linear Scan ASV (LSASV), scanning from −400 to +700 mV with a 4 or 8 V s^{-1} scan rate and 1.6 mV step. The solution was stirred during the deposition step and then held for 10 s at −400 mV before the stripping scan took place. All measurements were made in the presence of dissolved oxygen.

Fig. 2. Syringes loaded with 0.2, 0.4 and 1.0 g ImpAs used in this work. Column path lengths were 2.5, 5 and 12 mm respectively.

As(III) was determined after addition of 10 mM HCl and 10–20 μM hydrazine to prevent oxidation (Salaün et al., 2007) (Salaün et al., 2012), using a deposition potential of −0.7 V for 15s (SI Fig. S2). Total As was determined in 0.1 M HCl using a deposition potential of −1.3 V for 15s. In these conditions of acidity and pH, immediate oxidation of As(III) to As(V) by the oxidant produced at the auxiliary electrode ensures that all arsenic in the voltammetric cell is present as As(V) (Salaün et al., 2007). The blank electrolyte prior to addition of the sample was used for background subtraction. The As stripping peak was located at ca. +180 mV in 0.01M HCl and ca. +230 mV in 0.1M HCl. Peak height was used for quantification. As(III) and total As were determined by the method of standard additions, with a minimum of 2 additions of As(III) in each case (Gibbon-Walsh et al., 2011).

The working electrode was cleaned in 0.5 M H_2SO_4 by imposing a potential of −2.5 V for 30s followed by a CV scan between −200 and +1500 mV at a scan rate of 1000 mV s^{-1} (Salaün et al., 2012) (SI Fig. S3). Electrodes were cleaned at the start of each day, and sometimes between measurements if electrode sensitivity appeared diminished (i.e. after analysis of very high iron content synthetic waters).

2.4. Determination of photooxidation kinetics

Suspensions of 0.1 g L^{-1} Degussa P25 (TiO_2) and 10 mg L^{-1} As(III) (133 μM) were prepared in 10 mM HEPES (total volume 100 mL) and stirred overnight in the dark to achieve equilibrium adsorption. Beginning at $t = 0$, suspensions were irradiated by UV light ($\lambda = 368$ nm) with a power of 13.7 mW cm^{-2}. Aliquots were taken at regular intervals, with TiO_2 removed using a 0.45 μm nylon syringe filter (VWR 28145-489). Each aliquot was (a) analysed for total As by ICP-MS, (b) diluted from 1 mL to 10 mL with Milli-Q water and passed three times through a conditioned ImpAs syringe, then analysed by ICP-MS for 'As(III)', and (c) speciated by ASV. A single ImpAs syringe was used for all experiments. For each time series the value of k and its uncertainty were calculated as the slope of the linear regression and its standard error. Experiments were performed in duplicate to give a final average, and the final uncertainty determined as the difference between the maximum and average values of k.

2.5. Sampling at field sites and arsenic spike experiment

Groundwater was collected from a natural spring sourced from granite bedrock, and surface water from a stream feeding into the River Kennal, Cornwall, UK. Bottled mineral water from a French volcanic spring was purchased. These waters were filtered using a 0.45 μm nylon membrane. West Bengal groundwaters were sampled - well 3 (deep well, 400 feet), well 4 (shallow well) and STN13 (shallow well, 70 feet) in the village of Sahispur (23°04′16.9″N 88°36′33.4″E), and STN5 in the village of Chakudanga (480 feet, 23°04′57.7″N 88°36′09.0″E), both in the Nadia district of West Bengal, India. The sampling procedure was based on that of Gibbon-Walsh et al. (2011). Tube wells were pumped continuously for 6–15 min before collecting samples in opaque plastic bottles to prevent photooxidation of As(III). Samples were immediately spiked with either HCl (to pH 2) or 10 mM EDTA to prevent iron precipitation. Samples were filtered to remove solid particulates and bacteria. Acidified samples were pH neutralised by addition of NaOH before conducting the arsenic spiking experiment as ImpAs performs poorly under acidic conditions, owing to protonation of the pyridine groups (pKa = 5.2) disrupting the ImpAs metal-organic receptor (Moffat et al., 2014).

Natural samples were subdivided and spiked with arsenic stock solutions to give a wide range of As(III):As(V) ratios. The first half of each subsample was collected without further treatment (for determination of As(III) and total As by ASV, and total As by ICP-MS), whilst the second half was passed through a syringe loaded with 1g ImpAs for determination of "As(III)", with the results labelled as *ImpAs/ICP-MS*. Using ASV, As(III) was determined within 24 h of sampling and total As within 48 h. Samples were diluted at least 5 times with Milli-Q water during measurement by ASV to minimise matrix effects and the most concentrated samples were diluted 60–100 times to ensure analysis was made within the linear range of the method. Three ImpAs syringes were used to treat all natural media, separated into (i) oxic waters, (ii) anoxic samples without EDTA, and (iii) anoxic samples with EDTA. Absorbance at 254 nm was determined using a Jenway-7315 UV–vis spectrophotometer with Milli-Q water used for background subtraction.

2.6. Determination of total As by ICP-MS

Samples were acidified to 2% (v/v) HNO_3 and analysed using the Agilent 7900 quadrupole ICP-MS. Calibration curves of at least 5 points were obtained both with a single element arsenic standard (Fluka, 1000 ± 4 mg L^{-1}, traceCERT), and a multi-element standard (Inorganic Ventures, 10 μg mL^{-1}, NIST-traceable standard). Measurements were also normalised to internal standards (yttrium) and the uncertainty determined as the root-mean-square deviation (RSD) of each measurement. The detection limit for arsenic was 0.41 μg L^{-1} (5.5 nM).

3. Results and discussion

3.1. Demonstrating speciation by ImpAs chemisorbent

3.1.1. Speciation under equilibrium conditions

The first objective of this work was to investigate whether ImpAs can separate As(III) and As(V) from synthetic waters. Batch reactions under equilibrium conditions were used to verify that As(V)-selective ImpAs does not remove As(III) from solution, even after overnight shaking (in 10 mM HEPES) (Fig. 3a). Since separation of As(III) and As(V) fails when the sorbent is saturated, ImpAs was kept in excess. The speciation, expressed as the fraction of As(III) in each sample, was determined by Equation (1) and compared against the expected results (Fig. 3b).

$$Speciation\ (\%\,As(III)) = 100 \times \frac{[Total\ As\ (ImpAs\ treated)]}{[Total\ As\ (untreated)]} \qquad (1)$$

Using 1 g L^{-1} ImpAs, the linear regression gave a slope of 0.952 ± 0.049 (within 5% of the expected one-to-one calibration curve) with $R^2 = 0.992$. Equation (1) gave 2.9 ± 0.3% and 94.3 ± 2.2% As(III) for mixing fractions 0% and 100% As(III) respectively. Similar results were obtained using 20 g L^{-1} ImpAs: a calibration curve with a slope of 0.887 ± 0.022 with 3.5 and 92.6% As(III) at mixing fractions 0 and 100% As(III) respectively. These results indicate quantitative removal of As(V) and separation from As(III) within ±7%.

3.1.2. Implementation as an easy-to-use, portable device

Having verified that ImpAs can speciate arsenic under equilibrium kinetics, ImpAs was loaded into syringes to (i) provide a rapid and high throughput device for laboratory applications, and (ii) to provide portability for on-site applications. Syringes were first tested for As(V) removal in 10 mM HEPES with and without prior conditioning (i.e. resin wetting) (Fig. 3c). We first aimed to identify the appropriate amount of ImpAs for loading into 5 mL plastic syringes – balancing efficient removal with low material consumption. Since As(V) sorption is a function of contact time between sorbent and sample, syringes were prepared with 0.2 g (2.5 mm path length), 0.4 g (5 mm) and 1.0 g (12 mm) ImpAs.

Without prior conditioning As(V) removal was limited and the 1.0 g ImpAs syringe only removed 57.9 ± 2.0% As(V) in a single pass (Fig. 3c). This is likely due to pore channelling between resin beads, offering paths of least resistance through which influent contact with ImpAs is limited. However, when ImpAs was conditioned first, it demonstrated very efficient removal of As(V) (98.0 ± 1.8% with a single pass, using 1g ImpAs). When conditioned, increasing the mass of ImpAs also increased As(V) removal due to increased contact (Fig. 3c). In all cases ImpAs was unsaturated and so incomplete As(V) removal was due to kinetic limitations rather than limited capacity. Cross-contamination due to carry over was only identified for a single data point in Fig. 3c. Control experiments (N = 2) demonstrated that As(III) was neither removed nor oxidised when passed through the syringe (Fig. 3c, grey diamonds).

Having established efficient As(V) removal using ImpAs syringes in HEPES buffer solutions, more complex media were considered. Challenge Water (CW) is a synthetic groundwater used to test the performance of arsenic removal units (The NSF Joint Committee on Drinking Water Treatment Units, 2016), whilst synthetic groundwaters SGW-1 and SGW-2 were formulated using published data on West Bengal groundwater composition (McArthur et al., 2004) (Table 1). CW was high in sulphate, which is known to interfere with anion exchange resins (Pakzadeh and Batista, 2011), whilst SGW-1 was high in phosphate, a known competitor of As(V) for ImpAs binding sites (Moffat et al., 2014). ImpAs was effective in both CW and SGW-1 with 92.9 ± 1.1 (N = 2) and 96.9 ± 0.7% (N = 2) As(V) removed in a single pass (Fig. 3d), demonstrating that ImpAs-loaded syringes can speciate arsenic in the presence of inorganic groundwater species.

3.2. Optimising electrochemical speciation for challenging waters

The objective of this section was to optimise our portable voltammetric system for arsenic speciation in the challenging arsenic-contaminated waters of South Asia that often contain high levels of Fe(II) and Mn(II) (Gupta and Singh, 2018). In West Bengal and Bangladesh, concentrations of 60 μM Fe(II) (approximately 3.3 mg L^{-1}) and 20 μM Mn(II) (1.1 mg L^{-1}) are typical for arsenic contaminated groundwaters (McArthur et al., 2004) (Hug et al., 2008) (Ayers et al., 2016). There are only a few papers dealing with electrochemical speciation of arsenic in the groundwaters of South Asia (Rasul et al., 2002) (Paul et al., 2008) (Gibbon-Walsh et al., 2011), and they all differ in voltammetric methods and/or electrodes. Here, we tested the influence of high levels of Fe and Mn on the determination of As(III) and total As in synthetic groundwaters, under acidic conditions using fast linear scan ASV (4–8 V s^{-1}).

Addition of high levels of Fe(II) generally resulted in a decrease of the As(III) signal (Fig. 4a and 4b), e.g. a loss of *ca.* 40% for addition of 120 μM Fe(II) (6.6 mg L^{-1}). Even at 300 μM Fe(II), the arsenic peak remains well-shaped and standard addition can still be achieved for reliable arsenic determination. A peak at *ca.* +0.6 V whose intensity increased linearly with Fe additions was present on the stripping scan, but its potential was significantly more positive than that of the As peak. In the determination of total As, no significant decrease in As peak intensity was observed during addition of up to 300 μM Fe(II) (16.5 mg L^{-1}) (SI Fig. S6). Similarly, addition of up 100 μM

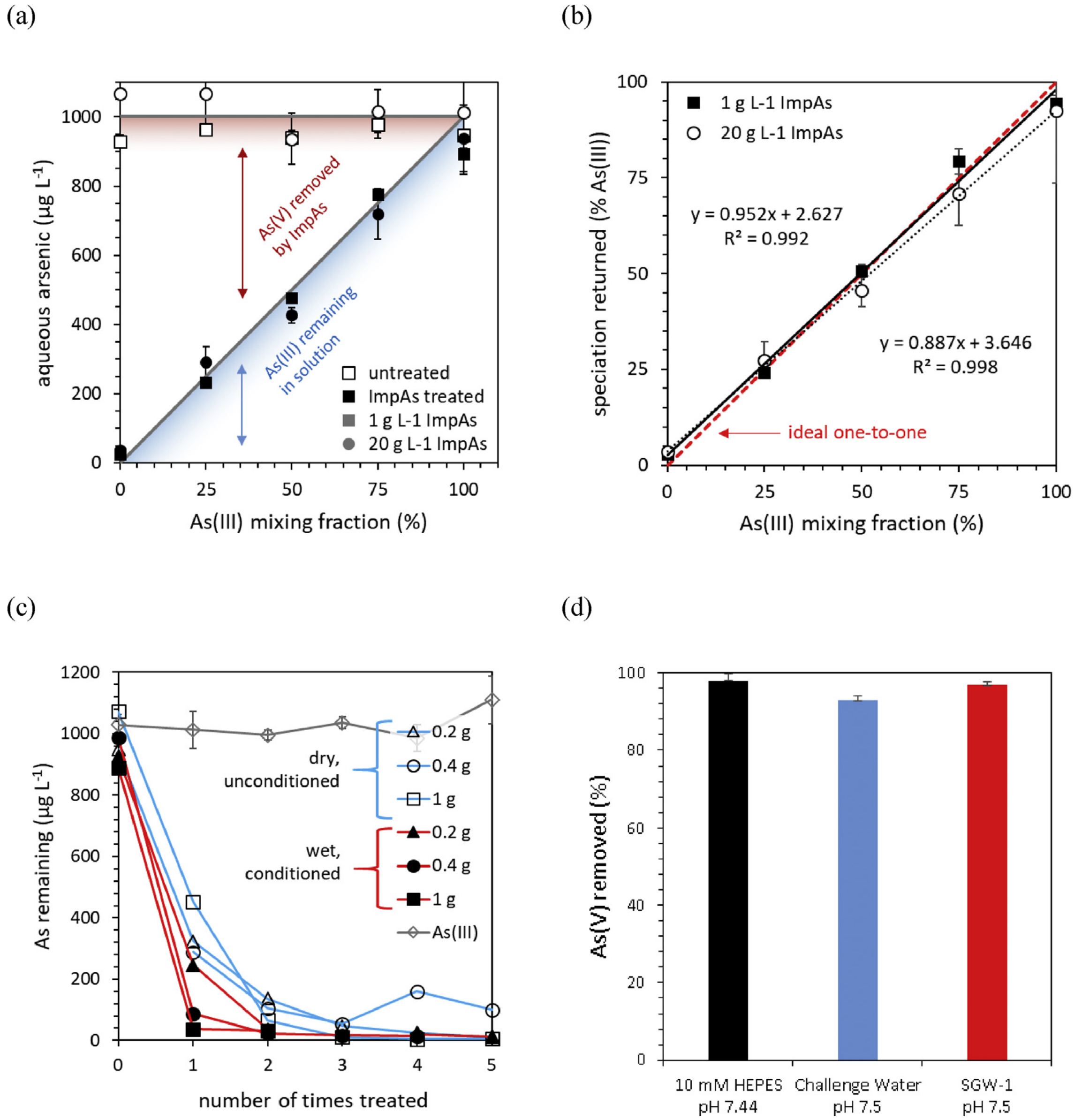

Fig. 3. ImpAs speciation method development. (a) The concentration of total As that remains in solution with and without addition of ImpAs as a function of As(III):As(V) mixing fraction, and (b) the resulting arsenic speciation calibration curves. (c) The removal of As(V) with sequential passes through syringes loaded with different masses of ImpAs. (d) As(V) removal efficiency in different media after a single pass through a syringe loaded with 1 g ImpAs (N = 2).

Mn(II) (5.5 mg L^{-1}) affected neither the As(III) nor the As(V) peak (SI Fig. S7).

Sensitivities and linear ranges were similar in synthetic groundwater (SGW-2) as in 10 mM HCl (Fig. 4c and 4d and SI Figs. S9–10). Detection limits were higher in synthetic groundwater than in blank HCl: for total As the LoD increased from 0.06 to 0.4 μg L^{-1} (0.8–5 nM) and for As(III) the LoD increased from 0.1 to 0.3 μg L^{-1} (1–4 nM) (SI Table S2). Within the linear range, the average uncertainty of measurement via the method of standard additions was ±6% (propagated from the standard error of the slope in the linear regression). In all cases detection limits were <1 μg L^{-1} indicating that arsenic contaminated waters can be speciated. This showed that the inorganic ions commonly encountered in South Asia, including natural levels of Fe(II) and Mn(II), do not significantly impact arsenic analysis by the method of standard additions under this voltammetric procedure.

3.3. Application 1: Determination of photooxidation rate constants in synthetic solutions

Photooxidation of As(III) using TiO_2 as a catalyst was investigated as one example application, aiming to highlight the advantages of ImpAs as a tool for simple and fast speciation. Remediation of As(III) contaminated waters is challenging since this species adsorbs poorly to sorbent media such as goethite (Qi and Pichler, 2017) and is hard to remove with membrane technology (Nicomel et al., 2015). A number of research groups have thus investigated the use of photocatalysts such as TiO_2 to oxidise As(III) to As(V) as a pre-treatment to reduce toxicity and improve adsorption (Fontana et al., 2018).

In this work the oxidation of As(III) to As(V) was successfully monitored using the ImpAs/ICP-MS procedure, with very similar results to those obtained by ASV (Fig. 5a). The reaction was modelled following pseudo-first order kinetics, with the rate

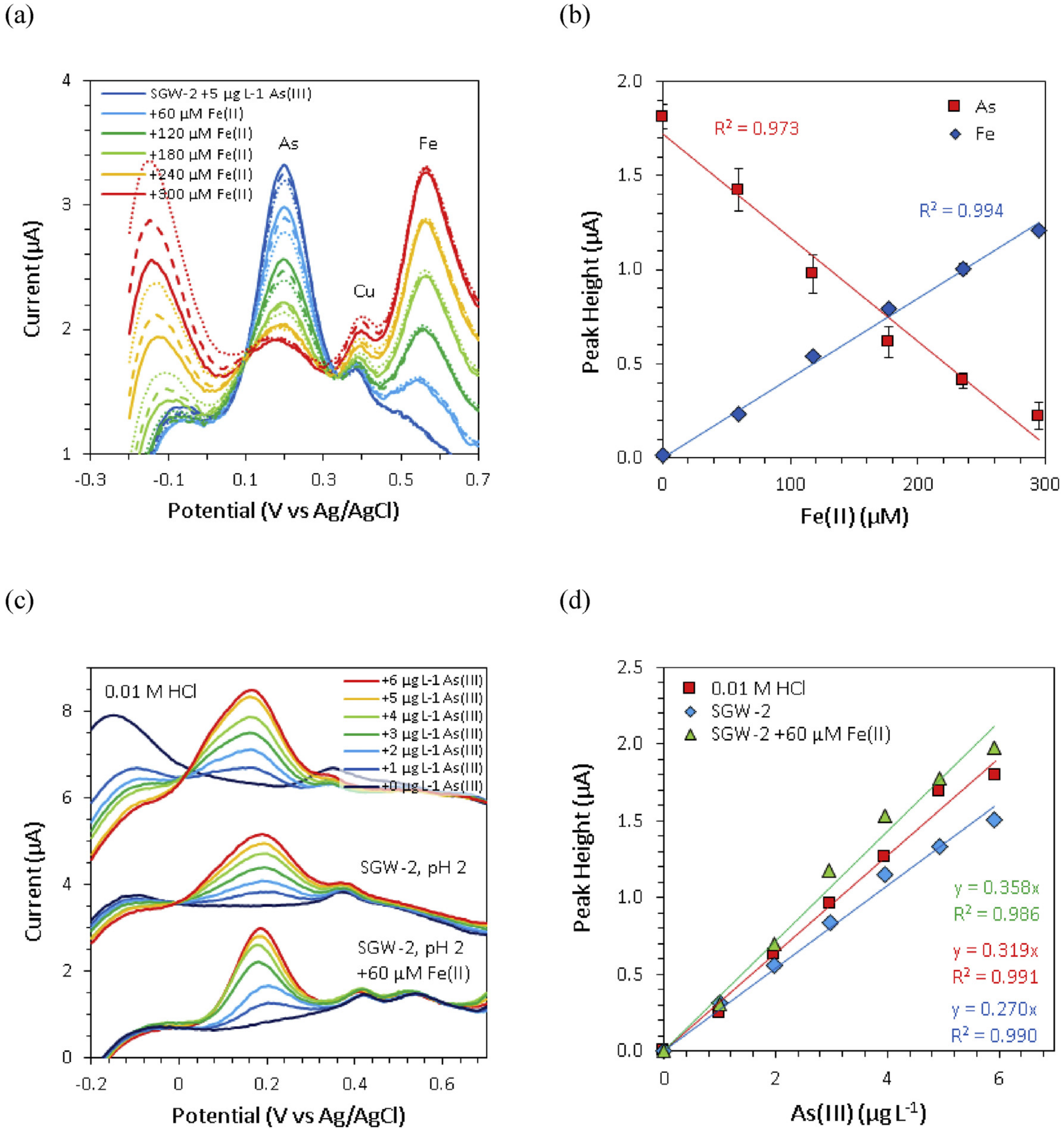

Fig. 4. Electrochemical method development. (a) and (b) show the stability of As stripping peaks (5 µg L^{-1} or 67 nM As(III)) in synthetic groundwater with increasing additions of Fe(II). For each 60 µM addition of Fe(II), three scans were made (solid, dashed, and then dotted line) to check for peak stability. (c) and (d) show the linear range of As(III) determination by ASV in 0.01 M HCl and synthetic groundwater with and without Fe(II) as additions of 1 µg L^{-1} As(III) (13 nM) are made. Similar results for total As are shown in the Supplementary Information. LSASV conditions: 15 s at −1.3 V (total As) or −0.7V (As(III)), 10s hold at −400 mV, stripping from −400mV to +700 mV at 4 V s^{-1}. Detection of As(III) was made at pH 2 with 20 µM hydrazine, and detection of total As was made at pH 1.

equation

$$-\frac{d[As(III)]}{dt} = k[As(III)] \tag{2}$$

where d[As(III)]/dt is the rate of change in the concentration of As(III) with respect to time, and k is the pseudo-first order rate constant (min^{-1}). The integrated solution to this equation is rearranged into the linear form

$$\ln\left(\frac{[As(III)]_t}{[As(III)]_0}\right) = -kt \tag{3}$$

where $[As(III)]_t$ and $[As(III)]_0$ are concentrations of As(III) at time ‘t’ and 0 respectively. Plotting Equation (3) in the linear form $y = mx + c$ indicated pseudo-first order kinetics, with $R^2 = 0.937 \pm 0.006$ using ASV measurements, and $R^2 = 0.981$ using ImpAs/ICP-MS (Fig. 5b). For each individual experiment the values of k determined by the two different analytical procedures were within error of one another (Fig. 5c). The final average of the two repeats gave $k = 0.0710 \pm 0.0019$ min^{-1} using ASV, and $k = 0.0725 \pm 0.0061$ min^{-1} using ImpAs/ICP-MS (Fig. 5c). Again, values of k were within error of one another, indicating that ImpAs successfully captured the same reaction kinetics as ASV.

3.4. Application 2: Speciation of natural waters

3.4.1. Spike recovery experiment

These experiments aimed to demonstrate that ImpAs selectively

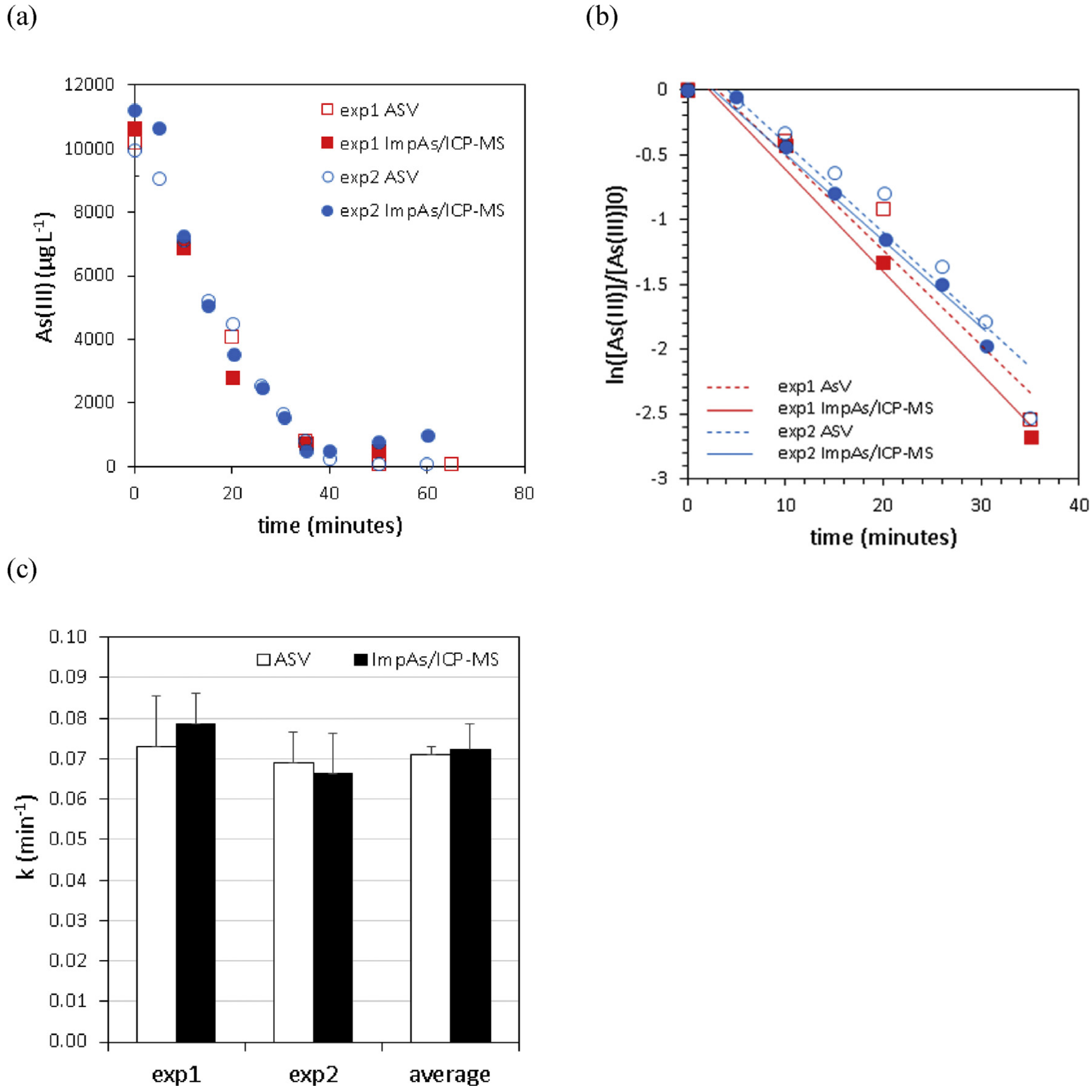

Fig. 5. Case study 1 – kinetics for the photocatalytic oxidation of As(III) over TiO_2, determined by ASV and ImpAs/ICP-MS. Conditions were 10 mg L^{-1} As(III), 0.1 g L^{-1} Degussa P25 TiO_2 powder, in 10 mM HEPES (pH 7.44). (a) Time series for photocatalytic oxidation of As(III) (two repeat experiments), (b) data fitted to a pseudo-first order kinetic model, and (c) comparison of rate constant, k, as determined by the two analytical methods. ASV measurements are shown as unfilled shapes, ImpAs/ICP-MS measurements are filled. Red squares indicate the first experimental repeat, and blue circles indicate the second experimental repeat. Solid lines and dashed lines indicate the linear best fit for ImpAs/ICP-MS and ASV results respectively.

removes As(V) from natural samples thus enabling speciation to be determined by subsequent ICP-MS analysis. Commercial bottled mineral water (France), groundwater from a spring and surface water from a stream (both from Cornwall, UK) were chosen as representative oxic waters. Four groundwaters sourced from tube wells in West Bengal were chosen as anoxic reducing waters with high concentrations of dissolved iron. After size filtration, clear groundwater samples from West Bengal required immediate acidification (to pH 2) with HCl or spiking with 10 mM EDTA to prevent formation of yellow-brown iron precipitates within a matter of minutes.

Results for three of these natural waters are shown in Fig. 6. For untreated samples ICP-MS showed that 100% of the As(V) spike added was recovered by total As determination, whilst ImpAs treatment removed all of the As(V) spike added. Both determination of total As in the untreated samples by ICP-MS and As(III) determination by ImpAs/ICP-MS were consistent with ASV analysis. Similar results were obtained for waters from both oxic and anoxic environments. No colour change in the solution was observed during the course of the experiment for these samples (though the resin became coated with a dark precipitate after treating large volumes of the West Bengal groundwater samples – SI Fig. S13).

3.4.2. *Limitations*

Samples preserved by acidification must be pH neutralised before treatment with ImpAs, to prevent disruption of the metal-organic receptor. Unlike the other West Bengal groundwaters, for STN5 rapid iron precipitation was visually observed both (i) immediately after sampling the water before acidification and (ii) within minutes of pH neutralisation. This sample showed a very high iron concentration (13 mg L^{-1} versus $\leq$ 5.0 mg L^{-1} for all other samples), and 99% of all arsenic present had been oxidised during storage. During the course of the STN5 spike experiment, the observed total As failed to match the quantity of As(V) added

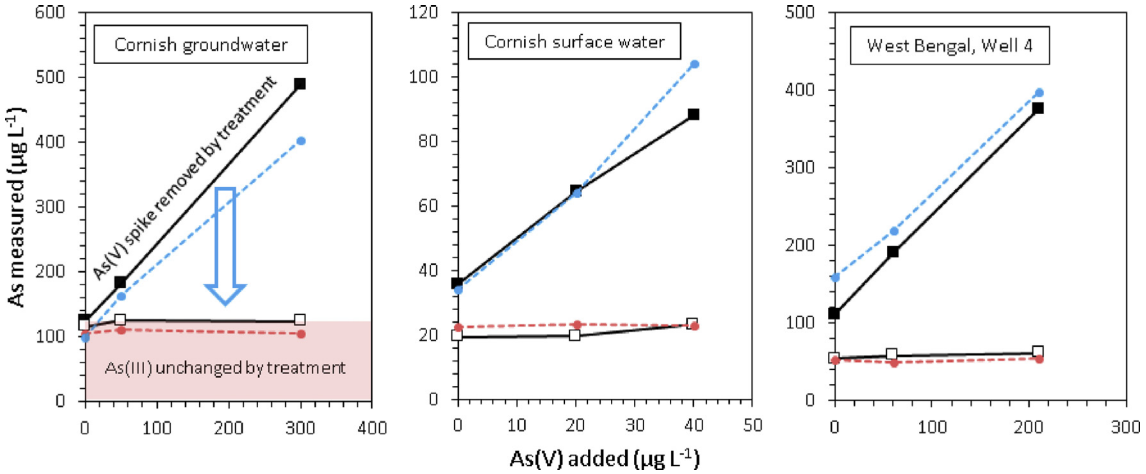

Fig. 6. Case study 2 – speciation in natural media. Samples were spiked with arsenic to obtain a mix of oxidation states and an ImpAs-loaded syringe used to remove As(V). By determining total As by ICP-MS before treatment with ImpAs (black filled squares) and after treatment (white squares) the speciation was determined. ASV determination is also given for comparison (dashed lines) with total As (blue) and As(III) (red).

(Fig. 7a) owing to loss of arsenic during iron precipitation. The concentration of As(III) was more stable, suggesting that losses of arsenic were primarily due to adsorption and co-precipitation of As(V), in line with previous findings (Gibbon-Walsh et al., 2011).

EDTA can be used instead of acidification to prevent iron precipitation. Whilst addition of EDTA prevented loss of iron both in standing samples and during ImpAs treatment (SI Fig. 14), EDTA presented a new problem. By complexing Zn(II) present in the ImpAs resin, EDTA limited the ability of ImpAs to retain As(V) (Fig. 7b). A discussion of why ImpAs performance was limited in the presence of EDTA, but not in the presence of weaker chelating agents such as dissolved organic carbon (e.g. humic acids) is given in the Supplementary Information (Figs. S15–S17).

3.5. *Comparison of ImpAs/ICP-MS with ASV for rapid, reliable and portable speciation of arsenic*

Good agreement was found in the speciation of synthetic waters using ImpAs/ICP-MS and ASV, generally within error of one another (Fig. 8a). The cross-calibration curve gave $R^2 = 0.967$. In the first case study, the difference between photooxidation rate constants determined by ASV and ImpAs/ICP-MS was insignificant - the difference of 2.0% was within error bounds, suggesting good accuracy. The precision of rate constants determined in duplicate by ImpAs/ICP-MS was slightly lower than those obtained by ASV (±8.4% versus ±2.7%).

For natural waters the speciation determined by ImpAs/ICP-MS and ASV also agreed, but with lower goodness of fit ($R^2 = 0.902$) (Fig. 8b). Importantly, there was no significant difference in the cross-calibration of ImpAs/ICP-MS and ASV speciation between oxic and anoxic water samples.

ImpAs/ICP-MS was much more time effective than ASV, requiring 30–60 s to condition the resin and 1 min to filter 5 mL of sample, plus 3 min analysis time by ICP-MS. ASV, meanwhile, required approximately 20 min experimental work to measure one sample in duplicate (35 s per scan with 15 scans to measure background, sample and 2 additions in triplicate). This highlights how chemisorbents such as ImpAs might enable high throughput

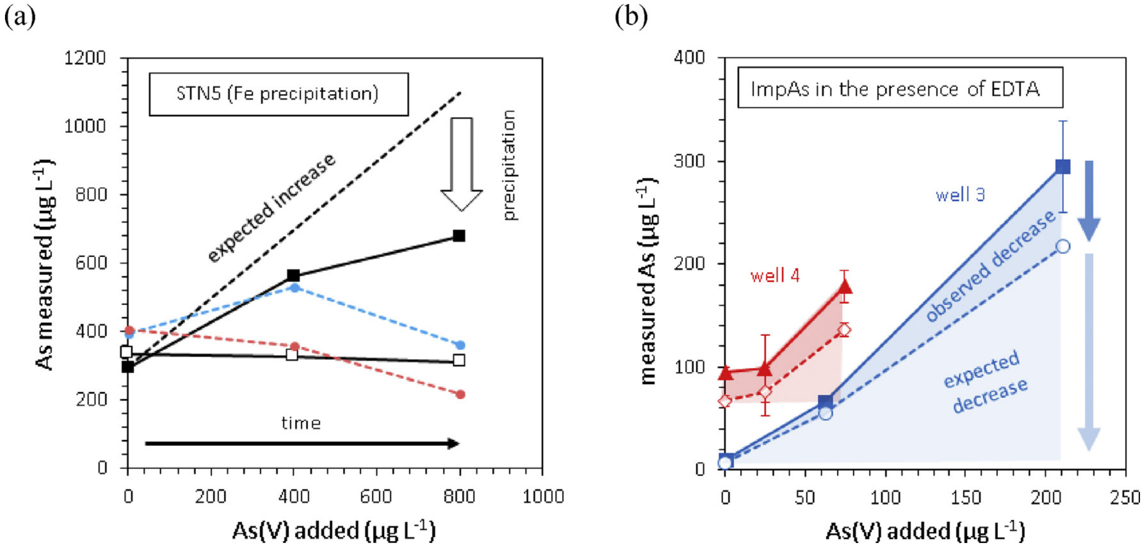

Fig. 7. Current limitations of speciation by chemisorbent. (a) Precipitation of iron during analysis of STN5 samples was associated with a loss of total As. (b) In the presence of 10 mM EDTA, ImpAs failed to remove all the As(V) spike, resulting in an overestimation of the proportion of As(III) present in the sample.

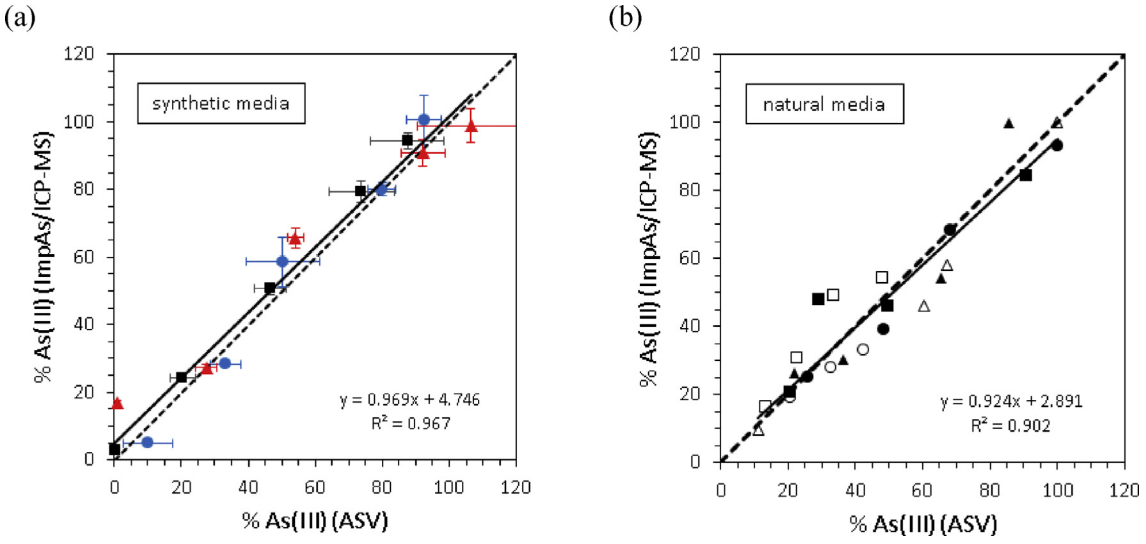

Fig. 8. Comparison of arsenic speciation determined using the developed ImpAs/ICP-MS and ASV methods in (a) synthetic and (b) natural samples. (a) Cross-calibration of arsenic speciation in 10 mM HEPES (black squares), CW (blue circles) and SGW-1 (red triangles). Error bars indicate the propagated uncertainty of each measurement. (b) Cross-calibration of arsenic speciation in natural media. Data points correspond to bottled mineral water (black squares), Cornish groundwater (black circles) and surface water (black triangles), and West Bengal groundwater samples Well 4 (white squares), STN13 (white circles) and STN5 (white triangles). Dashed lines indicate the ideal one-to-one cross-calibration, and solid black lines indicate the linear best fit.

applications in the laboratory. With a maximum As(V) capacity of 16 mg g^{-1}, a single syringe with 1.0 g ImpAs can theoretically treat a maximum 16 L water contaminated with 1000 μg L^{-1} As(V). Owing to the high sorption capacity of ImpAs, a single syringe can be reused to treat many samples - just three syringes were used to treat nearly all samples in this work – separated into (i) all synthetic media samples (at 1.0 g loading), (ii) all natural oxic waters, and (iii) all natural de-acidified West Bengal groundwaters, with little trace of cross-contamination between samples.

Speciation using handheld syringes loaded with ImpAs is highly portable – especially as a single syringe can treat many samples – and unlike ASV no hardware, batteries, or additional reagents are required. If coupled with a fast laboratory detection method (e.g. ICP-MS), high sample throughput can be achieved. In contrast, although ASV has lower sample throughput and requires more manual operation, ASV provides an immediate answer for on-site analysis and for near real-time monitoring of oxidation experiments. ASV is more appropriate for natural samples with high iron levels (>5 mg L^{-1}) where acidification or EDTA can be used to avoid precipitation.

4. Conclusions

This study aimed to develop the application of the As(V)-selective chemisorbent ImpAs as a fast, portable and cost-effective method to separate As(III) and As(V) from aqueous solutions (synthetic and natural), for applications in the design of arsenic treatment plants and monitoring campaigns in the field.

The key finding is that ImpAs can speciate inorganic arsenic in synthetic and natural waters at pH 7; this was true for both oxic waters and anoxic waters with $\leq$5 mg L^{-1} dissolved iron. We have shown here that chemisorbent materials offer an alternative and attractive approach towards the speciation of arsenic for on-site and laboratory applications, being simple, portable, quick and easy-to-use with little specialist knowledge required. In unstable waters where iron precipitation occurs within a few minutes, ASV is currently recommended as a portable and relatively low-cost solution for on-site arsenic speciation. Further work should consider the benefits and trade-offs between chemisorbents and other portable techniques for speciation, particularly other solid phase extraction techniques such as strong anion exchange resins.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The authors have the following patent: US 2017/0113949 A1, as already discussed in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.115650.

References

An, J., Lee, J., Lee, G., Nam, K., Yoon, H.O., 2015. Combined use of collision cell technique and methanol addition for the analysis of arsenic in a high-chloride-containing sample by ICP-MS. Microchem. J. 120, 77–81. https://doi.org/10.1016/j.microc.2015.01.001.

Ayers, J.C., Goodbred, S., George, G., Fry, D., Benneyworth, L., Hornberger, G., Roy, K., Karim, M.R., Akter, F., 2016. Sources of salinity and arsenic in groundwater in southwest Bangladesh. Geochem. Trans. 17, 4. https://doi.org/10.1186/s12932-016-0036-6.

Bednar, A.J., Garbarino, J.R., Burkhardt, M.R., Ranville, J.F., Wildeman, T.R., 2004. Field and laboratory arsenic speciation methods and their application to natural-water analysis. Water Res. 38, 355–364. https://doi.org/10.1016/j.watres.2003.09.034.

Benramdane, L., Bressolle, F., Vallon, J.J., 1999. Arsenic speciation in humans and food products: a review. J. Chromatogr. Sci. 37, 330–344. https://doi.org/10.1093/chromsci/37.9.330.

Borrill, A.J., Reily, N.E., 2019. Addressing the practicalities of anodic stripping voltammetry for heavy metal detection : a tutorial review. https://doi.org/10.1039/

c9an01437c.

Brainina, K.Z., Malakhova, N.A., Stojko, N.Y., 2000. Stripping voltammetry in environmental and food analysis. Fresenius' J. Anal. Chem. 368, 307—325. https://doi.org/10.1007/s002160000525.

Chai, L., Yang, J., Liao, F., Li, Q., Wang, Q., Liu, H., Dong, Q., Yin, Z., 2017. Kinetics and molecular mechanism of arsenite photochemical oxidation based on sulfate radical. Mol. Catal. 438, 113—120. https://doi.org/10.1016/j.mcat.2017.03.014.

Chen, S., Li, J., Lu, D., Zhang, Y., 2016. Dual extraction based on solid phase extraction and solidified floating organic drop microextraction for speciation of arsenic and its distribution in tea leaves and tea infusion by electrothermal vaporization ICP-MS. Food Chem. https://doi.org/10.1016/j.foodchem.2016.05.101.

Chen, Y.-W., Yu, X., Belzile, N., 2019. Arsenic speciation in surface waters and lake sediments in an abandoned mine site and field observations of arsenic ecotoxicity. J. Geochem. Explor. 205, 106349. https://doi.org/10.1016/j.gexplo.2019.106349.

Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713—764. https://doi.org/10.1021/cr00094a002.

Ding, W., Wang, Y., Yu, Y., Zhang, X., Li, J., Wu, F., 2015. Photooxidation of arsenic(III) to arsenic(V) on the surface of kaolinite clay. J. Environ. Sci. (China) 36, 29—37. https://doi.org/10.1016/j.jes.2015.03.017.

Fontana, K.B., Lenzi, G.G., Seára, E.C.R., Chaves, E.S., 2018. Comparision of photocatalysis and photolysis processes for arsenic oxidation in water. Ecotoxicol. Environ. Saf. 151, 127—131. https://doi.org/10.1016/j.ecoenv.2018.01.001.

Gibbon-Walsh, K., Salaün, P., Uroic, M.K., Feldmann, J., McArthur, J.M., Van Den Berg, C.M.G., 2011. Voltammetric determination of arsenic in high iron and manganese groundwaters. Talanta 85, 1404—1411. https://doi.org/10.1016/j.talanta.2011.06.038.

Gupta, A., Singh, E.J., 2018. Arsenic—iron relationships in aquifers of North East India: implications for public health and the environment. Environ. Manag. 1—7 https://doi.org/10.1007/s00267-018-0999-4.

Hering, J.G., Katsoyiannis, I.A., Theoduloz, G.A., Berg, M., Hug, S.J., 2017. Arsenic removal from drinking water: Experiences with technologies and constraints in practice. J. Environ. Eng. 143, 1—9. https://doi.org/10.1061/(ASCE)EE.1943-7870.0001225.

Huang, H., Dasgupta, P.K., 1999. A field-deployable instrument for the measurement and speciation of arsenic in potable water. Anal. Chim. Acta 380, 27—37. https://doi.org/10.1016/S0003-2670(98)00649-7.

Hug, S.J., Leupin, O.X., Berg, M., 2008. Bangladesh and Vietnam: different groundwater compositions require different approaches to arsenic mitigation. Environ. Sci. Technol. 42, 6318—6323. https://doi.org/10.1021/es7028284.

Johnston, R.B., Sarker, M.H., 2007. Arsenic mitigation in Bangladesh: National screening data and case studies in three upazilas. J. Environ. Sci. Heal. Part A 42. https://doi.org/10.1080/10934520701567155, 1889—1896.

Liang, C.P., Chen, J.S., Chien, Y.C., Chen, C.F., 2018. Spatial analysis of the risk to human health from exposure to arsenic contaminated groundwater: a kriging approach. Sci. Total Environ. 627, 1048—1057. https://doi.org/10.1016/j.scitotenv.2018.01.294.

Markley, C.T., Herbert, B.E., 2009. Arsenic risk assessment: the importance of speciation in different hydrologic systems. Water, Air, Soil Pollut. 204, 385—398. https://doi.org/10.1007/s11270-009-0052-6.

McArthur, J.M., Banerjee, D.M., Hudson-Edwards, K.A., Mishra, R., Purohit, R., Ravenscroft, P., Cronin, A., Howarth, R.J., Chatterjee, A., Talukder, T., Lowry, D., Houghton, S., Chadha, D.K., 2004. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: the example of West Bengal and its worldwide implications. Appl. Geochem. 19, 1255—1293. https://doi.org/10.1016/j.apgeochem.2004.02.001.

McGrory, E.R., Brown, C., Bargary, N., Williams, N.H., Mannix, A., Zhang, C., Henry, T., Daly, E., Nicholas, S., Petrunic, B.M., Lee, M., Morrison, L., 2017. Arsenic contamination of drinking water in Ireland: a spatial analysis of occurrence and potential risk. Sci. Total Environ. 579, 1863—1875. https://doi.org/10.1016/j.scitotenv.2016.11.171.

Mihucz, V.G., Enesei, D., Veszely, Á., Bencs, L., Pap-Balázs, T., Óvári, M., Streli, C., Záray, G., 2017. A simple method for monitoring of removal of arsenic species from drinking water applying on-site separation with solid phase extraction and detection by atomic absorption and X-ray fluorescence based techniques. Microchem. J. 135, 105—113. https://doi.org/10.1016/j.microc.2017.08.006.

Moffat, C.D., Weiss, D.J., Shivalingam, A., White, A.J.P., Salaun, P., Vilar, R., 2014. Molecular recognition and scavenging of arsenate from aqueous solution using dimetallic receptors. Chem. Eur J. 20, 17168—17177. https://doi.org/10.1002/chem.201404723.

Montoro Leal, P., Vereda Alonso, E., López Guerrero, M.M., Cordero, M.T.S., Cano Pavón, J.M., García de Torres, A., 2018. Speciation analysis of inorganic arsenic by magnetic solid phase extraction on-line with inductively coupled mass spectrometry determination. Talanta 184, 251—259. https://doi.org/10.1016/j.talanta.2018.03.019.

Naujokas, M.F., Anderson, B., Ahsan, H., Vasken Aposhian, H., Graziano, J.H., Thompson, C., Suk, W.A., 2013. The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem. Environ. Health Perspect. 121, 295—302. https://doi.org/10.1289/ehp.1205875.

Nicomel, N.R., Leus, K., Folens, K., Van Der Voort, P., Du Laing, G., 2015. Technologies for arsenic removal from water: Current status and future perspectives. Int. J. Environ. Res. Publ. Health 13, 1—24. https://doi.org/10.3390/ijerph13010062.

O'Reilly, J., Watts, M.J., Shaw, R.A., Marcilla, A.L., Ward, N.I., 2010. Arsenic contamination of natural waters in san juan and La Pampa, Argentina. Environ. Geochem. Health 32, 491—515. https://doi.org/10.1007/s10653-010-9317-7.

Okazaki, T., Wang, W., Kuramitz, H., Hata, N., Taguchi, S., 2013. Molybdenum blue spectrophotometry for trace arsenic in ground water using a soluble membrane filter and calcium carbonate column. Anal. Sci. 29, 67—72. https://doi.org/10.2116/analsci.29.67.

Pakzadeh, B., Batista, J.R., 2011. Impacts of cocontaminants on the performances of perchlorate and nitrate specialty ion-exchange resins. Ind. Eng. Chem. Res. 50, 7484—7493. https://doi.org/10.1021/ie102384h.

Paul, S.C., Rahman, M.A., Siddique, N., Alam, a M.S., 2008. Voltammetric study of arsenic (III) and arsenic (V) in ground water of Hajigonj and Kalkini in Bangladesh. Pak. J. Anal. Environ. Chem. 9, 49—55.

Qi, P., Pichler, T., 2017. Competitive adsorption of As(III), As(V), Sb(III) and Sb(V) onto ferrihydrite in multi-component systems: implications for mobility and distribution. J. Hazard Mater. 330, 142—148. https://doi.org/10.1016/j.jhazmat.2017.02.016.

Rabbani, U., Mahar, G., Siddique, A., Fatmi, Z., 2017. Risk assessment for arsenic-contaminated groundwater along River Indus in Pakistan. Environ. Geochem. Health 39, 179—190. https://doi.org/10.1007/s10653-016-9818-0.

Rasul, S.B., Munir, A.K.M., Hossain, Z.A., Khan, A.H., Alauddin, M., Hussam, A., 2002. Electrochemical measurement and speciation of inorganic arsenic in groundwater of Bangladesh. Talanta 58, 33—43. https://doi.org/10.1016/S0039-9140(02)00254-0.

Salaün, P., Gibbon-Walsh, K.B., Alves, G.M.S., Soares, H.M.V.M., van den Berg, C.M.G., 2012. Determination of arsenic and antimony in seawater by voltammetric and chronopotentiometric stripping using a vibrated gold microwire electrode. Anal. Chim. Acta 746, 53—62. https://doi.org/10.1016/j.aca.2012.08.013.

Salaün, P., Planer-Friedrich, B., van den Berg, C.M.G., 2007. Inorganic arsenic speciation in water and seawater by anodic stripping voltammetry with a gold microelectrode. Anal. Chim. Acta 585, 312—322. https://doi.org/10.1016/j.aca.2006.12.048.

Shahid, M., Niazi, N.K., Dumat, C., Naidu, R., Khalid, S., Rahman, M.M., Bibi, I., 2018. A meta-analysis of the distribution, sources and health risks of arsenic-contaminated groundwater in Pakistan. Environ. Pollut. 242, 307—319. https://doi.org/10.1016/j.envpol.2018.06.083.

Shankar, S., Shanker, U., Shikha, 2014. Arsenic contamination of groundwater: a review of sources, prevalence, health risks, and strategies for mitigation. Sci. World J. https://doi.org/10.1155/2014/304524, 2014.

Smedley, P., 2008. Sources and distribution of arsenic in groundwater and aquifers. Arsenic in Groundwater : a World Problem. International Association of Hydrogeologists, pp. 1—34, 9789080825826.

The NSF Joint Committee on Drinking Water Treatment Units, 2016. NSF/ANSI 53 - 2016 Drinking Water Treatment Units - Health Effects. NSF International Standard/American National Standard.

Voice, T.C., Flores del Pino, L.V., Havezov, I., Long, D.T., 2011. Field deployable method for arsenic speciation in water. Phys. Chem. Earth 36, 436—441. https://doi.org/10.1016/j.pce.2010.03.027.

Wang, Z., Bush, R.T., Liu, J., 2013. Arsenic(III) and iron(II) co-oxidation by oxygen and hydrogen peroxide: divergent reactions in the presence of organic ligands. Chemosphere 93, 1936—1941. https://doi.org/10.1016/j.chemosphere.2013.06.076.

Watts, M.J., O'Reilly, J., Marcilla, A.L., Shaw, R.A., Ward, N.I., 2010. Field based speciation of arsenic in UK and Argentinean water samples. Environ. Geochem. Health 32, 479—490. https://doi.org/10.1007/s10653-010-9321-y.

Zhao, L. yu, Zhu, Q. yun, Mao, L., Chen, Y. jun, Lian, H. zhen, Hu, X., 2019. Preparation of thiol- and amine-bifunctionalized hybrid monolithic column via "one-pot" and applications in speciation of inorganic arsenic. Talanta 192, 339—346. https://doi.org/10.1016/j.talanta.2018.09.064.