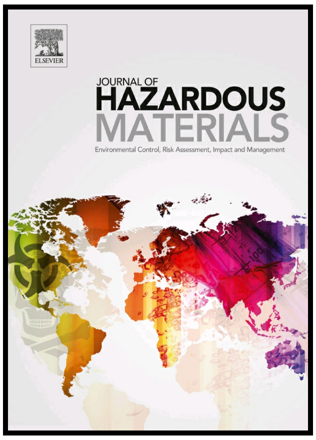

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Effect of speciation and composition on the kinetics and precipitation of arsenic sulfide from industrial metallurgical wastewater

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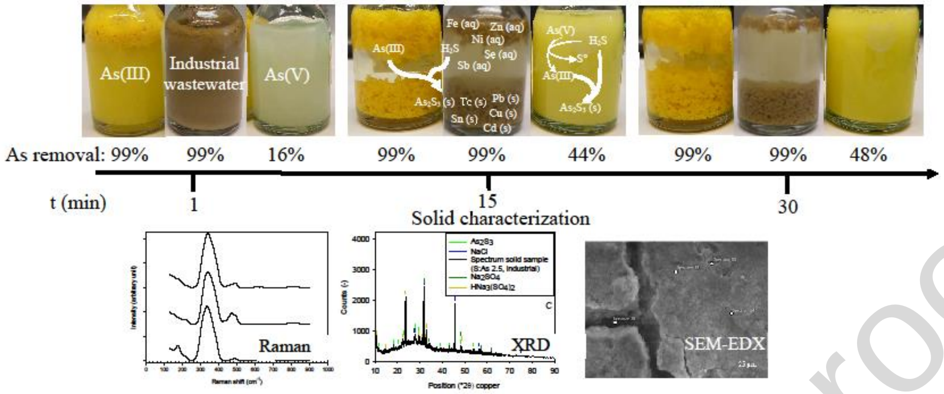
Graphical abstract



KEYWORDS: Arsenate reduction, selective metal precipitation, rate determining step, orpiment, metal sulfide

Abstract

Precipitation of arsenic as As_2S_3 produces little waste sludge, has the potential for low chemical consumption and for selective metal(loid) removal. In this study, arsenic removal from acidic (pH 2), metallurgical wastewater was tested in industrially relevant conditions. Sulfides added at a S:As molar ratio of 2.5 and 5 resulted in removal of 99 % and 84 % of As(III) and As(V). Precipitation of As_2S_3 from the As(III) and industrial wastewater containing 17% As(V) was nearly instantaneous. For the synthetic As(V) solution, reduction to As(III) was the rate limiting step. At a S:As ratio of 20 and an observed removal rate (k_2 = 4.8 (mol L^{-1}) h^{-1}), two hours were required to remove of 93% of arsenic from a 1 gAs L^{-1} solution. In the case of As(V) in industrial samples this time lag was not observed, showing that components in the industrial wastewater affected the removal and reduction of arsenate. Speciation also affected flocculation and coagulation characteristics of As_2S_3 particles: As(V) reduction resulted in poor coagulation and flocculation. Selective precipitation of arsenic was possible, but depended on speciation, S:As ratio and other metals present.

1. Introduction

Arsenic is a major pollutant in metallurgical waste and process waters. Roasting and smelting of ores, industrial by-products and e-scrap, processing of spent electrolytes and acid mine drainage result in arsenic rich wastewater, up to several grams per liter [1–5]. Due to its toxicity, the removal of arsenic is one of the main objectives of metallurgical wastewater treatment [6]. Treatment technologies such as sorption, coagulation and membrane separation are generally only used for removal of low levels of arsenic up to 30 μmol L^{-1} [7–10]. Three main technologies are suited for the removal of arsenic from acidic, arsenic rich wastewaters: precipitation as calcium arsenate, ferric arsenate or arsenic sulfide [11,12].

In the past, precipitation as calcium arsenate was preferred due to its multi-purpose nature and the supposed stability of the precipitates [11]. Addition of lime neutralizes the acidic wastewater and precipitates sulfates as gypsum, metals as hydroxides and arsenic as calcium arsenates [1,5]. This process is however associated with large consumption of calcium oxide, large volumes of waste sludge and loss of other, valuable metal(loid)s. Furthermore, recent studies have shown that calcium arsenates are less stable than expected due to the carbonation of calcium [3,13]. Co-precipitation of iron and arsenic is currently designated as the best available technology by the US environmental protection agency [14]. This technique requires the presence or addition of iron in/to the wastewater. Under ambient conditions, the resulting sludge is not stable for long term storage as reducing conditions can result in the reduction and mobilization of iron and arsenic [15,16]. New technologies have been able to produce stable crystalline bio-scorodite under ambient conditions, opening up new routes for treatment and disposal [3,17].

Precipitation as arsenic sulfide has three main advantages when compared with calcium and ferric arsenates: production of small amounts of waste sludge, the possibility of selective metal removal and the minimal addition of chemicals. Per mole of arsenic, As_2S_3 is 1.6 and 1.9 times lighter than $Ca_3(AsO_4)_2$ and $FeAsO_4 \cdot 2H_2O$, respectively, and the resulting sludge does not contain gypsum. Contrary to most metal sulfides, arsenic sulfide is insoluble at acid pH (< 6) and soluble in neutral or alkaline conditions. As a result selective precipitation is theoretically possible [4,18–22]. Finally, the required sulfides can be produced by reducing sulfates in wastewater, minimizing the need for consumables [23].

The design of an arsenic sulfide based process requires insight into reaction kinetics and required sulfide dosage. Presently, there are only a few studies on arsenic sulfide precipitation from arsenic rich wastewaters in conditions relevant for metallurgical operations [24]. Previous reports have been limited to synthetic water without other metal(loid)s embedded, low arsenic concentrations and circumneutral conditions, while industrial metallurgical wastewaters typically have a low pH, contain several grams of arsenic per liter and multiple competing metal(loid)s [24–26].

This study was conceived to shed light on arsenic sulfide precipitation from metallurgical wastewaters. First, synthetic acidic wastewaters containing As(III) and As(V) up to 1 and 5 g L^{-1} were used to evaluate the effect of speciation and S:As ratio on removal and kinetics. Subsequently, industrial wastewater containing a mixture of metal(loid)s was tested. Removal rate and efficiency were compared to those of earlier tests, taking into account the speciation of arsenic in industrial wastewater. Finally, the selective removal of arsenic in the presence of iron, tellurium, tin, copper, lead, cadmium, zinc, nickel, selenium and antimony was assessed.

2. Materials and methods

2.1. Stock preparation

Two stock solutions of As(V) and As(III) of 2 g L^{-1} and 30 gSO_4^{2-} L^{-1} were made by dissolving 18.18 g of $Na_3AsO_4 \cdot 7H_2O$ (>98 %, Sigma-Aldrich) and 7.00 g $NaAsO_2$ (>99 %, Sigma-Aldrich) in 43.75 mL H_2SO_4 (50 %, Carl Roth). A third stock solution of 5 g L^{-1} was prepared by dissolving 14.43 g $Na_2HAsO_4.7H_2O$ (>98 %, Sigma-Aldrich) and 29.36 $NaAsO_2$. NaOH pellets (VWR) were used to adjust the pH of the solution up to pH 2. The solution was diluted with demineralized water up to 2 L. 2 L of industrial metallurgical wastewater was collected from an industrial metal refining plant. Samples were stored in a closed container and shielded from light. Two stock solution of 1.35 mol L^{-1} and 5.35 mol L^{-1} HCl were made by diluting a 12 mol L^{-1} HCl solution (Sigma-Aldrich) in 500 mL of demineralized water.

For the experiments focusing at 1g L^{-1} arsenic, a 1.33 mol L^{-1} NaHS solution was prepared, while a stock solution of 6.67 mol L^{-1} NaHS was used for the experiments aiming at 5g L^{-1} arsenic. All NaHS solutions were used within 24 h. A Schott-bottle containing 100 mL of ultrapure water was sparged with argon for 20 min. 80 mg of NaOH was dissolved. 7.473 g and 37.336 g of NaHS (>99.3 %, Sigma-Aldrich) were added, resulting in two stock solution of 1.33 mol L^{-1} and 6.67 mol L^{-1} NaHS. Once all solids were dissolved, the bottle was wrapped in aluminum foil, closed with a rubber cap to enable sampling with a syringe and stored at 4 °C until the start of the experiment.

2.2. Kinetic experiments

Experiments were conducted in 20 mL penicillin bottles. Each bottle was used to obtain one sampling point. To evaluate the effect of sulfide dosing, six different doses of NaHS stock solution were tested, resulting in initial molar S:As ratios of 0, 1.5, 2.5, 5, 10 and 20. First, 10 mL of arsenic stock solution was added. Demineralized water and 1.35 mol L^{-1} HCl were added to the bottles, as indicated in Table S1. HCl was used to correct for pH changes due to the later addition of NaHS. Bottles were sparged with argon for 20 min and capped. Experiments were performed at room temperature in triplicate.

The experiment was initiated by adding the volume of NaHS indicated in Table S1 to the penicillin bottle, resulting in starting concentrations of 1 g L^{-1} and 5 g L^{-1} of arsenic. Bottles were sampled with a syringe at designated times and filtered over a 0.45 µm syringe filter (Chromafil PVDF, Macherey Nagel). pH and conductivity were measured within 15 minutes using Pt 1000 (pH, conductivity) and a SO70X gold (redox) electrodes and Metrohm 744 and Consort C6010 instruments (Table S15 - Table S20). The concentration of aqueous sulfides was modelled on the arsenic removal and stoichiometry resulting from the solid characterization.

2.3. Chemical analysis

Elemental analysis was preceded by digestion of the suspensions with H_2O_2 (30 %, Carl Roth) and HNO_3 (65 %, VWR) in a volumetric ratio of 2:1:1 (sample:H_2O_2:HNO_3) and heating the mixture to 65 °C for 2 h. The solution was subsequently diluted using 10 % HCl to a volumetric ratio of 1:10 for high arsenic concentrations (> 75 mg L^{-1}) and 1:5 for low arsenic concentrations (< 75 mg L^{-1}). Metal concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6000). The method was validated by applying the same protocol on unfiltered samples of industrial wastewater with an initial S:As ratio of 20 (Figure S1). Ion chromatography (IC) (ICS-2000, Dionex) was used to determine the concentration of As(V) in the industrial wastewater, similar to the protocol described in Yang et al (2016) [27].

2.4. Solid phase characterization

After 24 h, samples were filtered over a 1.5 µm glass microfiber Whatman™ filter. After rinsing 10 times with 10 mL of 0.5 mM HCl, solids were dried for 48 h in an anaerobic 5 L vessel, which was sparged with argon for 1 h in advance. Two AnaeroGen™ 3.5 L bags (Thermo Fisher) were placed in the vessel before closing to ensure anaerobic conditions. X-ray powder diffraction (XRD) was used to determine the precipitate mineralogy. Precipitates were visualized with scanning electron microscopy (SEM), combined with energy dispersive X-ray spectroscopy (EDX) to get a qualitative assessment of the elemental distribution and composition of the precipitates. A minimum of three locations were analyzed to acquire a more reliable measurement of the sample composition. Raman spectra were measured using a WITec Alpha300R+ spectroscope equipped with a 785 laser (Toptica). More information on the methodology used for solid characterization can be found in the supporting information (SI).

2.5. Simulations and statistics

A Pourbaix diagram simulating a S:As molar ratio of 1.5 was composed using FactSage 7.0 (Figure S4) [28]. Reactions and their associated Gibbs free energies were obtained from HSC under standard conditions [29]. Aqueous modelling software (OLI Studio 9.6) was used to simulate observed processes and reactions taking place (Figure S2 and Figure S3) [30]. SigmaPlot 13 was used for graphs and statistical analyses [31].

The second order rate constant k_2 was calculated using the following methodology, adapted from Atkins et al (2006) [32]. First, the natural logarithm of the ratio of sulfides ([Sulfides]) to arsenic ([As]) in mol L^{-1} at each timepoint (i in hours) was calculated and plotted as function of time (t_i). A linear equation was fitted ($R^2 = 0.98$) and the slope (a) was calculated.

$$\ln\left(\frac{[Sulfides]_i}{[As]_i}\right) = at_i + \ln(\frac{[Sulfides]_{0h}}{[As]_{0h}}) \qquad (1)$$

From this equation the second rate order constant (k_2) was calculated.

$$a = k_2([Sulfides]_{0h} - [As]_{0h}) \qquad (2)$$

$$k_2 = \frac{a}{([Sulfides]_{0h} - [As]_{0h})} \qquad (3)$$

The effect of the molar ratio of As(V):As(III), S:As and pH on the arsenate reduction reaction was assessed via the Nernst equation (equation (4)) in Figure S5 (R: ideal gas constant (J (Kelvin mol)$^{-1}$), T: temperature (Kelvin), z: number of electrons exchanged, F: Faraday constant (C mol^{-1})), taking into account the pKa_1's of H_2S (6.99), H_3AsO_4 (2.33) and H_3AsO_3 (9.22) [33,34].

$$E = E_0 - \frac{R\,T}{z\,F}\ln(\frac{[H_3AsO_3]}{[H_3AsO_4]\,[H_2S]}) \qquad (4)$$

3. Results and discussion

3.1. Effect of S:As ratio on precipitation kinetics in synthetic wastewater

In the case of synthetic As(III) wastewater, a molar S:As ratio ≥ 2.5 was required for the complete removal of arsenic (Figure 1). At a S:As ratio of 1.5, the theoretical equivalent molar ratio between S:As for As(III), only 70 % of arsenic precipitated, resulting in residual concentrations of 375 ± 15 mg L^{-1}. At molar S:As ratios ≥ 2.5, arsenic was removed below concentrations of 0.75 ± 0.75 mg L^{-1}. Precipitation of arsenic from synthetic As(III) was almost complete after 1 min (Table S3) and therefore only these data points are shown in Figure 1. These results were also confirmed at higher concentrations: at a concentration of 5 g L^{-1} and a S:As ratio of 5, all As(III) was removed within 1 min (see Figure S6).

Previous studies and simulations (Figure S2 and Figure S4) have shown that precipitation of As(III) and sulfides is dominated by formation of As_2S_3, indicated by reaction (5) [21,22,35–37].

$$3\ H_2S + 2\ H_3AsO_3 \rightarrow As_2S_3 + 6\ H_2O \qquad (\Delta G^0=-137.59\ \text{kJ mol}^{-1}) \qquad [29] \qquad (5)$$

At low molar S:As ratios, our results are in agreement with previous studies [24]. However, at S:As molar ratios > 4, Eary et al (1992) (pH 4) and Wilkin et al (2003) (pH 7 – 10) reported an increase in As_2S_3 solubility, which is not reflected in our data [21,38]. At pH 5 Webster et al. (1990) observed similar behavior for crystalline orpiment. Similar to our results at pH 2.1 ± 0.4, Webster et al. (1990), however, did not observe an increase in solubility at a pH of 1.5 [35]. At lower pHs relevant for metallurgical wastewaters, soluble arsenic-sulfide complexes are less stable [22,23,39,40]. Such destabilization may explain why high molar S:As ratios (up to 20) in our results were not associated with lower removal efficiencies.

In the case of As(V) (Figure 2), the majority of the arsenic was removed below concentrations of 150 ± 75 mg L^{-1} when S:As molar ratios ≥ 5 were used. At lower molar ratios of S:As, less arsenic was removed. Compared to the control, no significant removal (ANOVA, $p = 0.65$) was observed when a molar S:As ratio of 1.5 was maintained. At a molar S:As ratio of 2.5, 35 % of arsenic was removed, resulting in a residual concentration of 600 ± 150 mg L^{-1}. Higher molar S:As ratios of 10 and 20 resulted in residual concentrations of 75 ± 30 mg L^{-1} and 75 ± 7.5 mg L^{-1}.

The higher required molar S:As ratio conforms with the reduction of As(V) to As(III) coupled to sulfide oxidation (reaction (6a)), and subsequent precipitation according to reaction (6b) or the direct precipitation of As_2S_5 (reaction (7) and Figure S3) [24,26,41,42]. Despite negative Gibbs free energies, a stoichiometric excess of sulfide was required to achieve complete arsenic removal within the duration of the experiment. The total reduction potential of reaction (6a) is also dependent on the ratio of As(V) to As(III), the ratio of S:As(V) and the pH. At higher As(V):As(III), high S:As(V) ratios and lower pH, the reduction potential will become more favorable (see Figure S5). However, given the fast precipitation of As(III), the direct effect of the As(V):As(III) ratio will be limited. As(III) may affect the reduction potential by lowering the concentration of sulfides, since precipitation as As_2S_3 will also lower the amount of sulfides in solution.

$$H_2S + H_3AsO_4 \rightarrow S^0 + H_3AsO_3 + H_2O \qquad (\Delta G^0 = -82.38\ \mathrm{kJ\ mol^{-1}}) \qquad (6a)$$

$$H_2S + 2\ H_3AsO_3 \rightarrow As_2S_3 + 6\ H_2O \qquad (\Delta G^0 = -137.59\ \mathrm{kJ\ mol^{-1}}) \qquad (6b)$$

$$5\ H_2S + 2\ H_3AsO_4 \rightarrow As_2S_5 + 8\ H_2O \qquad (\Delta G^0 = -77.25\ \mathrm{kJ\ mol^{-1}})\ [29] \qquad (7)$$

At molar S:As ratios > 2.5, removal of arsenic from wastewater was complete after 2 h. In solution containing a mixture of As(V) and As(III), a lag of at least 1 h was also observed, indicating that this lag in arsenic removal is also present in solutions containing high arsenic concentrations and mixtures of trivalent and pentavalent arsenic (Figure S6). This relative slow precipitation may indicate that reduction of As(V) to As(III) (reaction (6a)) is the rate limiting step in the removal of As(V) [24]. Once reduced, As(III) precipitated quickly as As_2S_3 (reaction (6b)). Exclusion of direct precipitation of As_2S_5 (reaction (6)) requires characterization of solids however, which will be provided later in the manuscript. Assuming arsenic precipitated according to reaction (6), the incomplete removal may also have been due to incomplete reduction at low molar S:As ratios. The Pourbaix diagram in Figure S4 shows that, at molar S:As ratios ≥ 1.5, As_2S_3 precipitation is dominant below 1.1 V (vs standard hydrogen electrode). When molar S:As ratios of 1.5 and 2.5 were applied however, maximum redox potentials of 114 ± 16 mV and 55 ± 13 mV were measured. Additionally, Rochette et al (2000) showed that at a S:As ratio of 2 complete arsenic reduction was achieved [26]. Given these observations, reduction of As(V) to As(III) may have been dominant over direct precipitation of As_2S_3 due to the stability of As(III) and intermediate sulfur-arsenic complexes at low molar S:As ratios [26].

Removal of arsenic occurred faster at higher S:As ratios. At a molar S:As ratio of 20, a second order exponential relationship (k_2 = 4.8 (mol $L^{-1})^{-1}$ h^{-1}) explained 98 % of the observed variation [24]. Intermediate sulfur-arsenic complexes and free As(III) are less stable at high molar S:As ratios and low pH [22,23,26,39]. Due to this decrease in stability, As_2S_3 precipitation became more dominant and occurred faster at high molar S:As ratios and low pH [43]. Overall, removal of arsenic is highly dependent on speciation, S:As ratio and pH. By manipulating these parameters, it is possible to minimize reaction time and, as a result, to minimize reactor size and capital costs.

3.2. Arsenic sulfide precipitation in industrial wastewater

Experiments were repeated with industrial wastewater from a metal refining plant to assess the viability of this removal method in industrial relevant conditions and to evaluate the impact of other metal(loid)s, speciation and increased salinity (Table S18 - Table S20). Initial element concentrations and sample compositions have been provided in SI (Table S4 - Table S14). The behavior of arsenic, iron, tellurium, tin, copper, lead, cadmium, zinc, nickel, selenium and antimony in industrial wastewater was assessed as a function of the various S:As ratios (Figure 3). Excluding antimony, residual elemental concentrations after 2 h are shown.

The behavior of arsenic closely approximated the trends observed during synthetic As(III) experiments (Figure 1). Removal of arsenic and most elements was nearly immediate. At a molar S:As ratio of 2.5 mol mol^{-1} complete removal of arsenic was achieved, while at a S:As ratio of 1.5, only 70 % was removed, down to a residual concentration of 307 ± 67 mg L^{-1}. At a molar S:As ratio of ≥ 2.5, arsenic was removed to 6 ± 1 mg L^{-1}. IC analysis showed that 17 % of arsenic was present as As(V). Based on the lag in arsenic removal observed in the synthetic As(V) solution and synthetic mixtures of As(V) and As(III), it might be expected that S:As ratio and time required for removal would be higher in industrial wastewater due to the presence of 17 % As(V). This was however not observed. One or multiple components in the industrial wastewater may have affected the reduction of As(V) to As(III) and removal of arsenic, though this requires additional research. While elements such as selenium, tellurium, iron, antimony and zinc have been shown to catalyze either sulfide oxidation or sulfide interchange reactions, the catalysis of arsenate reduction by metal(loid)s remains a yet unexplored field that requires further investigation [44–46]. Such effects could impact the economics of arsenic sulfide removal from metallurgical wastewater significantly, as faster kinetics will result in smaller reactor sizes and lower capital costs.

Iron, zinc, nickel and selenium remained in solution. Tellurium and copper precipitated completely under all tested conditions, whereas precipitation of tin, lead, cadmium and antimony was dependent on the S:As ratio. The majority of these trends can be explained by the solubility of various metal sulfides. At the observed pH of 1.2 ± 0.3, arsenic sulfides and copper sulfides are the least soluble (solubility product, K_{sp}: $10^{-62.51}$ and 8 10^{-37} respectively, see Table S23), followed by lead sulfide (Ksp: 3 10^{-28}), cadmium sulfide (Ksp: 10^{-27}). Zinc sulfide (Ksp: 3 10^{-23}), nickel sulfide (Ksp: 4 10^{-20}) and iron sulfide (Ksp: 8 10^{-19}) remained in solution as these compounds are soluble in acid conditions [19,47,48]. The removal mechanisms for tin and tellurium remain unclear, though removal as tin and tellurium sulfide is possible [49–51]. While reduction by H_2S has been described for the similarly behaving selenium, an adequate description for tellurium requires additional research [52].

The S:As ratio affected the solubility of lead, tin, cadmium and antimony: up to a S:As ratio of 2.5 residual concentrations of lead and tin decreased, whereas cadmium and antimony concentrations reached a minimum at a S:As ratio 5. The solubility products of cadmium and tin sulfide (Ksp: 10^{-25}) are somewhat intermediate between copper sulfide and iron sulfide, which might help explain the increased removal observed at higher sulfide dosing [53]. At a S:As ratio of 20 the residual concentration of nickel increased, possibly due to the formation of small nickel sulfide particles or of polysulfide complexes, though the stability of such complexes at low pH requires further investigation [54–57]. Antimony showed similar trends as arsenic, i.e. an increased removal with increasing sulfide concentrations. Based on the low solubility product of Sb_2S_3 (Ksp: 10^{-25}) higher removal of antimony might be expected [33]. However, the concentration of dissolved antimony was already low at the start (0.31 ± 0.03 mg L^{-1}), providing a possible explanation for the limited removal. However, removal of antimony was only complete after 2 h. The time lag observed in the precipitation of antimony may imply a similar reduction mechanism to As(V) (Table S13). Further research, including determination of the antimony speciation, could confirm such behavior [58,59].

Differences in solubility resulted in a certain degree of selectivity towards arsenic: nickel, zinc, iron and selenium can be recovered separately from arsenic after As_2S_3 precipitation. Elements such as copper and tellurium co-precipitated with arsenic and, unless the precipitate is treated, will be lost when the sludge is disposed. Additional research could result in improved selectivity towards tin, lead and antimony and enhance the sole removal of arsenic, e.g. by varying pH, S:As ratio and reaction time.

3.3. Characterization of solid precipitates

All diffractograms displayed a primary peak at 18.55° and secondary peaks indicative of As_2S_3 (Figure 4, Figure S7). In the case of As(V), elemental sulfur was also observed. Besides As_2S_3, As(III) oxides such as As_2O_3 and As_4O_6 were also detected. It is likely that these oxides were the byproduct of exposure to oxygen prior to the XRD. Nevertheless, no As(V) oxides were detected and the reduced nature of the oxides is indicative of the reduction process described in reaction (6). These observations confirm reaction (5) in the case of As(III) and reaction (6) in the case of As(V), while excluding reaction (7) and computer simulations (Figure S3) [41,42]. Salts such as NaCl, Na_2SO_4 and $HNa_3(SO_4)_2$ were also detected in the diffractograms. These salts are likely the result of insufficient rinsing of the solids prior to drying. Additional information on the diffractograms can be found in the SI (Tables S22 - 29).

Comparison of Raman spectra (Figure 5) to spectra of several As-S-O species (As_8S_9, As_4S_5, AsS, As_2S_3, As_2O_3 and S) and data reported in literature showed that the broad peaks centered at 335 – 341 cm^{-1} was best explained by amorphous As_2S_3, also reported as g-$As_{40}S_{60}$ [26,60–63]. The small displacement of the spectrum of the industrial sample may be due to small differences in measuring conditions such as temperature or humidity. The small secondary peak at 489 – 491 cm^{-1} could be attributed to S-S vibrations due to the oxidation of excess sulfides or the formation of As-S-S-As bridges [63]. In the case of As(V) an additional peak at 472 cm^{-1} can be discerned, indicating the presence of elemental sulfur [64]. An additional, unidentified peak at

153 cm^{-1} was observed in the spectrum of the industrial wastewater. Taking into account the diffractograms from the XRD, these results indicate that reaction (5) in the case of As(III) and reaction (6) in the case of As(V) are the dominant pathways.

SEM-EDX was used to visualize and get an indication of the molar S:As ratio in the precipitates (Figure 6, Figure S8, Table S21). The S:As ratio in the precipitates from the synthetic As(III) solution approximated 1.5 ± 0.05 mol mol^{-1}, indicative of the presence of As_2S_3. The S:As ratio in the industrial precipitates appeared to be higher at 1.7 ± 0.2 and 2.0 ± 0.4 mol mol^{-1}. Similarly, the EDX indicated a higher S:As ratio in precipitates of the As(V) solution, approximating a molar ratio of 2.40 ± 0.09 and 2.5 ± 0.3 for S:As ratios of 5 and 20 respectively. This increase was likely caused by the presence of elemental sulfur S^0 interspersed with As_2S_3 precipitates, as no individual S^0 particles could be observed (Figure 6E). Given that 17% of arsenic in industrial wastewater was present as As(V), the molar S:As ratio of 1.7 ± 0.2 correspond well to the expected stoichiometric value of 1.67. At higher sulfide dosing, the elevated S:As ratio of 2.0 ± 0.4 in the precipitate may be the result of the precipitation of additional metal or metalloid sulfides, of unintentional oxidation of surplus sulfides during rinsing or a consequence of the qualitative nature of energy dispersive X-ray spectroscopy.

The different composition of the solid precipitates may explain the difference in visual appearance. The solids of As(III) wastewater were orange-yellow in color (Figure 6A), typical of orpiment [65]. Elemental sulfur in solids from As(V) wastewater may cause the bright yellow color shown in Figure 6B. The brown color of the industrial precipitates (Figure 6C) was likely caused by the co-precipitation of other elements. Small, metastable crystals from the As(III) wastewater coagulated over time (see flocs in Figure 6A and Figure S8A, B and C), while such coagulation did not occur in the experiments with As(V) wastewater (Figure 6B and Figure S8D, E and F). In a previous study precipitates from As(III) wastewater displayed better coagulation and flocculation properties and a more neutral zeta potential. Particles from As(V) solutions are electrostatically repelled due to their negative charge, while particles from the As(III) solution did not repulse each other as strongly, allowing the formation of larger flocs. Particles from As(V) wastewater were also smaller in size, which was confirmed by visual observations and SEM images in this study (Figure 6 and Figure S8) [24]. Sulfide overdosing (*i.e.* high sulfide to metal ratios) is known to result in smaller metal sulfide particles and poor flocculation and coagulation [18,66,67]. Given that As(V) reduction to As(III) is slow compared to the fast precipitation of As(III) as As_2S_3, temporal S:As(III) ratios were likely higher in As(V) experiments than in experiments with synthetic As(III) or industrial wastewater. In the As(V) experiments, the supply of As(III) was slow due to the rate limiting reduction of As(V). Any As(III) resulting from the reduction quickly precipitated as As_2S_3, keeping the As(III) concentration in solution low and S:As(III) ratio high.

The Raman spectra, XRD and EDX indicated the presence of As_2S_3 in both industrial and synthetic samples. Presence of elemental sulfur was confirmed in the synthetic samples containing As(V). These results confirm the hypothesis that As(III) precipitated as As_2S_3 (reaction (5)) and that this precipitation was preceded by a reduction of As(V) to As(III) in the case of As(V) containing samples, with the concomitant oxidation of H_2S to elemental sulfur (reaction (6)). Consequentially, models that postulate direct precipitation of As_2S_5 (Figure S3) need to be reconsidered [41,42]. Taking into account the observed kinetics, the reduction of As(V) to As(III) is the rate limiting step in the removal of arsenic from As(V) containing wastewaters.

4. Conclusions

This study shows that precipitation of As_2S_3 can efficiently remove arsenic from metallurgical streams: it produces little waste sludge and some selectivity towards other metal(loid)s is possible. To translate such a process from lab-scale setup with synthetic wastewater to a larger and continuous system treating industrial wastewater, several factors have to be taken into account. First, speciation is an important factor: In the case of As(V) containing industrial wastewaters, reduction of As(V) to As(III) may require increased S:As ratios and longer reaction times, resulting in poor settling/coagulation, high required hydraulic retention times and increased capital costs [24]. In those cases, it may be interesting to use a two stage approach where As(V) is first reduced to As(III) at low S:As ratios and precipitated as As_2S_3 in a second stage. However, our results showed that the removal of As(V) from complex industrial wastewater requires further investigation and cannot be merely approximated by synthetic tests. A time lag and increased S:As ratio were not observed as expected in the industrial wastewater containing As(V).

Besides speciation, pH also has a significant effect on arsenic sulfide precipitation. Removal of arsenic from As(V) containing wastewater occurs faster at low pH, As_2S_3 precipitates are more stable in acidic environments and at pH 2 or lower and no increase in As_2S_3 solubility at S:As ratios > 4 is observed [21,26,35,38,68]. Finally, by focusing on complex wastewaters containing multiple metal(loid)s, future research can improve selectivity by varying parameters such as pH, S:As ratio and reaction time, additionally boosting the possible recovery of valuable metal(loid)s embedded in metallurgical wastewater.

Associated content

Eight figures, thirty tables and three texts are included in the SI.

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Figure captions

Figure 1: Dissolved arsenic concentrations after the addition of sulfides at varying molar S:As ratios in a synthetic As(III) solution of pH 2.1 ± 0.4. after 1 min (*N* = 3).

Figure 2: Dissolved arsenic concentrations as a function of time after the addition of sulfide at varying molar S:As ratios in a synthetic As(V) solution, including the simulated arsenic concentrations based on the second order model for the S:As ratio of 20 (pH 1.8 ± 0.4, N = 3).

Figure 3: Behavior of metal(loid)s after the addition of various amounts of sulfides (expressed as initial S:As ratio) at pH 1.2 ± 0.3 (after 2 h, excluding Sb (0 h)). A) Residual concentrations of arsenic, B) iron, tellurium, tin, C) copper, lead, cadmium, zinc, D) selenium, nickel and antimony (N = 3). Note the different scales in the graphs.

Figure 4: X-ray diffractograms (XRD) of the arsenic precipitates S:As molar ratio of 2.5. A) Synthetic As(III) wastewater B) Synthetic As(V) wastewater C) Industrial wastewater.

Figure 5: Raman spectra of the arsenic precipitates S:As molar ratio of 2.5. 1) Synthetic As(III) wastewater 2) Synthetic As(V) wastewater 3) Industrial wastewater.

Figure 6: A-C) Close up (30 min) and (D-F) scanning electron microscopic (SEM) image of precipitates formed during the experiments with an initial S:As molar ratio of 20. A,D) Synthetic As(III) wastewater, B,E) Synthetic As(V) wastewater, C,F) Industrial wastewater. White dots denote the location of the energy dispersive X-ray spectroscopy (EDX) spectra (Table S21).

Figures

Figure 1.

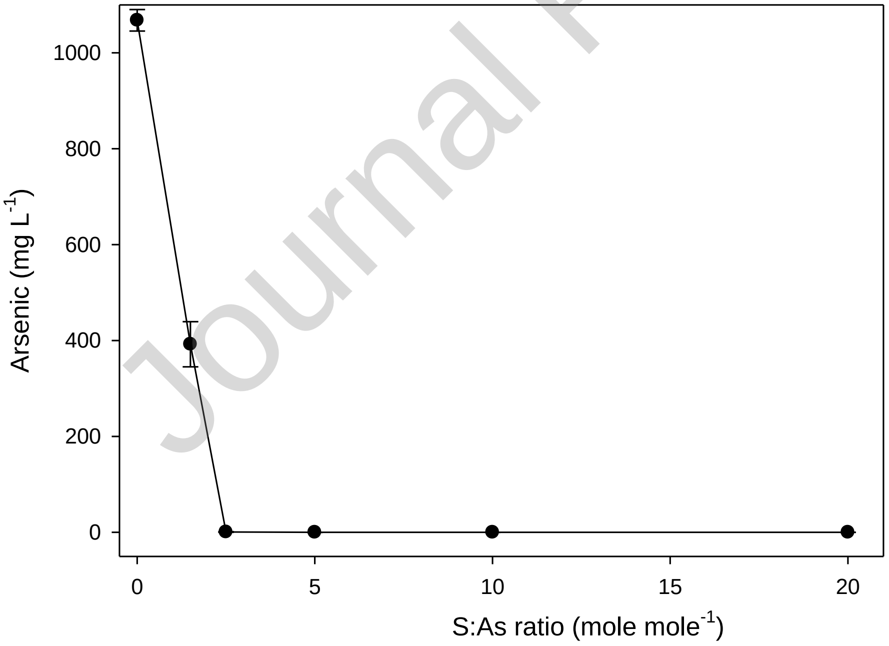


Figure 2.

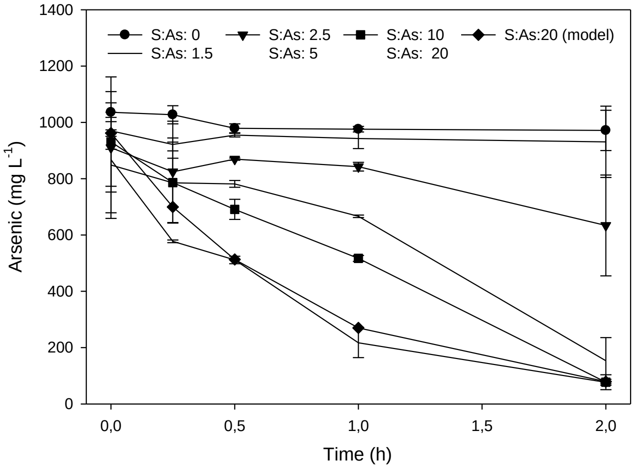


Figure 3.

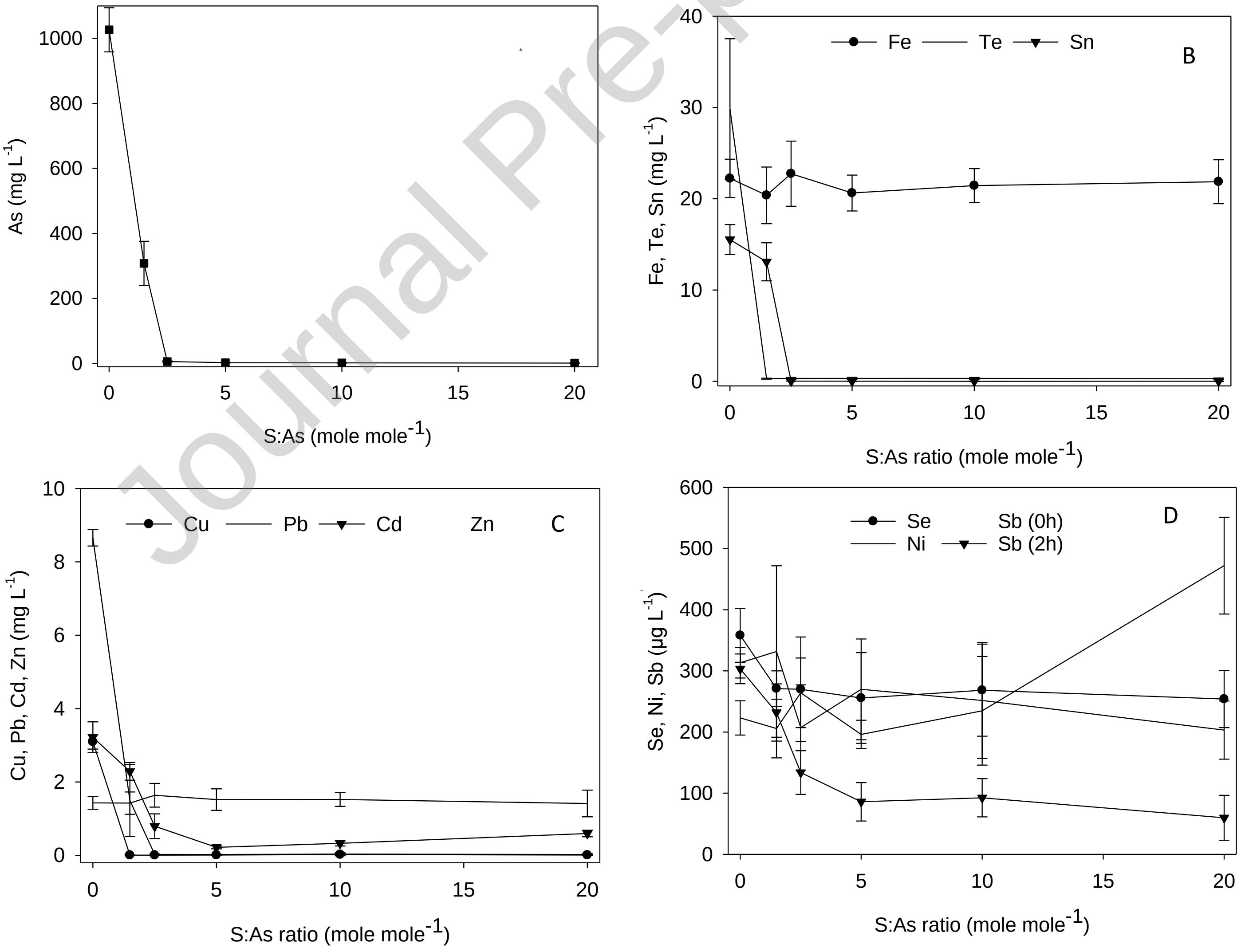


Figure 4.

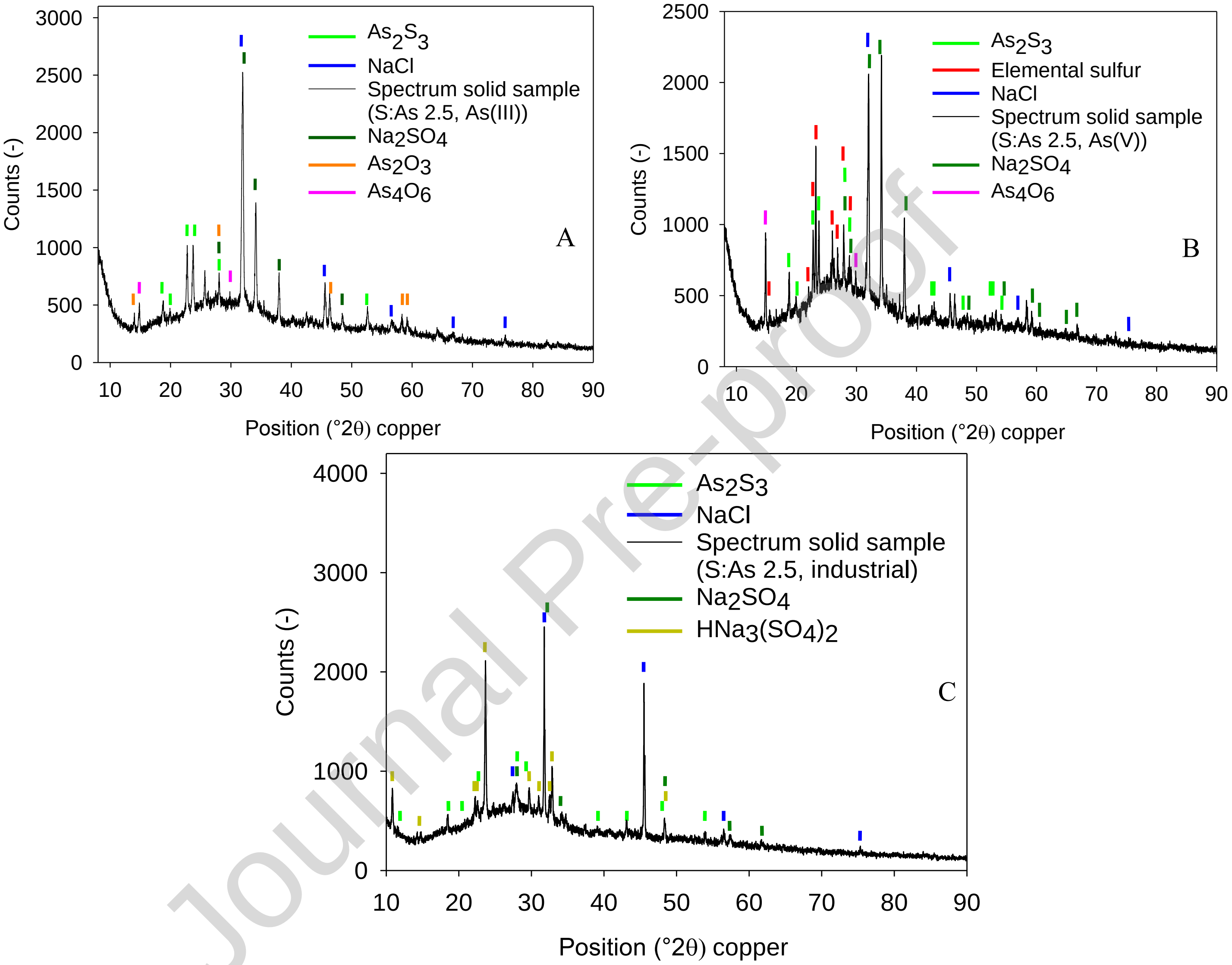
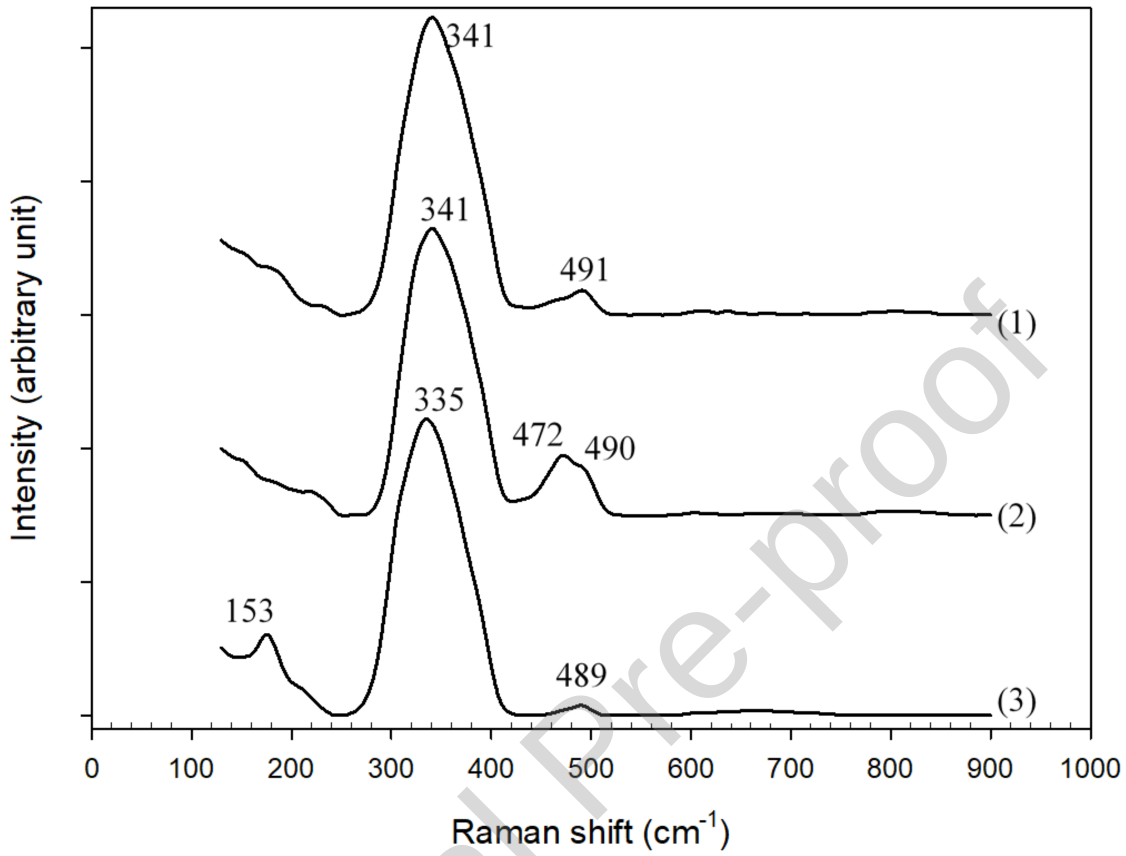
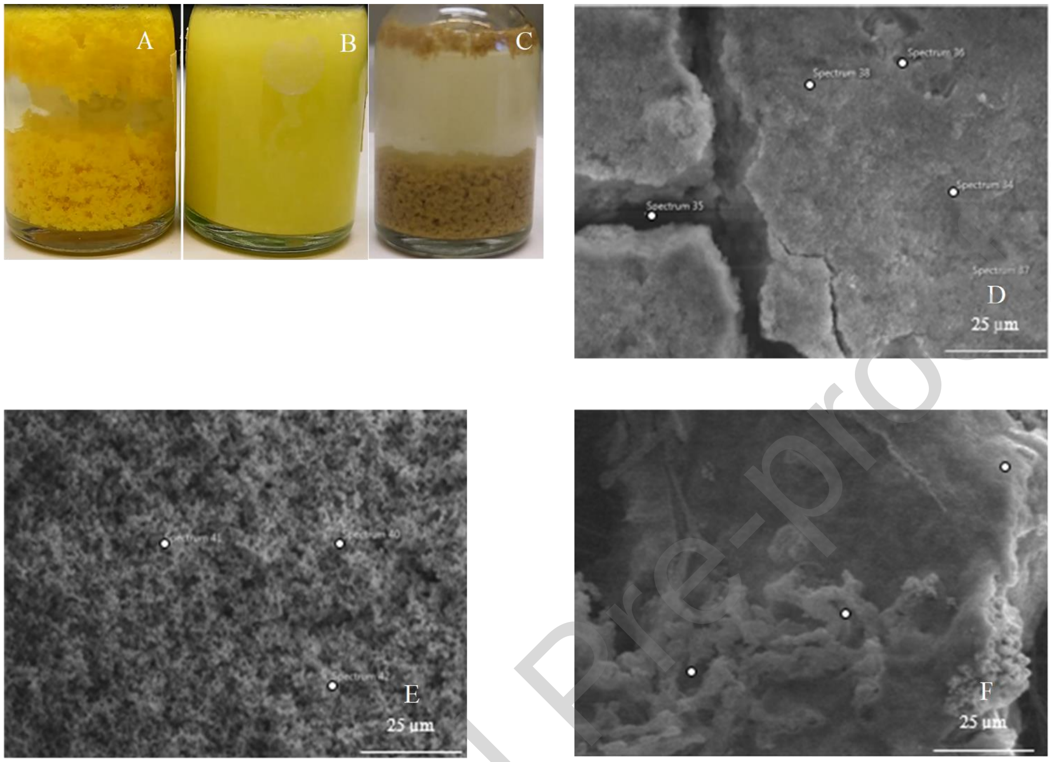

A
Counts (-)
0
500
1000
1500
2000
2500
3000
10
20
30
40
50
60
70
80
90
Position (°2θ) copper
As2S3
NaCl
Spectrum solid sample (S:As 2.5, As(III))
Na2SO4
As2O3
As4O6
B
Counts (-)
0
500
1000
1500
2000
2500
Position (°2θ) copper
As2S3
Elemental sulfur
NaCl
Spectrum solid sample (S:As 2.5, As(V))
Na2SO4
As4O6
C
Counts (-)
0
1000
2000
3000
4000
Position (°2θ) copper
As2S3
NaCl
Spectrum solid sample (S:As 2.5, industrial)
Na2SO4
HNa3(SO4)2

Figure 5.



341
341
491
335
472
490
153
489
(1)
(2)
(3)
Intensity (arbitrary unit)
0
100
200
300
400
500
600
700
800
900
1000
Raman shift (cm^{-1})

Figure 6.


A
B
C
Spectrum 36
Spectrum 38
Spectrum 34
Spectrum 35
Spectrum 37
D
25 µm
Spectrum 41
Spectrum 40
Spectrum 42
E
25 µm
F
25 µm

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- Arsenic sulfide precipitation was tested in industrial relevant conditions
- As(V) reduction to As(III) is the rate limiting step in the precipitation of As_2S_3
- As(V) reduction in synthetic wastewater results in poor coagulation and flocculation
- As(V) in industrial wastewater did not result in a removal lag and poor coagulation
- Selective metal precipitation is dependent on the applied S:As ratio