TWO-STAGE TREATMENT OF HIGH ARSENIC SYNTHETIC MINE WATER AT COLD TEMPERATURE

A.L. Mackie¹ and M.E. Walsh¹, *M. Laliberté² and M. Couture²

¹Department of Civil and Resource Engineering, Dalhousie University
1360 Barrington Street, Rm D215
PO Box 15 000, Halifax, NS, CA B3H 4R2

²Veolia Water Solutions & Technologies Canada, Inc.
4105 rue Sartelon
Saint-Laurent, QC, CA H4S 2B3
(*Corresponding author: Marc.Laliberte@veoliawater.com)
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ABSTRACT

Arsenic is a highly toxic element and a known human carcinogen. It is often a contaminant in mine water discharges, particularly from gold mining and roasting operations, and has been found at concentrations as high as 4 g/L. Increasingly stringent controls on the concentration of arsenic allowed to be discharged into the environment cannot always be met by current treatment processes and thus enhanced technologies are required to achieve low treated effluent concentrations at reasonable costs. A novel two-step physicochemical treatment process was developed and tested at the bench-scale using synthetic mine water solutions (SMWs) in order to reduce arsenic concentrations in treated effluent to exceed current discharge regulations. The process includes chemical coagulation with ferric sulphate and ballasted flocculation for enhanced solid-liquid separation. The SMW contained 59 ± 2 mg/L arsenic with a slightly alkaline pH. The effect of arsenic speciation on the process was tested by using either arsenite, As(III), or arsenate, As(V), in the SMW solutions. Tests were performed at cold temperature (3 ± 1 °C) to ensure the process’ efficacy year-round in northern climates. Arsenic in As(V) SMW solutions was removed to a final total concentration of 0.0054 ± 0.002 mg/L, almost half the current recommended allowable drinking water concentration of 0.010 mg/L. As(III) was removed to a concentration below the Metal Mining Effluent Regulations’ (MMER) current limit of 0.50 mg/L, to 0.32 ± 0.06 mg/L, with double the coagulant dose used in Stage 1 for As(V) removal. Oxidant addition at a concentration of 5 mg KMnO₄/L in Stage 2 resulted in final total arsenic concentrations of 0.017 ± 0.002 mg/L and pH adjustment with lime in Stage 2 resulted in 0.0415 ± 0.0007 mg As/L in treated As(III) SMW. Both of these modifications to the process reduced arsenic concentrations to below proposed new MMER limits (i.e., 0.10 mg/L). This two-stage treatment process was shown to reduce arsenic concentrations to well below current treatment guidelines while reducing or eliminating chemical oxidant demand.

KEYWORDS

Arsenic, Ferric sulphate, Ferric hydroxide, Coagulation, Mine water, Ballasted flocculation, Actiflo®

INTRODUCTION

Arsenic is often found as a minor contaminant in mine drainage, but can reach concentrations of several grams per litre in waters at gold-mining and -leaching operations (Clark & Raven, 2004; Wang & Mulligan, 2006). Arsenic is highly toxic, especially in its reduced form (i.e., arsenite or As(III)), and a mixture of both common inorganic aqueous species, As(III) and As(V), can often be found in both oxidizing and reducing waters (Raven, Jain, & Loeffert, 1998; Bednar, Garbarino, Ranville, & Wildeman, 2005; Sharma & Sohn, 2009). The Canadian MMER state, among other requirements, that mine effluents must not be acutely toxic to certain aquatic species, have a pH between 6.5 and 9.5, and have a maximum monthly average arsenic concentration of 0.50 mg/L (Fisheries Act, 2002). A review of the MMER is currently underway which could see the allowable arsenic concentration further reduced to 0.10 mg/L in mine water discharges. For comparison, the Guidelines for Canadian Drinking Water set a limit for arsenic of 0.010 mg/L, and the Canadian Council of Ministers of the Environment (CCME) guideline for the protection of freshwater aquatic life, 0.005 mg/L (CCME, 2007; Health Canada, 2012).

The US EPA’s Best Demonstrated Available Technology (BDAT) for arsenic removal from
wastewater is by co-precipitation with ferric hydroxide. This technology incorporates the use of a ferric coagulant (i.e., chloride or sulphate) and pH adjustment with lime or caustic to precipitate ferric hydroxide flocs which specifically adsorb arsenic from the wastewater. This process is the one used most often for arsenic removal from mine water (Harris, 2003; Twidwell, Robins, & Hohn 2005; Jia & Demopoulos 2008). Any As(III) present in the waste stream is transformed to As(V), which is generally more easily removed, by chemical oxidation prior to co-precipitation processes (Bowell, 2003; Twidwell et al., 2005).

The objective of this study was to remove arsenic from high concentration-arsenic SMW in a two-stage treatment process simulated at bench-scale. The goal was to reduce arsenic concentrations to well below current treatment guidelines while reducing chemical oxidant demand. We also investigated the effectiveness of the treatment process with respect to arsenic speciation (i.e., As(III) versus As(V)).

EXPERIMENTAL ANALYSIS

Materials

We designed the SMW solutions to simulate high-arsenic mine water from a former gold mining and roasting operation in northern Canada, with an arsenic concentration of 59 ± 2 mg/L and a pH of 7.9 ± 0.1. Separate solutions containing arsenic in the form of arsenite (using arsenic trioxide, Anachemia Chemicals) and arsenate (using sodium arsenate, Anachemia Chemicals) were used to test the effect of arsenic speciation on the process. SMW also contained calcium (210 ± 12 mg/L), magnesium (63 ± 4 mg/L), sodium (230 ± 73 mg/L), sulphate (520 ± 120 mg/L), and chloride (250 ± 40 mg/L), and had an alkalinity of 260 ± 18 mg/l as CaCO$_3$. All chemicals used were reagent A.C.S. grade. Veolia Water Solutions & Technologies (VWS) provided ferric sulphate coagulant (Hydrex 3253), anionic polymer (Hydrex 3551), and microsand (Actisand™, nominal diameter 100 µm). A 1 % w/v solution of hydrated lime (Ca(OH)$_2$) was used for pH adjustment. A 0.5 % w/v solution of potassium permanganate (KMnO$_4$) was used in Stage 2 tests with oxidation.

Methods

We performed a series of jar tests to simulate the two-stage treatment train. Stage 1 consists of coagulation with ferric sulphate followed by pH adjustment with lime and Stage 2 consists of coagulation with ferric sulphate, followed by pH adjustment or chemical oxidation where noted. We used ballasted flocculation and sedimentation for treated water clarification in both stages. We simulated the Actiflo® ballasted flocculation process at the bench-scale following procedures developed and validated by VWS (Desjardins, Koudjonou, & Desjardins, 2002). The Actiflo® process incorporates microsand into the flocculation step, generating flocs that are denser and therefore settle faster than in traditional clarification processes. Sand is separated from the precipitated sludge in a hydrocyclone for reinjection into the process. An overview of the Actiflo® process is shown in Figure 1. We used a Phipps and Bird model 7790-100 4-paddle jar tester with 600 mL glass beakers to perform the batch tests, with a constant mixing speed of 150 rpm or G-value of approximately 100 s$^{-1}$.

Testing was done at 3 ± 2 °C to ensure the process' efficacy year-round in northern climates because coagulation/flocculation treatment processes usually result in worse outcomes (i.e., higher residual contaminants) at colder temperature. The poorer treatment is due to slowed precipitation and adsorption kinetics as well as increased water viscosity which reduces coagulant dispersion in the reaction vessel and slows settling rates (Kang & Cleasby, 1995; Desjardins et al., 2002). Temperature was controlled using a chiller attached to a circulating water bath in which the beakers were placed.

Figure 2 is a schematic of the two-stage treatment process evaluated in this study. Chemical additions were timed to simulate a 40 m/h rise rate and were added in the following order: coagulant (t = 0), hydrated lime (Stage 1) or oxidant (Stage 2, test dependent; t = 2 min), microsand and half the polymer dose (t = 7 min), remaining polymer dose (t = 12 min), and finally a 3 minute settling period (t = 15 min). In each treatment stage, 1 mg/L polymer and 10 g/L microsand were used; 400 µL/L of coagulant, equal to
75.6 mg/L as iron and a Fe/As molar ratio of 1.7, was used in Stage 1 and 100 µL/L in Stage 2. In the first set of experiments, Stage 1 only, the lime dose was varied from 20 to 1000 mg/L as Ca(OH)$_2$ in order to determine the pH of maximum arsenic removal. In the second stage, the impact of oxidation on arsenite removal was investigated with tests on As(III) SMW run with and without KMnO$_4$. Tests were performed in duplicate, unless otherwise indicated.

Figure 1 – Actiflo® clarification process overview (VWS, 2013)

Figure 2 – Process flow diagram
Analytical

We measured turbidity of clarified water samples with a HACH 2100N turbidimeter and pH with a HACH HQ40D multimeter and PHC101 probe. Total metals of the clarified samples were measured by an external accredited laboratory using ICP-MS for arsenic and ICP-OES for all others (AGAT Laboratories Ltd, Saint-Laurent, QC). Where indicated, arsenic concentrations were measured in-house using a Thermofisher ICE3000 atomic adsorption spectrophotometer with flame analysis (i.e., AA). Speciation of arsenic was not analysed, however oxidation of arsenic is extremely slow and As(III) SMW solutions were treated within 3 days to minimize oxidation of As(III) to As(V) before treatment.

RESULTS

Stage 1 pH Curve Tests

Treated and clarified As(V) SMW samples had total arsenic concentrations after Stage 1 ranging from 0.232 to 0.833 mg/L and lime dose (100 to 400 mg/L as Ca(OH)$_2$) did not have any effect on arsenic removal. Samples run without lime addition had an average final arsenic concentration of 0.30 ± 0.06 mg/L, indicating that the majority of arsenate was removed during the initial 2 minute coagulation period (pH = 5.2 ± 0.2), with subsequent increases in pH having only a slight impact on treatment performance in Stage 1 of the process. Residual iron concentrations averaged 0.11 ± 0.03 mg/L for tests with pH adjustment while 0.7 ± 0.2 mg Fe/L remained in the samples treated without lime addition. Turbidities in the treated effluent from Stage 1 ranged from 0.61 to 0.89 NTU and showed no correlation to final total metals concentrations.

The treated As(III) SMW samples showed a distinct maximum removal of arsenic at a pH of 9.6 ± 0.1 (lime dose = 200 mg/L; Figure 3). The lowest final arsenic concentration was still above the Stage 1 target concentration of 1 mg As/L (i.e., 8.1 ± 0.6 mg/L), therefore we doubled the coagulant dose to 800 µL/L (i.e., 152 ppm Fe, Fe/As molar ratio = 3.4) for subsequent tests. The same trend was found at this coagulant dose, with a maximum removal at pH 9.5 ± 0.2 (lime dose = 400 mg/L; Figure 3). Final total iron concentrations ranged from 0.347 to 0.727 mg/L, following a similar pattern to residual arsenic concentrations (i.e., minimum at pH = 9.5). Turbidities ranged from 0.50 to 10.1 NTU and were highest at higher lime doses (i.e., 1000 mg Ca(OH)$_2$/L).

![Figure 3 – Total arsenic concentrations in As(III) SMW after Stage 1 treatment at 3 °C](image-url)
Two-Stage Treatment Tests

Results from the two-stage treatment tests are shown in Table 1. Stage 1 treatment doses for As(V) SMW were 400 µL/L of coagulant and 200 mg/L Ca(OH)$_2$; As(III) SMW Stage 1 treatment doses were 800 µL/L of coagulant and 400 mg/L Ca(OH)$_2$. All Stage 2 tests used 100 µL/L of coagulant. As(V) SMW tests had no pH adjustment in Stage 2 except the lowering due to coagulant addition (i.e., no lime addition). We initially ran As(III) tests without pH adjustment or oxidant addition in Stage 2 (As(III)a; Table 1). We also tested oxidation using 5 mg/L potassium permanganate without pH adjustment (As(III)b; Table 1) and pH adjustment using 40 mg/L Ca(OH)$_2$, in order to target arsenite removal, without oxidant addition (As(III)c; Table 1) in Stage 2 in order to determine the conditions giving the lowest residual arsenic concentrations.

### Table 1 – Two-stage treatment test results

<table>
<thead>
<tr>
<th>SMW</th>
<th>pH Stage 1</th>
<th>pH Stage 2</th>
<th>KMnO$_4$ dose (mg/L)</th>
<th>Final total arsenic (mg/L)</th>
<th>Arsenic % removal</th>
<th>Final total iron (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>9.7 ± 0.0</td>
<td>6.3 ± 0.2</td>
<td>0</td>
<td>0.0054 ± 0.0002</td>
<td>99.99</td>
<td>&lt; 0.300</td>
</tr>
<tr>
<td>As(III)a</td>
<td>9.5 ± 0.2</td>
<td>5.5 ± 0.4</td>
<td>0</td>
<td>0.32 ± 0.06</td>
<td>99.45</td>
<td>&lt; 0.300</td>
</tr>
<tr>
<td>As(III)b</td>
<td>9.5 ± 0.2</td>
<td>5.5 ± 0.4</td>
<td>5</td>
<td>0.017 ± 0.002</td>
<td>99.97</td>
<td>&lt; 0.300</td>
</tr>
<tr>
<td>As(III)c</td>
<td>9.5 ± 0.2</td>
<td>9.3 ± 0.0</td>
<td>0</td>
<td>0.042 ± 0.001</td>
<td>99.93</td>
<td>&lt; 0.300</td>
</tr>
</tbody>
</table>

DISCUSSION

The difference in removal between As(V) and As(III) found during pH curve testing is consistent with previous studies on arsenic co-precipitation/adsorption with ferric hydroxide (Raven et al., 1998; Goldberg & Johnston, 2001; Bowell, 2003; Qiao, Jiang, Sun, Sun, Wang, & Guan, 2012). These previous studies indicated that As(V) is more easily removed than As(III), which requires higher coagulant doses and higher treatment pH, which is in agreement with the results of this study. The main mechanism for arsenic removal during treatment with ferric coagulants is by adsorption to precipitates, though removals are generally higher during co-precipitation than adsorption onto preformed ferric hydroxide precipitates, due to the increased surface area available and the ability for arsenic to be incorporated into the solids during co-precipitation (Hering, Chen, Wilkie, Elimelich, & Liang, 1996; Harris, 2003; Jia & Demopoulos, 2005; Mercer & Tobiason, 2008; Qiao et al., 2012). The incorporation of calcium has also been shown to increase adsorption of arsenic to ferric hydroxide precipitates and the stability of the resulting sludge (Hering et al., 1996; Jia & Demopoulos, 2005; 2008).

Arsenate has been shown to be removed to maximum levels at a pH between 3.5 and 6.5 at room temperature. Below a pH of approximately 4, ferric sulphate hydrolysis presents higher concentrations of soluble ferric species, resulting in no surface (i.e., Fe(OH)$_{3(s)}$) for adsorption reactions to take place. Above pH 4, the negative charges on the surface of the ferric hydroxide precipitates increase (point of zero charge [PZC] ≈ 8.0) and electrostatic repulsion between the precipitate and the arsenic anions also increases (Nishimura & Umetsu, 2000; Wang, Nishimura, & Umetsu, 2000; Bowell, 2003; Pakzadeh & Batista, 2011; Qiao et al., 2012). The results of the current study are in agreement with previous research in that the coagulation pH of Stage 1 tests with As(V) SMW was 5.2 ± 0.2, and increasing pH with lime addition after the initial two minute coagulation period did not substantially affect arsenic removal.

Arsenite has been shown to be maximally adsorbed at room temperature at a pH near its first acid dissociation constant (pKa = 9.2), where the non-ionic (i.e., H$_2$AsO$_3^-$) and mono-anionic (i.e., H$_3$AsO$_4^-$) forms of the weak acid are in equilibrium. This equilibrium is necessary for the efficient adsorption of weak acids above the PZC of the adsorbent (Hingston, Posner, & Quirk, 1972; Sigg & Stumm, 1981; Raven et al., 1998; Jain, Raven, & Loeffert, 1999). This is near the pH of maximum arsenite removal found in this study at 3 °C (i.e., 9.5 ± 0.2). Though arsenic speciation was not measured and no precautions against oxidation were taken during testing, the reaction of the As(V) and As(III) SMW is significantly different with regards to treatment pH and therefore little to no oxidation is assumed to have occurred.
The oxidant dose used in this study for treatment of As(III) SMW in Stage 2, 5.0 mg/L KMnO₄, is significantly reduced from what would be required if oxidation were to take place at the head of the treatment process, before bulk removal of arsenic, as is frequently implemented (Bowell, 2003; Twidwell et al., 2005; Guan, Ma, Dong, & Jiang, 2009; Wang, Gong, Liu, Liu, & Qu, 2011). Additionally, overdosing of KMnO₄ was apparent due to the persistent pink colour of samples and residual manganese concentrations of 1.27 ± 0.05 mg/L (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2012). We did not attempt to optimize oxidant dose during this study. Adjusting the pH in Stage 2 to approximately what was found during Stage 1 pH curve testing as the pH of minimum residual arsenic (i.e., 9.3) resulted in greater arsenic removal than was found in unoxidized samples, though not quite as great as that found in tests incorporating oxidation. Further optimization of lime and coagulant doses would most likely increase arsenite removal without the need for chemical oxidation, although further study would be required to confirm this. The increase in removal of arsenic in Stage 2 tests incorporating chemical oxidation or pH adjustment also indicates that significant oxidation of As(III) did not take place prior to treatment.

CONCLUSIONS

This study demonstrates that arsenic in synthetic mine water can be removed to less than the current (i.e., 0.50 mg/L) and potential revised MMER guidelines (i.e., 0.10 mg/L) using the two-stage treatment process outlined in this study. Tests using As(V) SMW resulted in an average residual arsenic concentration of 0.0054 ± 0.0002 mg/L, which is less than the current drinking water maximum arsenic guideline of 0.010 mg/L. Tests using As(III) SMW resulted in higher final arsenic concentrations (i.e., 0.32 ± 0.06 mg/L) which were reduced to 0.017 ± 0.002 and 0.042 ± 0.001 mg/L using chemical oxidation and pH adjustment, respectively, in Stage 2 of the process. Arsenic speciation was not measured, however little to no natural oxidation of As(III) is assumed to have occurred prior to or during treatment. Oxidant demand can be reduced or eliminated by this novel two-stage process, depending on treatment goals and the As(III)/As(V) ratio in the contaminated water. The benefit of not using a chemical oxidant may outweigh the cost of the increased coagulant required for treatment of high-arsenite mine waters. Further testing is needed to determine the effect of temperature on the process, as well as optimization of coagulant and lime doses.

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REFERENCES


