



Article Leaching Performance of Nanotechnology-Induced High-Arsenic-Bearing Tooeleite-like Mineral Nanowaste

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Abstract: For arsenic decontamination from groundwater, arsenic crystallization is becoming adopted due to its sustainability and economic benefits. However, arsenic crystallization technology is a two-step process, which makes it complex and generates hazardous waste. Successful efforts toward making it a single-step process are presented here. The addition of nanorods and ball-milled zinc sulfide nanoparticles to arsenic-contaminated water result in highly monodispersed and high-arsenic-containing mineralized nanowaste with a crystalline structure similar to the mineral Tooeleite ((Fe³⁺₆(As³⁺O₃)₄SO₄(OH)₄·4H₂O)). This study reports the results of a short-term stability test based on a toxicity characteristic leaching procedure and a long-term stability test of the mineralized synthetic nanowaste produced from water treatment. The Tooeleite-like mineralized nanowaste passed short-term stability tests. Arsenic in the leachate were found to be 1.1 ± 0.2 mg L⁻¹ and 4.8 ± 0.3 mg L⁻¹ from waste generated by the nanorod and ball-milled nanoparticles, respectively. The crystallinity was well preserved, as observed from the post-stability-test diffraction patterns, consequently proving that the waste product can be non-hazardous and therefore would not require any secondary treatment before final disposal.

Keywords: arsenic; mineralized nanowaste; high stability; low solubility

1. Introduction

Arsenic (As) is among the most toxic contaminants in groundwater, owing to its widespread presence in aquifer rocks and anthropogenic activities [1]. As is introduced to the environment through many agricultural and industrial sources discharging arsenic-based compounds, mixing with water streams, or leaching into groundwater [2]. The detrimental impacts of arsenic depend on the concentration of arsenic and its chronic exposure to humans [3]. Exposure to arsenic can cause skin cancer, cancer of the bladder, diabetes, and lung diseases [4]. It may also affect the photosynthesis of plants and prove lethal to many aquatic organisms [5].

There has been intense research on suitable arsenic remediation methods. For the effective adoption of the developed technologies in many African/Asian countries, cost-effectiveness and easy-to-use alternatives are preferred. Many adsorbents have been used to remove arsenic from water, yielding attractive removal rates with very little/minimal investment [6,7]. However, the post-handling of the used adsorbent is another serious concern due to the leaching of arsenic [8,9]. It should also be noted that the reduced form, As(III) is much more toxic than As(V), making the removal of As(III) a primary concern [10]. However, the literature further suggests that the adsorption/fixation of As(III) is more challenging than As(V). At the same time, the As(III) species is generally higher in concentration than As(V) in groundwater [11]. The charge neutrality at near-neutral pH accounts



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for the lower fixation rate of As(III) and makes it more mobile than As(V) [12,13]. Considering these points, adsorption seems to be an ineffective methodology for removing As(III). A lack of knowledge about the desorption of arsenic from the adsorbent makes adsorption-based decontamination processes further unappealing/undesirable [14–16]. In brief, minor changes in the chemical or environmental parameters (pH, redox potential, natural organic matter (NOM), competitive ions) may result in controlling the adsorption/desorption of arsenic [17].

The post-handling of waste is generally carried out by performing the solidification/stabilization of arsenic, which, if mismanaged during waste handling, may become a much more significant concern [18,19]. Other alternatives for removing arsenic are cement encapsulation/vitrification [20], which are either expensive or not commercially available. The literature further reveals that arsenic removal via the arsenic crystallization technique (ACT) is increasingly becoming adopted due to its sustainability and effective removal rate [21]. In brief, ACT involves the conversion of arsenic to waste minerals with high arsenic content and long-term stability, which would show low arsenic solubility when disposed of as municipal solid wastes. However, ACT is a two-step process (removal followed by mineralization), and it has its limitations [22]. These steps of ACT (1) are complex and time-consuming, (2) require hazardous waste handling due to possible leaching, (3) are costly, and (4) are ineffective when there is a low concentration of arsenic in the waste or a high waste volume.

Considering the complexity of ACT for the effective arsenic removal from iron (Fe)/ arsenic-contaminated water, a synthetic waste material similar in crystallinity to that of the natural arsenic-bearing mineral Tooeleite can be produced using specialized nanostructures of zinc sulfide (ZnS) as the precursor [11]. The synthetic nanosized waste is similar to Tooeleite, and it is also found to be nanoscale with higher stability than natural Tooeleite [23]. Unlike the Tooeleite mineral, the developed Tooeleite-like mineral waste also lacks sulfate ions [11]. The current process encounters the limitations associated with the ACT by making it an advanced single-step ACT process. It is also worth mentioning that the resulting Tooeleite-like mineral has arsenic in the form of As(III), while Tooeleite contains a combination of As(III) and As(V). The presence of arsenic in the reduced form within Tooeleite-like mineral waste makes its stability imperative due to As(III)'s higher desorption rate and toxicity. The principal objective of this study was the stability analysis of the developed waste in assessing the leachability/release of As(III) from and the geochemical changes that may occur in landfill situations. This article compares the stability of the wastes generated from the treatment of arsenic-contaminated water utilizing specialized lab-synthesized ZnS nanorods and a readily available, cost-effective ZnS ball-milled nanomaterial. The results from this study can be used to evaluate whether the product waste can be efficiently and sustainably handled.

2. Materials and Methods

2.1. Materials

Octadecylamine (ODA) (Sigma, Kawasaki, Japan, >99%), potassium ethyl xanthogenate (Sigma, >96%), and zinc acetate dihydrate (Sigma, Kawasaki, Japan, 98%) were used as received. The ODA was stored in argon for the entire time before use. Ethanol absolute (VWR International, Radnor, PA, USA, Normapur) and chloroform (Emparta ACS, Sigma-Aldrich, St. Louis, MO, USA) were used for synthesis. KOH (Chem Labs, Faridabad, Haryana, India, 85%), As₂O₃ (Nice Laboratories, Bangalore, India, ~99.5%), and FeCl₃ (Sigma-Aldrich, St. Louis, MO, USA, Reagent grade 97%) were used for preparing the arsenic and iron solution, and ZnS (10 μ m, Sigma-Aldrich, St. Louis, MO, USA 99.99% trace-metal basis) bulk-size hexagonal crystalline phase was used for the effortless production of nanoparticles utilizing the top–down approach. Deionized water (resistivity 18.2 M Ω cm) was used to make artificial arsenic-contaminated water from a Millipore filter system. Glacial acetic acid (Sigma-Aldrich, St. Louis, MO, USA, ACS Reagent, ≥99.7%) and sodium hydroxide (NaOH) (Sigma-Aldrich, St. Louis, MO, USA, ACS reagent ≥ 97%) were

used to make leaching solutions for short-term and long-term stability tests. Planetary ball mills (Pulverisette 7 premium line, Fritsch GmbH, Idar-Oberstein, Germany) were used for ball milling the bulk ZnS for the production of nanoparticles. A Millipore Swinny stainless steel syringe filter holder for 13 mm membrane filters, with a Millipore Durapore HVLP 13 mm diameter filter with a pore size of $0.45 \,\mu$ m, was used to extract the leachate. An Orion StarTM A221 pH Portable meter was used for measuring the pH of leachate solutions.

2.2. Mineralized Nanowaste Formation

2.2.1. ZnS Precursor Synthesis

ZnS nanorods of average size 8–10 nm in length and 1–2 nm in diameter were prepared according to Belman et al. (2011) [24]. Briefly, the nanorod precursor, zinc-ethylxanthate, was produced by mixing 3.00 g of potassium ethyl xanthogenate and 2.05 g of zinc acetate dihydrate in water. Before use, the precursor was filtered, which was followed by filtration, repeated washing, and vacuum drying. Nanorods of ZnS were prepared by dissolving 0.08 g of the dried precursor zinc-ethylxanthate into 1.53 g of molten ODA under argon gas at 100 °C. Before adding the precursor, ODA was exposed to a CO₂ atmosphere for 30 min. After adding the precursor, the temperature was increased to 105 °C for 5 min and then quickly increased to 130 °C for another 10 min, and then the reaction was stopped. The nanorods were collected by flocculating the sample with ethanol and later separating it with the help of a centrifuge [25]. Finally, the nanorods were redispersed in chloroform, which was followed by drying and stored in a vacuum prior to its use and characterization.

We tested the cost-effectiveness of methods for producing specialized nanorods, ZnS nanoparticles, by the top–down route (such as ball milling), where 10 µm sized bulk materials were dry ground in a planetary ball-mill machine to form nanoparticles ranging from 15 to 500 nm in diameter [26]. Briefly, powder ZnS was accurately weighed and then transferred to a hardened chrome-steel vial of 80 mL volume. The vial with lid was perfectly sealed and mounted on the rotating disk of the ball mill. The ball-to-powder ratio was 16:1, and the high-energy ball-milling was carried out at 400 rpm for 210 min. After the prerequisite milling, ZnS particles were collected from the vial and sampled for characterization of the crystalline phase in X-ray diffraction and imaging to note the particle size formed under transmission electron microscopy.

2.2.2. One-Step Arsenic Bearing Waste Generation

High arsenic-containing, monodispersed, Tooeleite mineral-like waste was generated when iron and As(III) containing water were treated with ZnS nanorods [11]. Iron and As(III) containing water were synthetically prepared from As_2O_3 and FeCl₃ salt and neutralized by 1 N KOH solution. These solutions were treated with 1.0 mg of ZnS nanorods (AF-NR = Arsenic + Ferric NanoRods) and 1.0 mg of ZnS ball-milled (AF-BM = Arsenic + Ferric Ball Milled) at 70 °C for 3 h, which precipitated high-arsenic-bearing nanowaste. The generated mineralized nanowaste was collected after filtering (Whatman42 filter paper) the reaction mixture and dried under vacuum. The yield of the generated waste under different ZnS treatments and consequent Fe:As ratios was recorded. The crystalline structure of each resultant waste was similar to the natural As(III) bearing mineral Tooeleite. The stability tests were carried out on the generated mineralized nanowaste (AF-NR and AF-BM). The residues formed after 3 h of reaction were collected after filtering the solution through a Whatman 42 filter paper. The collected residues were air-dried, as is typically the case in an actual treatment facility, and used for different stability tests.

2.3. Short-Term Stability Test

The Toxicity Characteristic Leaching Procedure (TCLP), which was developed by the United States Environmental Protection Agency or US EPA (detailed in US EPA Method 1311) [27], is one of the most commonly used procedures to check the stability of wastes. The TCLP test is intended to represent the average leachate concentration over the assumed 3 to 10 years of the leaching period, not the peak concentration. Briefly, in TCLP, glacial acetic acid and sodium hydroxide buffer at pH 4.93 \pm 0.05 were used. Acetic acid was chosen because it is considered the most prevalent form of acid in municipal solid waste (MSW) leachate. TCLP was conducted for 18 ± 2 h, and a 20:1 liquid/solid (L/S) ratio by weight was adopted for waste extraction. The US EPA suggested this ratio for suitability in simulating a mismanaged solid waste processing facility. The TCLP methodology assumes a 3 m landfill depth, 100 cm annual rainfall, 5% co-disposal with municipal waste, 100% rain percolation through the landfill, 1 g-cm⁻³ waste density, and three years of leaching. The 20:1 ratio of the TCLP methodology represents a significantly more extended leaching period of approximately 3–10 years. The TCLP tests were performed following the standard method [28] in an end-over-end instrument at 30 ± 2 rotations per minute (RPM). The buffer solution was prepared by mixing 5.7 mL of glacial acetic acid in 500 mL reagent water, which was followed by the addition of 64.3 mL of 1 N NaOH solution and later diluting it to a volume of 1000 mL. After 20 h of the run, the solid–liquid slurry mixture was filtered using a 0.45 µm membrane filter in a Swinny stainless steel syringe filter. Quantitative analysis of the filtered sample was carried out to determine the amount of arsenic leached out and further compared with the USEPA TCLP test's standard limit for As, which is 5 mg L^{-1} (only below this level of leaching concentration can the waste be classified as non-hazardous).

A modified short-term TCLP was also performed by increasing the L/S ratio to 200:1, which was used for the long-term leaching test, keeping other parameters such as pH, time, and RPM similar. A higher volume of added liquid should ensure more leaching due to a greater solid–liquid interaction. However, an increased volume of liquid will decrease the concentration of arsenic, and this result was compared with the long-term stability test, where 200:1 L/S was maintained. After 20 h of rotation, the tests were stopped, and leachate was extracted for quantitative analysis. The tests were repeated thrice to check the reproducibility of the results.

2.4. Long-Term Stability Test

Unlike short-term stability tests, no definitive tests define long-term stability. Shortterm stability tests like TCLP may be unsuitable for evaluating long-term behavior, as the solid waste residues may undergo chemical changes with time due to pH (pH 3 to 5), temperature, and prevailing redox potential [29]. Furthermore, the specific test conditions may not represent the actual disposal conditions under which the solid waste residues are stored in the open and can be affected by acid precipitation [30–32]. A separate methodology was adopted to understand the long-term stability of the developed mineralized nanowaste. The long-term stability test was carried out for 200 days at four different pH conditions. Instead of glacial acetic acid, concentrated Suprapur HNO₃ and NaOH were used to obtain the desired pH levels (4, 5, 7, and 9). HNO₃ was chosen as it closely resembles acid rain [33]. Here, like the modified short-term leaching test, the liquid:solid ratio was maintained at 200:1. A higher volume ensured enough liquid was available for the longer timeline of the test. The tests were repeated in an end-over-end rotation at four different pH levels, which were chosen to cover the entire pH range that can be present in a landfill. The wide pH range also ensured that different anionic and neutral forms of As(III) and As(V) (if formed by the oxidation of As(III) in a long-term study) can be studied. Leachate collection and analysis were carried out throughout the 200 days of the experiment with a 0.45 μ m pore size filter paper in a Swinny stainless steel syringe filter. The volume of leachate solution removed from the container was replaced with a fresh pH solution. The solid filtered onto the filter paper was also returned after leachate extraction. This reintroduction of fresh pH solution and the degraded solid residue ensured (i) maintenance of the same pH throughout the experiment, (ii) an L:S ratio of 200:1, and (iii) the presence of already degraded developed waste until the 200th day.

2.5. Characterization of Samples

The quantitative analysis for the total arsenic and iron of these leachates was carried out by ICP-OES (Perkin-Elmer Optima 2100 DV, Hong Kong, China), ICP-MS instruments (iCAP-RQ ICP-MS Thermofisher, Waltham, MA, USA). The samples were prepared following standard protocol. Five-point calibration was completed to obtain the unknown concentrations. The data were cross-checked using standard certified reference materials (CRMs) with a recovery of 98%. An internal standard (Indium) was added to each sample to check the data reproducibility. Powder X-ray diffraction (PXRD) of the slightly pressed dried residues and after short-term leaching tests were carried out at a 0.775 Å wavelength of Indian beamline, Photon Factory, KEK, Japan, and at a 0.6635 A wavelength of RRCAT, Indore, India, respectively. The morphology, composition, and structure of nanorods, ball-milled nanoparticles, AF-NR, and AF-BM were probed in a JEOL-JEM 2100F electron microscope using a 200 kV electron source ultrahigh-resolution transmission electron microscope (UHR FEG-TEM), which was equipped with energy-dispersive X-ray spectroscopy. X-ray photoelectron spectroscopy (XPS) experiments were carried out in an Omicron photoemission spectrometer equipped with an EA-125 analyzer and Mg K_{α} X-ray source to collect iron 2p and arsenic 3d core level spectra of the generated AF-NR and AF-BM waste. All statistical correlations were carried out in Origin Pro Version 2020b (9.75) software by Origin Lab (Northampton, MA, USA).

3. Results and Discussion

3.1. Characteristics of Mineralized Nanowaste

The PXRD data (Figure 1a) obtained at the 0.775 Å wavelength for both the nanowastes-AF-NR and AF-BM—matched the crystalline structure of the natural arsenic-bearing mineral Tooeleite [11]. However, the generated waste did not have sulfate in the crystalline structure as observed in the Tooeleite mineral (general formula $Fe_6(AsO_3)_4SO_4$ (OH)₄.4H₂O). The TEM images (Figure 1b,c) for AF-NR (=nanowaste from ZnS nanorod treatment) and AF-BM (=nanowaste from ball-milled ZnS nanoparticles), respectively, reveal rice-like spindles-shaped particles of average length of ~700 nm. The inset of Figure 1b,c shows the actual waste product, which is yellowish for AF-NR and yellowishorange color for AF-BM, while both were in powder form. However, the product formed by nanorod treatment, viz AF-NR particles, showed better monodispersity, well-maintained morphology, and smooth edges compared to the ball-milled treated waste product AF-BM. The XPS analysis (Figure 1d,e) shows that the form of iron in both solid wastes is Fe(III) (binding energy of ~711.2 eV ($2p_{3/2}$) and ~724.5eV ($2p_{1/2}$)), and the form of arsenic is mainly in the As(III) (binding energy of ~44.6 eV) oxidation state. The elemental ratio of Fe:As in the solids was obtained from XPS peaks, which were normalized by considering the photoionization cross-section for the specific core. The elemental ratio was found to be 1.6:1 for AF-NR, whereas in AF-BM, it was found to be 2.4:1. AF-BM seemed to contain a higher amount of iron in the generated waste, which may explain the orange tinge in the final product. AF-BM can also contain ferrihydrite nanominerals, which are presumed to be the pathway to form Tooeleite [23]. The yield of waste was significantly (p < 0.01) higher in ball-mill ZnS nanoparticle-treated arsenic–iron solution (50.5 ± 1.2 mg) compared to the nanorod-treated solution (46.7 \pm 1.0 mg) from the same starting concentration of iron and arsenic. However, the arsenic removal rate was above ~95% for ZnS nanorod-treated water and above ~86% in ZnS ball-mill-treated water.

The formed nanospindles' crystalline structure from either treatment closely resembled the natural arsenic-bearing mineral Tooeleite. However, the morphology and size of the mineral is quite different from abiotic or biotic Tooeleite mineral [34,35]. Furthermore, the generated waste has no sulfate anion in its structure, which is an integral part of naturally occurring Tooeleite minerals and may have been substituted by arsenite anion, as observed previously [35]. The same study also suggested that sulfate-free Tooeleite minerals may have more significant potential in arsenic removal and immobilization, as the coordination structure of sulfate-free Tooeleite is close to the ideal crystal structure [35], which should be the case in the present study. Moreover, the well-controlled morphology, monodispersity, and smooth edges observed in the nanowaste generated from ZnS nanorods can provide higher stability toward the leaching of arsenic from the nanowaste structure.



Figure 1. Shows (**a**) powder X-ray diffraction pattern of generated waste AF-BM and AF-NR taken at 0.775Å wavelength with identified hkl plane corresponding to Tooeleite, shows TEM images of (**b**) AF-NR, (**c**) AF-BM, inset shows actual product; (**d**,**e**) shows binding energy of iron 2p and arsenic 3d of AF-BM and AF-NR, obtained from X-ray photoelectron spectroscopy.

3.2. Short-Term Stability Test

Quantitative analysis confirmed that AF-NR and AF-BM mineralized nanowastes convincingly pass the TCLP test. Figure 2a shows the quantitative result of the short-term stability test obtained following the standard US EPA TCLP and modified TCLP method in the AF-NR and AF-BM waste products. The concentration of arsenic leached out from the AF-NR was 1.1 \pm 0.2 mg L⁻¹, which was below the allowed range of 5.0 mg L⁻¹ (blue dotted line from Figure 2a). A comparison of leaching from AF-NR against the literature-reported leaching of bulk actual Tooeleite mineral suggests that the leaching from AF-NR is almost 100 times below the leaching observed in reported studies [22,33] and almost ten-fold less than the sulfate-free Tooeleite mineral [35]. In the 2018 study, Yang et al. observed that arsenic showed a lower tendency to leach from the waste as the pH of the waste generation reaction increased, which is in line with the present observations [35]. The nanotechnology-induced synthesis of a Tooeleite mineral-like (highly monodispersed) solid [11] may be much more stable than Tooeleite synthesized conventionally at low pH [22]. The waste produced from the cost-effective water treatment with ball-milled ZnS nanoparticles, AF-BM, was just below the limit of 5 mg L^{-1} . The concentration of arsenic was found to be 4.8 ± 0.3 mg L⁻¹. However, this concentration was also below the observed leaching concentration in sulfate-free and sulfate-bearing Tooeleite minerals, which ranged from 14.1 (at pH 1.94) to 35.9 (at pH 1.89), depending on the pH. Therefore, the ZnStreated production of sulfate-free Tooeleite was more attractive than sulfate-Tooeleite for arsenic immobilization.



Figure 2. Shows (**a**) Toxicity Characteristic Leaching Procedure (TCLP) test arsenic leaching concentration of AF-NR and AF-BM nanowaste, the blue dotted line represents the TCLP test level above which an arsenic-bearing waste can be termed hazardous; (**b**) shows the amount of arsenic lost with respect to initial arsenic present in the wastes after the TCLP test and the corresponding As:Fe ratio of AF-NR and AF-BM; (**c**) shows powder X-ray diffraction patterns of wastes after the TCLP test at a 20:1 liquid:solid ratio and modified TCLP at a 200:1 liquid:solid ratio, obtained at 0.6635 Å wavelength, with identified hkl plane to show that post-TCLP, the product primarily holds a Tooeleite structure.

A comparison between the modified TCLP ratio (200:1) and standard TCLP ratio (20:1) for both cases reveals that the leaching was within the standard TCLP limit (Figure 2a). The pH of the final solution was observed to be 3.2 ± 0.5 in the standard TCLP test and 4.2 ± 0.7 in the modified TCLP test and was different from the previous observation of the Tooeleite-mineral leaching test [33], where the pH varied from 4.6 to 7.4. This acidic change in pH of the buffer could be attributed to the nanostructure of mineralized nanowaste, which may facilitate hydroxyl ion adsorption on the surface and/or the formation of iron (oxy) hydroxide from the leached Fe, forming at very low pH [36]. However, a complete understanding of pH reduction in leaching analysis warrants further study.

The Fe:As ratio was higher in the final waste product AF-BM compared to AF-NR (Figure 2b). AF-BM leached out five times more arsenic with respect to initial arsenic content in the solid than AF-NR. The morphology and the irregular structure of the AF-BM waste may have facilitated easier dissolution, as irregular edges can provide more surface area for the buffer to enhance dissolution. The XRD data obtained at 0.6635 Å wavelength (Figure 2c) show that even after a rigorous US EPA TCLP test, the AF-NR and AF-BM residue has a crystalline feature, suggesting that the crystal dissolution is incomplete, and the structure is stable enough to hold arsenic in a mineralized form. The normalized intensity of AF-NR and AF-BM for the TCLP test (20:1) and modified TCLP test (200:1) shows the peaks observed in the Tooeleite mineral. However, AF-BM has lost more crystallinity than AF-NR nanowaste after the TCLP test; the most intense peak of Tooeleite at 001 (hkl) was significantly less in intensity in AF-BM. Peaks of AF-BM also presented a wider FWHM compared to AF-NR, which suggests a reduction in particle size post-TCLP test.

3.3. Long-Term Stability Test

3.3.1. Arsenic Leaching Using Inorganic Acid

In the first 24 h of the long-term stability test, leached arsenic was 2.5 times higher than in the short-term TCLP test for AF-NR and 1.5 times higher for AF-BM at pH 5. This indicates that an inorganic acid environment can enhance the leaching of arsenic from the crystalline structure. The cumulative concentration (Figure 3) of leached arsenic in the long-term stability test varied widely at different pH solutions. In the AF-NR sample, the amount of total arsenic leached was approximately ten times higher than that of the short-term stability test; in AF-BM, it was three times higher. Under all pH conditions, AF-BM showed a significantly higher (2 to 4 times) potential to leach arsenic than AF-NR. The results show that arsenic leaching is more acid-dependent than pH-dependent, with leaching higher in inorganic acid even in the first 24–108 h of the test. Thus, changing the acid form (here, HNO₃ was used instead of glacial acetic acid) for maintaining the pH can significantly affect arsenic leaching from the waste product.

At pH 4, the leached As concentration from the AF-BM solid was found to plateau within the 10th day of the long-term stability test, with negligible leaching until day 200. In the case of AF-NR at pH 4, the leaching of arsenic was slow at the beginning, and the leaching was enhanced on day 87 of the experiment. A similar trend was observed for the pH 5 system, where AF-BM showed pronounced leaching and plateaued by day 28, whereas AF-NR showed slow leaching throughout the experiment period. It seems that at acidic pH for inorganic or organic acid (of TCLP test), AF-NR can hold arsenic better into its structure than AF-BM. After the decontamination procedure, the nanorod treatment seems to generate a more stable nanowaste. At all the pH values after 115 days, both AF-BM and AF-NR solids leach in a similar pattern, which may signify that the structural transformation for AF-NR is near completion and this transformation is pH dependent. However, it would be hard to predict the true nature of structural change after a long-term stability test, as sample volumes were low and powder diffraction was not feasible. Arsenic leaching was observed after 115 days of experiments for all pH values, suggesting that the structure is more labile to dissolution after this prolonged test under varied pH conditions. The system, maintained at pH 7, followed a similar leaching rate for both wastes. Still, the

leachate arsenic concentration was slightly less in AF-NR than in AF-BM, but the difference was insignificant. The basic pH 9 behaved differently than acidic or neutral pH, where both the systems showed continuous leaching for the entire experiment timeline. At pH 9, AF-BM showed a significantly higher tendency to leach than AF-NR; the final leachate concentration of arsenic was highest in both wastes at pH 9.



Figure 3. Shows concentration of arsenic in the leachate of long-term stability test of AF-NR and AF-BM under (**a**) pH 4, (**b**) pH 5, (**c**) pH 7, and (**d**) pH 9.

A huge difference was observed in comparing the amount of arsenic leached from AF-NR and AF-BM samples, (Figure 3) irrespective of the pH or the time of analysis. The most pronounced effect is observed within the first 56 days of the long-term stability test, where AF-BM samples leached arsenic almost 2.5–3 times more than that from the AF-NR sample, suggesting better stability for AF-NR waste. There are no guidelines to compare these long-term stability tests; however, these tests indicate that more than 5 mg L⁻¹ may occur within the first 28 days at neutral pH regardless of the process used. Therefore, the generated waste may be hazardous when stored in the open for an extended period. Changing the acid from an organic form, which emulates mainly landfill conditions, to an inorganic one emulating acid rain changes the amount of arsenic leached back in any pH range (although pH 5 for the long-term test will be best suited for comparison). Therefore, a thorough study in developing the true leaching test is urgently needed to ensure the proper handling of As-rich waste formed in the present study.

3.3.2. Iron Leaching Using Inorganic Acid

The cumulative concentration of iron in the leachate was comparable to arsenic (Figure 4), which was similar to previous observations [37]. The AF-BM waste, which contained higher iron in its structure, showed a more significant iron dissolution than AF-NR under all pH conditions. Iron leaching from AF-BM is almost four times higher than that from AF-NR. Under all pH conditions, arsenic concentration in leachate shows a significantly strong correlation with iron concentration for both AF-NR (pH 4 r = 0.79, pH 5 r = 0.97, pH 7 r = 0.99, pH 9 r = 0.88, p < 0.05 in all pH) and AF-BM (pH 4 r = 0.93, pH 5 r = 0.92, pH 7 r = 0.93, pH 9 r = 0.88, p < 0.05 in all pH). In the acidic pH, the tendency of iron to leach was higher due to the higher dissolution rate of iron-bearing minerals.

AF-BM has a higher potential to leach iron in all the pH and followed a similar trend under all pH conditions. However, AF-NR showed limited iron leaching and had the highest iron leaching in pH 5 and 7. The leaching of iron in pH 9 was negligible for AF-NR. AF-NR's tendency to leach iron under all pH conditions seems to be pronounced at the later stage of the experiment. Iron leaching in both wastes was lowest at pH 9. This lower iron concentration at high pH may be due to the tendency of iron to precipitate oxides and hydroxides at high pH, which may not have passed through a 0.45 µm filter and, thus, cannot be measured quantitatively if the product is filtered.



Figure 4. Shows concentration of iron in the leachate of long-term stability test of AF-NR and AF-BM under (**a**) pH 4, (**b**) pH 5, (**c**) pH 7, and (**d**) pH 9.

The tendency of AF-NR to leach less arsenic and iron from its structure indicates that the end-waste product AF-NR, from ZnS nanorod-treated arsenic-containing water is a better-quality waste and should ensure easier handling. Short- and long-term studies find AF-NR to be more stable and have less potential for leaching arsenic. The better morphology and monodispersity of AF-NR compared to AF-BM can be the primary reason for the higher stability of the generated waste, as both were produced under similar treatment conditions. This study does indicate that Tooeleite-like mineral waste devoid of sulfate ions has better stability than sulfate mineral, and future research can focus on developing a large-scale (kg production level) system to generate a one-step arsenic decontamination processes, producing stable, non-hazardous waste. These methods can be cost-effective and may address the arsenic issue in poor-income and developing nations, where the arsenic contamination issue is most prevalent.

4. Conclusions

Our results indicate that the highly monodispersed Tooeleite mineral-like nanowaste formed after treatment with ZnS nanorods will pass US EPA TCLP tests, and ZnS ball-milled produced nanowaste is close to the TCLP leaching limit. The nanowaste formed had a very high content of arsenic in it when compared to other wastes of arsenic treatment for the same amount of waste. If the present treatment method is used on a larger scale, the resulting waste can be easily dumped back into the environment without further pre-treatment (like solidification/stabilization). As it is a single-step process of mineralization, the effective cost may decrease where a two-step process (removal of arsenic and immobilization of removed arsenic in the waste) is used. Nanotechnology-induced As mineralization can provide a sustainable future for routine treatment processes requiring the generation of a stable waste product.

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