Surface complexation modeling of the removal of arsenic from ion-exchange waste brines with ferric chloride

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ABSTRACT

Brine disposal is a serious challenge of arsenic (V) removal from drinking water using ion-exchange (IX). Although arsenic removal with ferric chloride ($FeCl_3$) from drinking waters is well documented, the application of $FeCl_3$ to remove arsenic (V) from brines has not been thoroughly investigated. In contrast to drinking water, IX brines contain high ionic strength, high alkalinity, and high arsenic concentrations; these factors are known to influence arsenic removal by $FeCl_3$.

Surface complexation modeling and experimental coagulation tests were performed to investigate the influence of ionic strength, pH, Fe/As molar ratios, and alkalinity on the removal of arsenic from IX brines. The model prediction was in good agreement with the experimental data. Optimum pH range was found to be between 4.5 and 6.5. The arsenic removal efficiency slightly improved with higher ionic strength. The Fe/As ratios needed to treat brines were significantly lower than those used to treat drinking waters. For arsenic (V) concentrations typical in IX brines, Fe/As molar ratios varying from 1.3 to 1.7 were needed. Sludge solid concentrations varying from 2 to 18 mg L^{-1} were found. The results of this research have direct application to the treatment of residual wastes brines containing arsenic.

1. Introduction

Arsenic removal from high ionic strength solutions is a major challenge for various water treatment technologies, including ion-exchange (IX), activated alumina adsorption, reverse osmosis, and nanofiltration [1]. These treatment processes, when used for arsenic removal, produce arsenic-laden residual wastes, which must be properly disposed of to prevent further contamination of the environment [1]. Because of its high toxicity [2–4], the maximum contaminant level (MCL) in the U.S. for arsenic in drinking water was set by the U.S. Environmental Protection Agency (EPA) at 10 μg L^{-1} on January 18, 2001, and water treatment plants in the U.S. have had to comply with the new regulation since January 23, 2006 [2]. Ion-exchange (IX) is one of the best available technologies to remove As(V) from water due to its excellent efficiency and flexible application to small size treatment plants [1,3–5].

Conventional strong base anion (SBA) exchange resins and specialty resins have been utilized to efficiently remove As(V) (i.e., $HAsO_4^{2-}$ and $H_2AsO_4^-$ species) from waters [3,6–9]. As(III) must

be oxidized to As(V) prior to ion-exchange treatment, because SBA exchange resin is only efficient in removing As(V) [5,7,10].

Spent IX resin beds must be regenerated, generally, using sodium chloride for the process to be economically viable. The regeneration process produces brine solutions with high concentrations of As(V), alkalinity, and ionic strength [1]. The high ionic strength is associated with the use of NaCl brine for resin regeneration. The waste brines have high alkalinities because ion-exchange resins exchange bicarbonate present in the water. During regeneration bicarbonate is then released to the waste brine. According to the Resource Conservation and Recovery Act (RCRA) of the United States, brines generated from arsenic removal ion-exchange plants are considered hazardous if they contain more than 5 mg L^{-1} of arsenic [10]. The cost of disposal and handling of hazardous wastes are drastically higher than that for non-hazardous wastes [11].

As(V) can be removed from waters and brines using ferric chloride ($FeCl_3$) coagulation, which produces arsenic-iron hydroxide sludge that generally passes the Toxicity Characteristic Leaching Procedure (TCLP). The TCLP test determines whether a waste is hazardous [12–15]. As(V) removal with ferric chloride from drinking water is a well documented process and has been studied for many years [16–23]. Adsorption is believed to be the major mechanism for As(V) removal by coagulation with ferric chloride [12,23–25]. However, very few studies have addressed the removal of arsenic from ion-exchange brines. Contrary to drinking water, ion-exchange brines contain high alkalinity, high ionic-strength,

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Constituent	Unit	Concentration
As(V)	mg L^{-1}	5–120
Alkalinities as CaCO$_3$	g L^{-1}	1–10
Sulfate	g L^{-1}	4.8–48
pH	–	8–10
NaCl	g L^{-1}	40–120
Ionic strength	M	0.6–2.1

and arsenic concentrations in the mg L^{-1} range; these factors are known to influence arsenic removal by ferric chloride. Therefore, the optimum conditions for arsenic removal from brines with ferric chloride are likely to be different from those for drinking water.

The arsenic concentrations in waste brines from typical IX plants in the U.S. will have As(V) concentrations in the mg L^{-1} range (Table 1), which are several orders of magnitude greater that those found in drinking waters. Therefore, there is a need to evaluate how As(V) removal from brines with ferric chloride is affected by initial As(V) concentration. Steinwinder and Zhao [13] and An et al. [26] have recently studied the removal of As(V) from a recycled IX brine containing 300 mg L^{-1} of As(V) using ferric chloride. Mercer and Tobiason [15] have studied the removal of As(V) from membrane concentrates. These concentrates may contain ionic strengths similar to those found in IX brines. However, the As(V) concentrations in membrane concentrates (0.5 mg L^{-1}) are much lower than IX brines (10–120 mg L^{-1}).

Mercer and Tobiason [15] found that increasing the ionic strengths from 0.2 to 1.5 M did not affect the removal efficiency of As(V) from concentrates, and increasing the ionic strength from 0.008 to 1.5 M caused a slight increase in the removal efficiency. Xu et al. [27] reported that increasing the ionic strength increased the adsorption of As(V) on two types of soil. Although alkalinity favors HFO formation after addition of ferric chloride [13], it inhibits sorption onto goethite [28–30] or HFO [20,31,32]. pH is directly related to carbonate alkalinity, and high carbonate alkalinity tend to produce high pH values.

This research addresses As(V) removal from IX brines using ferric chloride. A two-layer surface complexation model was used to predict As(V) removal under various scenarios. Laboratory coagulation experiments were performed to evaluate how accurately the model can predict As(V) removal from ion-exchange brines. The modeling and experimental results were used to investigate the effects of important parameters, including pH, initial As(V) concentration, ferric chloride dosage, ionic strength, and alkalinity on the As(V) removal by FeCl$_3$ coagulation. In addition, the quantity of sludge generated in the treatment process was determined for varying ferric chloride dosages and initial As(V) concentrations.

2. Experimental

2.1. Synthetic brine preparation and reagents

To determine the range of major parameters to be evaluated, the composition of several brines from operating ion-exchange plants in Arizona and California were investigated (Table 1). Table 1 was used in this research to guide appropriate concentration ranges to be used in modeling and in the coagulation experiments.

All solutions were prepared using high grade deionized (DI) water. The glassware was acid washed. To prepare the synthetic brines, reagent-grade 99.9% NaCl granules (EMD Chemicals) was added to deionized water to obtain a primary stock solution of 120 g L^{-1} NaCl, which was diluted as needed to prepare brines containing 40, 60, and 80 g L^{-1} NaCl. Sodium bicarbonate (NaHCO$_3$,

EMD Chemicals) was used to prepare a 61 g L^{-1} HCO$_3$$^{-}$ stock solution, which was used to provide the alkalinity in the brines solutions. A primary stock solution (1000 mg L^{-1}) for As(V) was prepared using sodium hydrogen arsenate granules (Na$_2$HAsO$_4$.7H$_2$O, Alfa Aesar, Ward Hill, MA). A 1000 mg L^{-1} As(V) stock solution was utilized to prepare the synthetic brine solutions. A fresh ferric chloride stock solution (100 g L^{-1}) was prepared the day of the experiments from a drinking water-grade ferric chloride solution (536 g L^{-1} of FeCl$_3$ from Kemira Water Solutions).

2.2. Experimental procedure

A series of coagulation batch experiments were conducted on synthetic brine solutions using a PB-700 standard JarTester from Phipps & Bird (Richmond, VA). Coagulation was performed with 2 min rapid mix of ferric chloride at 12 rad s^{-1} (G = 158 s^{-1}) followed by a 30 min slow mix at 3 rad s^{-1} (G = 20 s^{-1}) for flocculation with 250 mL of the synthetic brine solutions. Hundred milliliters of homogenously mixed brine was collected for solid analysis. Next, the remaining solution was allowed to settle for 30 min before sampling for arsenic analysis.

Forty-five milliliters of the untreated and treated brine solutions were collected to determine arsenic concentrations. The samples were centrifuged at 367 rad s^{-1} for one hour using a Sorvall Legend RT Bechtop centrifuge to separate the liquid from the solids. Samples were acidified with nitric acid (pH < 2) and stored in the refrigerator at 4 °C.

The pH of the solutions was measured before adding ferric chloride, and after the coagulation process. A series of titration curves were constructed for brine solutions of different pH values, which were used to anticipate the pH reduction due to application of a known concentration of ferric chloride. The final pH of each solution was adjusted to the desired values using either acid or base, while allowing for the anticipated pH decrease caused by ferric chloride addition.

2.2.1. Coagulation batch experiments to investigate the effects of pH

Eighteen coagulation experiments were performed at six different final pH values (1.5–12.5) at three levels of ionic strengths (0.1, 0.8, and 1.5 M). Initial arsenic concentration and alkalinity in all batches were 49.2 mg L^{-1} (0.66 mM) and 5.0 g L^{-1} as CaCO$_3$, respectively, which are the mean values found in typical IX brines (Table 1). Ferric chloride was applied at a constant dosage of 140 mg L^{-1} (2.5 mM) FeCl$_3$ (as Fe), corresponding to the Fe/As molar ration of 3.8.

2.2.2. Coagulation batch experiments to validate the modeling of As(V) removal

Eighteen coagulation batch experiments were performed for each initial As(V) concentration of 10, 42, or 92 mg L^{-1}, including six batch experiments at three levels of ionic strength (0.1, 0.8, and 1.5 M). Ferric chloride dosages in the range of 8–62 mg L^{-1}, 27–173 mg L^{-1}, and 55–242 mg L^{-1} (as Fe) were added to brines containing initial As(V) concentration of 10, 42, or 92 mg L^{-1}, respectively. The pH of all solutions was adjusted to a constant pH of 5.5 ± 0.1.

In addition, forty-two batch experiments were conducted to remove varying concentrations of As(V) from the synthetic brine solutions containing 60 g L^{-1} NaCl (1.2 M ionic strength) and 2.5 g L^{-1} as CaCO$_3$ initial alkalinity by addition of various dosages of ferric chloride. Seven batch experiments were carried out for each initial As(V) concentrations of 12, 21, 39, 57, 79, and 119 mg L^{-1} by adding ferric chloride dosages in the range of 12–41 mg L^{-1}, 12–68 mg L^{-1}, 15–160 mg L^{-1}, 15–190 mg L^{-1},

20–190 mg L^{-1}, 25–190 mg L^{-1}, respectively. Duplicate experiments were performed to assure the quality of data. The pH of brines was adjusted to 6.5 ± 0.1.

2.2.3. Coagulation batch experiments to evaluate the effects of alkalinity

Eighteen coagulation batch experiments were performed for an initial arsenic concentration of 47.7 mg L^{-1} and 0.8 M ionic strength for 2.5, 5, and 10 g L^{-1} as CaCO$_3$ alkalinities without pH adjustments. The final pH was not controlled during the coagulation process.

2.3. Analytical methods

Arsenic analyses were conducted within two weeks of sample collection. Samples were diluted for the measurements and the diluted samples contained 40 or 80 g-NaCl L^{-1}. Arsenic concentrations in the cleared liquid part of the samples were measured by ICP (Inductively coupled plasma Spectrophotometer) (Thermo Electron Iris Advantage) according to method 3125 [33]. The wavelength of 189.04 nm was used for arsenic measurements. The detection limit for arsenic measurement in water was 0.001 mg L^{-1}. The detection limit of 0.01 mg L^{-1} was selected for arsenic measurements in brines with background correction to compensate for NaCl interference. Brine samples were diluted with acidified deionized water 10 or 20 times to minimize the effect of NaCl on the ICP torches, thereby reducing the cleaning requirements.

The concentration of total iron in the prepared stock solution was measured by flame atomic absorbance spectrometry (AAnalyst 100 from PerkinElmer) following standard procedures (Method No. 3111 B) [33] prior to its use. Three calibration standards and the wave length of 248.3 nm were used for the measurements.

The pH of the solutions was measured by an Orion 920A+ pH meter equipped with an Orion 8102BNUWP probe from Thermo Electron Corporation, USA. The total suspended solids (TSS) in the samples were determined according to method 2540 D [33] using 0.45 μm filters.

2.4. Surface complexation modeling

A two-layer surface complexation model incorporated into MINEQL+, v. 4.6 [34], was utilized in this research to model As(V) removal from brines. The results of the laboratory coagulation batch experiments were compared to the results of the simulations to evaluate how well the MINEQL+ simulations fit the experimental results. The two-layer surface complexation model and the database of Dzombak and Morel [24] were utilized by Hering et al. [23] to predict arsenic removal by ferric chloride from drinking water with very low ionic strengths. The solution and surface reactions, and respective equilibrium constants for arsenate, iron, carbonate, and water are presented in Schecher and McAvoy [34], Boccelli et al. [35], and Hering et al. [23]. In the model, a mole of ferric chloride added to the solution yields 0.55 mg L^{-1} hydrous ferric oxide (HFO) or 89 g-HFO per mol-Fe [23,24]. A surface area of 600 m^2 g-HFO^{-1} [24,34] was used in the surface complexation model.

MINEQL+ utilizes the Davis equation to calculate the activity coefficients for various components. The Davis equation works well for ionic strength values less than 0.5 M, and usually, Pitzer equations are recommended to calculate the activity coefficients in high ionic strength solutions [36]. However, Xu [36] reported that a conventional extended Debye–Hückel equation (similar to Davis equation) was adequate to model ion-interactions in NaCl-dominanted brines with ionic strengths of up to 1.5 M. The ion-exchange brines in this research are NaCl-dominant with ionic
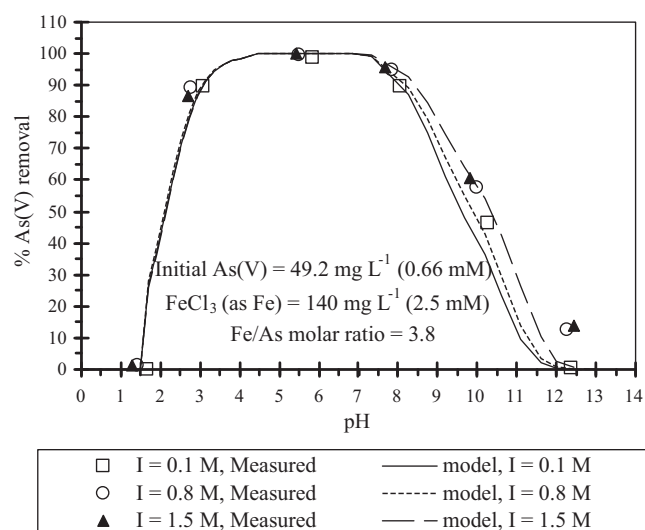
Fig. 1. Effect of pH and ionic strength on the adsorption of As(V) onto ferric hydroxide precipitates for an initial As(V) concentration of 49.2 mg L^{-1} and FeCl$_3$ (as Fe) dosage of 2.4 mM.

strengths of less than (or equal to) 1.5 M. Therefore, the incorporated Davis equation in MINEQL+ is likely to be adequate to calculate the activity coefficients of the adsorption process.

2.5. Statistical analysis

The As(V) removal efficiencies of the model and the experimental data were compared using analysis of variance (ANOVA) and regression analysis at different ionic strengths of 0.1, 0.8, 1.2, and 1.5 M (separately). The null hypothesis was that the modeling fits the experimental data when the coefficient (β) of the linear regression line ($Y = \beta X$) equals to 1. A t-test analysis (paired two-sample) was performed for means of the removal efficiencies among brines with 0.1, 0.8, and 1.5 M ionic strengths. The goal was to evaluate whether an increase in ionic strength resulted in higher As(V) removal efficiencies.

3. Results and discussion

3.1. Effect of pH on As(V) removal from brines with ferric chloride

Fig. 1 shows the percent arsenic removal from the synthetic ion-exchange brine as a function of pH at ionic strength levels of 0.1, 0.8, and 1.5 M for As(V) and FeCl$_3$ (as Fe) dosages of 0.66 mM and 2.5 mM (Fe/As molar ratio of 3.8), respectively. The lines in the graph represent surface complexation modeling and it will be discussed later. The symbols represent experimental data. Nearly one hundred percent As(V) removal from the brine was achieved at the pH range of 4.5-6.5. An interesting feature of Fig. 1 is that it forms a plateau at the optimal pH removal range. It follows that the same percent removal can be achieved at the lower pH range (i.e., pH 4.5) and the upper range (i.e., pH 6.5). Since IX brines have high pH values (i.e., 8–10) and there is a cost associated with acid use to lower the pH, in practice, operating at higher pH values is desirable.

Very poor As(V) removals are achieved at pH < 3.8 and at pH > 7.8. The reason for the drastic decrease in the removal efficiency when pH increased from 7.8 to 12.5 is surface charge reversal of HFO at pH values higher than the pzc of HFO (i.e. 7.9) [37]. Steinwinder and Zhao [13] showed that As(V) removal efficiency with FeCl$_3$ from an ion-exchange brine containing 300 mg L^{-1} As(V) at Fe/As molar ratio of 5 decreased from 100% to 30% when pH increased from 6 to 11.5. Clifford et al. [14] showed that As(V)
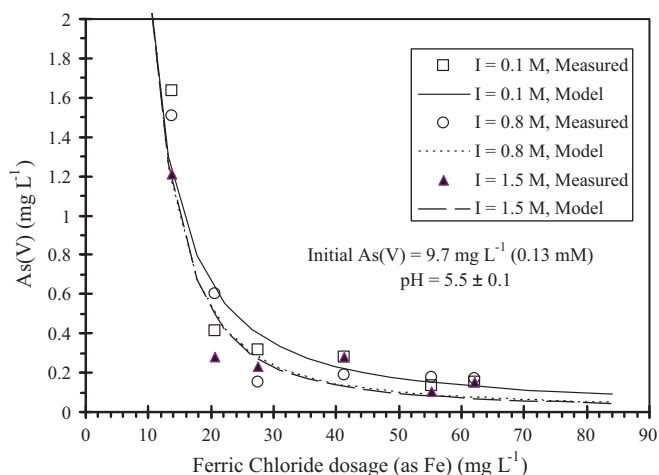
Fig. 2. Remaining arsenic(V) concentrations as a function of ferric chloride and ionic strength for an initial As(V) concentration of $9.7\,mg\,L^{-1}$, initial alkalinity of $5\,g\,L^{-1}$ as $CaCO_3$, and pH of 5.5.

removal efficiency with $FeCl_3$ from a brine containing $3.45\,mg\,L^{-1}$ As(V) at Fe/As molar ratio of 20 decreased from 99.7% to 71.8% when pH increased from 6.2 to 8.5. In this study, at an ionic strength of 0.8 M, the As(V) removal efficiency decreased from 99.6% at pH 5.5 to 57.5% or 12.3% when the pH was increased to 10 and 12.2, respectively.

The data in this study revealed that when the pH decreased from 3.5 to 1.5, As(V) removal efficiency reduced drastically from 95% to 0%. Although decreasing the pH of IX brines to such low levels would not be economically feasible or desired, two factors explain the lower to null removal of As(V) at these low pH values. Firstly, at pH < 4, the dihydrogen arsenate species transforms to the non-ionic and non-adsorbable species of As(V), arsenic acid (H_3AsO_4), which predominates at pH < 2.5. Secondly, at pH < 1.5, HFO does not form, that there is no surface for As(V) to be adsorbed to and iron from $FeCl_3$ is present as the dissolved species (Fe^{3+} and $FeOH^{2+}$). Reduced removal of As(V) by $FeCl_3$ at acidic pH values has been reported by others [38,39].

The finding presented herein indicates that to treat ion-exchange brines, the pH, which are typically between 8 and 10, must be lowered. In view of the fact that acids used to lower pH are costly, a pH of 6.5 would be desirable for 100% removal. In this study, the TCLP limit of $5\,mg\,L^{-1}$ of As(V) was achieved at pH 7.8, indicating that IX brine treatment to reach TCLP limits is efficient at pH below 7.8. It should be noted that As(V) removal from IX brines is possible at pH 8 to 10 at a lower efficiency.

3.2. Effects of ionic strength, initial As(V) concentration, and ferric chloride dosage on removal

Figs. 2–4 depict arsenic removal from the synthetic brine with increasing $FeCl_3$ addition for a fixed pH of 5.5, three initial arsenic concentrations (i.e., $9.7\,mg\,L^{-1}$, $42.3\,mg\,L^{-1}$, $97.9\,mg\,L^{-1}$), and ionic strengths of 0.1, 0.8, and 1.5 M. In the figures, symbols represent experimental data and the lines are surface complexation modeling prediction. As it will be discussed later in Section 3.3, the model fits the experimental data very well.

As(V) removal for brines with 0.1, 0.8, and 1.5 M ionic strengths were compared statistically (Table 2). The small P values of 0.0158 and 0.0224 (<0.05) indicate that increasing the ionic strength of brines from 0.1 M to 0.8 or 1.5 M promoted a statistical difference in the As(V) removal efficiencies. Notwithstanding its statistical significance, the arsenic removal efficiency increased only slightly (1.6% and 1.7%) when the ionic strength was increased from 0.1 to
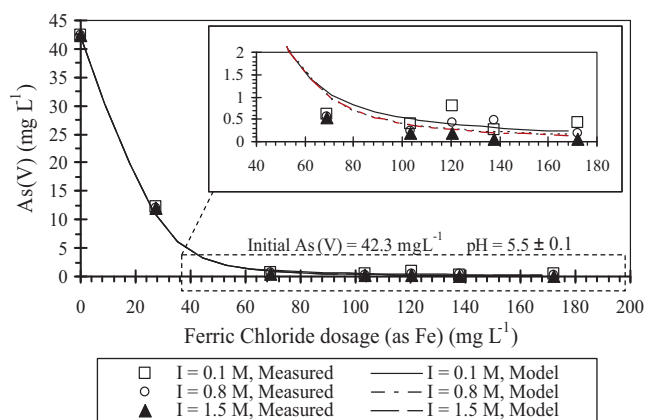
Fig. 3. Remaining arsenic(V) concentrations as a function of ferric chloride and ionic strength for an initial As(V) concentration of $42.2\,mg\,L^{-1}$, initial alkalinity of $5\,g\,L^{-1}$ as $CaCO_3$, and pH of 5.5.
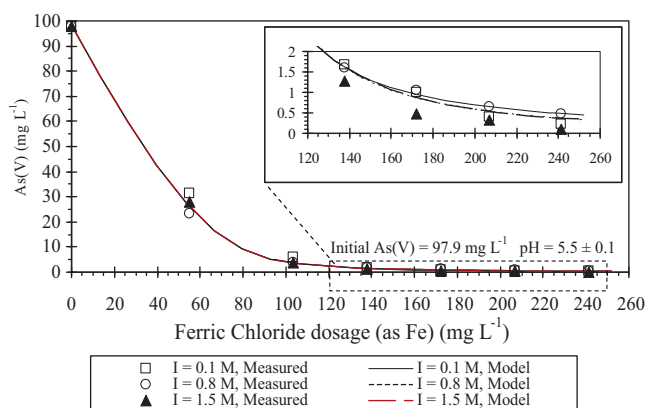
Table 2
Results of paired t-test for As(V) removal efficiencies for brines with ionic strengths of 0.1, 0.8, and 1.5 M.

Parameter	t-Test analysis between		
	0.1 M and 0.8 M	0.1 M and 1.5 M	0.8 M and 1.5 M
Observations	27	27	27
t-Stat	−2.2711	−2.1088	−0.2704
P one-tail	0.0158	0.0224	0.3945
t Critical one-tail	1.7056	1.7056	1.7056
P two-tail	0.0317	0.0448	0.7890
t Critical two-tail	2.0555	2.0555	2.0555

0.8 M and 1.5, respectively. There is no statistically significant difference (P value = 0.3945 > 0.05) found between the As(V) removal efficiency for brines with 0.8–1.5 M ionic strength. The increase in As(V) removal efficiency at higher ionic strength can be explained by the compression of the electric double layer that results in the faster formation of larger amounts HFO [15,40–42].

The $FeCl_3$ dosages which were used in this study aim at removing arsenic to levels that meet the TCLP standard and to levels below the TCLP standard that would allow for alternative ways to dispose of the brine.

Table 3 depicts Fe/As ratios to achieve remaining As(V) concentrations of $5\,mg\,L^{-1}$ and $0.5\,mg\,L^{-1}$ for pH 5.5, different ionic strengths, and different initial As(V) concentrations. For brines with lower arsenic concentration (i.e. $9.7\,mg\,L^{-1}$), approximately three

Fig. 4. Remaining arsenic(V) concentrations as a function of ferric chloride and ionic strength for an initial As(V) concentration of $97.9\,mg\,L^{-1}$, initial alkalinity of $5\,g\,L^{-1}$ as $CaCO_3$, and pH of 5.5.

Table 3
Ferric chloride dosages for brines with pH of 5.5 and different ionic strength needed to lower As(V) to 5 mg L^{-1} or 0.5 mg L^{-1}.

As(V) (mg L^{-1})	pH	I (M)	Remaining As(V) = 5 (mg L^{-1})		Remaining As(V) = 0.5 (mg L^{-1})	
			FeCl$_3$ as Fe (mg L^{-1})	Fe/As	FeCl$_3$ as Fe (mg L^{-1})	Fe/As
9.7	5.5	0.1	8.1	1.1	25.6	3.5
		0.8–1.5	7.8	1.1	23.9	3.3
42.3	5.5	0.1	53.3	1.7	86.9	2.8
		0.8–1.5	53.0	1.7	75.3	2.4
97.9	5.5	0.1	108.8	1.5	201.0	2.7
		0.8–1.5	100.9	1.4	171.2	2.3

times more FeCl$_3$ is needed to achieve 0.5 mg L^{-1} remaining As(V) as compared to 5 mg L^{-1}, the TCLP limit (Table 3). For initial As(V) concentrations between 42.3 mg L^{-1} and 97.9 mg L^{-1}, which are typical of most ion-exchange brines, only about 1.5 times more FeCl$_3$ is needed to achieve 0.5 mg L^{-1} remaining As(V) as compared to 5 mg L^{-1}. It has been reported that addition of FeCl$_3$ at a Fe/As molar ratio of 2 to a recycled IX brine with initial As(V) concentrations of 300 mg L^{-1} resulted in remaining As(V) concentration of <3 mg L^{-1} [13]. This result is consistent with previous findings [32,49,50] that lower Fe/As ratios are needed to remove higher concentrations of arsenic from waters as compared to arsenic removal from drinking waters (Table 7).

In this research, adsorption densities to attain 0.5 mg L^{-1} As(V) were 0.29 mol As(V) per mol Fe and 0.43 mol As(V) per mol Fe when initial As(V) concentrations were 9.7 mg L^{-1} and 97.9 mg L^{-1}, respectively. The higher adsorption densities achieved for higher ferric chloride dosages explain the larger removal efficiencies obtained by Fe/As ratios that are not directly proportional to the concentration of arsenic present in the brine. Adsorption densities of 0.16–0.25 mol As(V) per mol Fe have been reported for HFO when treating drinking water with low concentrations of As(V) [32,43]. In addition, very high adsorption densities, ~1 mol As(V) per mol Fe, were reported when very high concentrations of As(V) were present [32]. Moreover, at higher FeCl$_3$ (as Fe) dosages (10–100 mg L^{-1}), the solubility diagram for iron species shows the formation of the large amount of Fe(OH)$_3$-"sweep flocculation." [5]. Therefore, at higher FeCl$_3$ dosages, more HFO surfaces are available for As(V) adsorption.

The final desired level of arsenic in a brine treated with ferric chloride will depend on approved disposal methods available in individual municipalities. In states where non-hazardous brines could be disposed of by alternative means (e.g. discharged into sewer lines), water utilities may consider applying higher Fe/As ratios to obtain wastes with much lower As(V) concentration, without increasing their FeCl$_3$ consumption much.

3.3. Two-layer surface complexation modeling

The results of coagulation batch experiments were used to validate the surface complexation model utilized in this research. Predicted and experimental values of As(V) removal efficiency were statistically compared (Table 4). Analysis shows that the surface complexation model used in this research is in good agreement with the experimentally determined data points. The coefficient of determination (R^2) value between the predicted and observation values was 0.9920. This indicates the model is reliable. Statistical F tests revealed that F values are greater than F_{crit} values. There was no evidence of lack of fit. The determined P values are less than 0.05, specifying that the model is significant at 95% confidence level.

Fig. 5 is a surface plot of As(V) removal efficiency predicted by the surface complexation model at pH 6.5 and ionic strength of 1.2 M for different initial As(V) concentrations and varying FeCl$_3$ (as Fe) dosages from 0 to 200 mg L^{-1}. For approximately 10 times increase in initial As(V) concentration, the Fe/As molar ratio needed

is only about 1.4 times higher (Fig. 5.). To achieve a remaining As(V) concentration of 0.5 mg L^{-1} the Fe/As molar ratios are approximately 3–4 times those needed for a remaining concentration of 5 mg L^{-1}.

Table 5 also shows that the lower the remaining As(V) concentration desired, the greater the Fe/As molar ratio needed. For a remaining As(V) concentration of 0.01 mg L^{-1} and an initial As(V) concentration of 12 mg L^{-1}, the Fe/As molar ratio needed is 75.6 which is 5 times greater than that (15.0) needed for initial As(V) concentration of 119 mg L^{-1} (Table 5).

By comparing the data presented in Tables 3 and 5, it can be seen that As(V) removal was slightly more effective at pH 5.5 than 6.5. For brines with initial As(V) concentrations of 9.7–97.9 mg L^{-1}, to obtain a remaining As(V) concentration of 5 mg L^{-1}, 1.1–1.4 Fe/As was required at pH 5.5 while 0.9 to 1.3 Fe/As was needed at pH 6.5. Clifford et al. [14] reported that for a brine containing 3.45 mg L^{-1} As(V) and 20 Fe/As, As(V) removal efficiency was 98.0% and the As(V) removal efficiency increased to 99.5% when pH decreased to 5.5.

The highest removal efficiencies from several published studies on arsenic removal from residual wastes and their associated data are shown in Table 6. As(V) concentrations in IX brines (up to 120 mg L^{-1}) are three orders of magnitude greater than those found in drinking water (up to 120 μg L^{-1} [44]), and more ferric chloride is required for brine treatment. However, the required Fe/As molar ratios vary between 1.4 and 84 (Table 6) for brines, which are less than the molar ratios required (14–312) (Table 7) for arsenic treatment of drinking water. Typical ferric chloride dosages of 5–30 mg L^{-1} are used in drinking water operations (MWH, 2005). Higher coagulant dosages [116–3192 mg L^{-1} FeCl$_3$ (as Fe)] are required for arsenic removal from brines compared to reported dosages required for the treatment of drinking waters [3–61 mg L^{-1} FeCl$_3$ (as Fe)]. The required Fe/As molar ratios are smaller for high concentrations of arsenic (Table 6).

Experimental results of several studies on the removal of As(V) from drinking waters are summarized in Table 7. Typical dosages of FeCl$_3$ (as Fe) are 1–21 mg L^{-1}, and Fe/As molar ratios are 25–572 (Table 7). Optimal Fe/As molar ratios of 20 [45] and 25 [46] were proposed to remove typical concentrations of arsenic in drinking waters without pH adjustment.

3.4. Effects of initial alkalinity

Table 8 shows the percent As(V) removal efficiency as a function of FeCl$_3$ (as Fe) added to the solution for alkalinities of 2.5, 5, and 10 g L^{-1} as CaCO$_3$, initial As(V) concentration of 48 mg L^{-1}, and ionic strength of 0.8 M. It was found that increasing alkalinity from 1 to 5 or 10 g L^{-1} as CaCO$_3$ resulted in decreased arsenic removal efficiency. As(V) removal efficiency decreased from 99.1% to 97.8% when the alkalinity increased from 2.5 to 10 g L^{-1} as CaCO$_3$. The reason for the decrease in efficiency with increased alkalinity is the higher final pH values resulted from higher alkalinity in this research. High carbonate alkalinity would produce high pH values, which are not favorable for the adsorption of arsenic onto

Table 4
Statistical evaluation for fitness of the surface complexation model to experimental data.

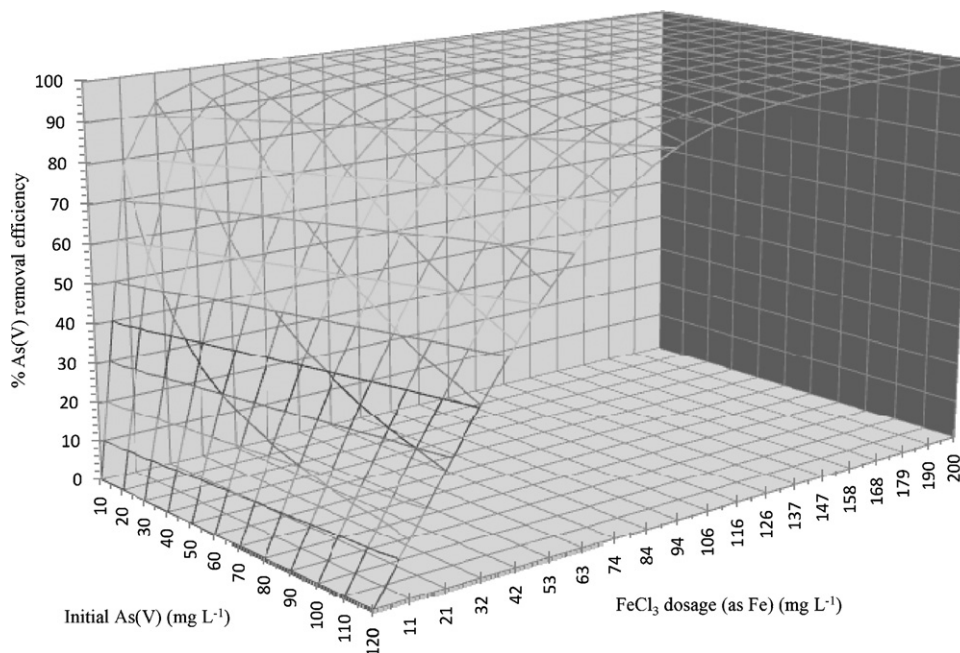| Source	Df[a]	SS[b]	MS[c]	F[d]	P
Regression[e]	1	129,220	129220	14507.19	<0.0001
Residual error	121	1078	9	–	
Lack-of-fit	108	1062	10	8.08	<0.0001
Pure error	13	16	1	–	
Total	122	130,298	–	–	

[a] Degree of freedom.
[b] Sum of squares.
[c] Mean of squares.
[d] $F_{critical} = < 0.0001$.
[e] $R^2 = 0.9920$; R^2 (adjusted) = 0.9920.

Fig. 5. Percent arsenic(V) removal as a function of ferric chloride dosage and initial As(V) concentration at a constant ionic strengths of 1.2 M, initial alkalinity of 5 g L^{-1} as CaCO$_3$, and pH of 6.5.

Table 5
Predicted Fe/As molar ratios to lower As(V) in brines with ionic strength of 1.2 M to 5, 0.5, and 0.01 mg L^{-1} for varying initial As(V) concentrations and a pH of 6.5.

Initial As(V) (mg L^{-1})	Remaining As(V) = 5 (mg L^{-1}) Fe/As	Remaining As(V) = 0.5 (mg L^{-1}) Fe/As	Remaining As(V) = 0.01 (mg L^{-1}) Fe/As
12	0.9	3.5	75.6
21	1.1	3.5	52.8
39	1.2	4.1	34.0
57	1.3	3.8	25.7
79	1.3	3.6	20.3
119	1.3	3.7	15.0

Table 6
Summary of studies on arsenic removal by ferric chloride for reverse osmosis (RO) and ion exchange (IX) waste residuals.

Residuals	FeCl$_3$ (as Fe) (mg L^{-1})	pH	Initial As(V) (mg L^{-1})	Fe/As molar ratio	% As(V) removal efficiency	Reference
RO	4.42	6.2	0.5	12	98	[17]
RO	31	6.2–8.1	0.5	84	100	[17]
IX	51	5.5	3.45	20	99.5	[16]
IX	127	5.2	3.45	50	99.7	[16]
IX	34	6.2	10.5	4.4	87.8	[1]
IX	167	5.6	11.3	20	99.7	[16]
IX	62	5.5	9.7	8.5	98.5	This study
IX	32	6.5	12	3.5	95.8	This study
IX	34	8.8	33.2	1.4	86.9	[1]
IX	172	5.5	42.3	5.5	99.8	This Study
IX	241	5.5	97.9	3.3	99.9	This Study
IX	442	6–7	300	2	>99	[15]
IX	1105	9	300	5	>99	[15]
IX	1105	3–6.5	300	5	>99	[15]
IX	4421	3–11	300	20	>99	[15]

Table 7
Summary of studies on arsenic removal by ferric chloride for drinking waters.

Study Type	FeCl$_3$ (as Fe) (mg L^{-1})	pH	Initial As(V) (mg L^{-1})	Fe/As molar ratio	% As(V) removal efficiency	Reference
Bench scale Synthetic water	1.7	7	20	115	100	[21]
Pilot Groundwater	2.7	7.9	21	174	98	[51]
Pilot Groundwater	2	6.4	33.7	81	97	[17]
Bench scale Groundwater	1.4	7	37.5	51	100	[52]
Bench scale Synthetic water	7.4	7.1	40	251	95	[8]
Bench scale Synthetic water	3	6.5	50	81	98	[16]
Pilot Groundwater	20.7	7.3	90	312	99	[8]
Pilot Groundwater	5.2	6	90	78	96	[8]
Bench scale Synthetic water	1.7	7	100	23	100	[21]
Bench scale Synthetic water	1	6	100	14	95	[20]
Bench scale Groundwater	6.7	6.8	300	30	99.3	[46]

Table 8
Percent As(V) removal efficiency and respective final pH values as a function of FeCl$_3$ (as Fe) dosage added to brines with 48 mg L^{-1} As(V), 0.8 M ionic strength and varying initial alkalinities.

Fe (M)	Fe/As	Init. Alk. 2.5 g L^{-1} as CaCO$_3$		Init. Alk. 5 g L^{-1} as CaCO$_3$		Init. Alk. 10 g L^{-1} as CaCO$_3$	
		% As(V) removal	Final pH	% As(V) removal	Final pH	% As(V) removal	Final pH
0	0	0.0	8.5	0.0	8.5	0.0	8.5
0.6	1.0	27.0	8.3	31.5	8.5	53.7	8.5
1.2	1.9	66.1	8.1	80.8	8.2	71.4	8.4
1.9	2.9	90.1	7.8	91.1	8.1	83.0	8.3
2.5	3.9	97.6	7.6	95.8	8.0	90.9	8.2
3.1	4.8	98.5	7.4	96.8	7.8	93.2	8.1
3.7	5.8	99.1	7.3	99.0	7.6	97.8	7.8

HFO [20,31,32]. This implies that IX brines with higher alkalinities require higher dosage of ferric chloride than IX brines with low alkalinities.

In removing arsenic by ferric chloride coagulation, the pH of the waste brine can be lowered by acid addition or by addition of higher concentrations of FeCl$_3$. This is the case because ferric chloride has an acidic character and its addition result in pH reduction. Therefore, water plants treating IX brines for As(V) removal may lower the pH of the brine with an acid or with excessive FeCl$_3$ dosages. Each of these choices has advantages. Because ferric chloride is relatively inexpensive, acid use is associated with higher operating cost. Using excessive dosages of FeCl$_3$ results in the generation of larger amounts of sludge, which have to be disposed off. Depending on the brine characteristics, an economic evaluation is needed to determine the best alternative to lower the pH of the brine.

3.5. Sludge Solids generated from the coagulation treatment

The total suspended solids for the coagulation batch experiments shown in Figs. 1–4 and Table 8 were measured. Coagulation in brines with high ionic strengths (0.8–1.5 M) produced larger flocs, which could be removed by the 0.45 μm filter. However, flocs formed in the brine with 0.1 M ionic strength passed through a 0.45 μm filter and several hours later formed in the filtrate from the solution. This observation suggests that in lower ionic strength brines, longer flocculation times should be provided for floc growth to assure more efficient solid/liquid separation. Mercer and Tobiason [15] also reported that higher ionic strengths lend themselves to better flocculation of particles allowing formation of larger floc sizes and subsequent more efficient solid/liquid separation.

Fig. 6 shows the total suspended solids generated for a brine with 1.5 M ionic strength, varying initial As(V) concentrations, and varying Fe/As molar ratios. The amount of sludge produced increased significantly with increasing Fe/As ratios and initial arsenic concentration. The amounts of solid generated in brines with initial As(V) concentrations of 42.3 mg L^{-1} and 97.3 mg L^{-1} were statistically different ($P = 0.015 < 0.05$).

In Fig. 6 it can be observed that the amount of solids produced tends to a stable constant value as the Fe/As molar ratios increase. For the brines with initial As(V) concentration of 42.2, and 97.9 mg L^{-1}, the solids concentration stabilizes after Fe/As ratios
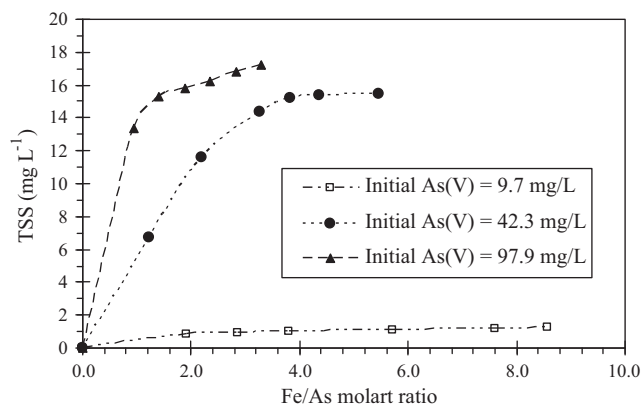
Fig. 6. Total suspended solids concentration (TSS) as a function of Fe/As molar ratio and initial As(V) concentration at $I = 1.5$ M and pH 5.5.

of 2.5 and 4.2, respectively. The amounts of sludge produced in the removal of 9.7, 42.2, and 97.9 mg L^{-1} As(V) with 1.5 M ionic strength were 1.3, 15.5, and 17.3 mg L^{-1}, respectively. The results also shown that the residual waste brine generated in the treatment of ion-exchange brine contained As(V) concentrations lower than the required TCLP limit. MacPhee et al. [1] reported that approximately 9 mg L^{-1} of sludge produced when 17–69 mg L^{-1} of FeCl$_3$ (as Fe) was used to treat IX brines containing initial As(V) concentrations of 10.5–24.8 mg L^{-1} and pH of 9.0–9.7.

Although the amount of sludge solids generated in the removal of arsenic from brines has been estimated in this research, the final disposal of the sludge and its stability was not investigated. However, it constitutes an important portion of residual management and recent studies have attempted to address these issues [47,48].

4. Conclusions

The following are the conclusions of this research:

1. As(V) removal from IX brines is a pH dependent process. The optimum pH range (maximum removal) of the adsorption process was found to be 4.5–6.5. However, the process was also efficient at higher pH (<8.5) values when higher dosages of ferric chloride were applied. Because IX brines typically have pH values between 8 and 10, lowering the pH is needed for effective arsenic removal.

2. The surface complexation model used to model adsorption of As(V) onto HFO was in good agreement with the results of the experimental results from batch coagulation tests. Therefore, the modeling can be used to assist the water industry in determined FeCl$_3$ dosages and pH values needed to achieve desired arsenic removals from ion-exchange brines.

3. The removal efficiency of As(V) by ferric chloride coagulation slightly increased when ionic strength of the brine was increased from 0.1 M to 0.8 M or 1.5 M, respectively. No significant improvement in removal efficiency was observed for ionic strength increased above 0.8 M.

4. Increasing alkalinity from 5 to 10 g L^{-1} as CaCO$_3$ slightly decreased the removal efficiency of As(V) with ferric chloride coagulation.

5. The ferric chloride dosages needed to remove arsenic to TCLP limits is not directly proportional to the higher As(V) concentrations found in brines. For arsenic concentrations typical of ion-exchange brines, Fe/As ratios of about 1.2–4 are sufficient to achieve remaining As(V) concentrations that meets or exceeds the required TCLP limit.

6. However, if IX brines were to be treated to achieve the MCL for drinking waters, lower Fe/As molar ratios would be required for higher arsenic levels. This is the case because smaller amounts of solids are formed for lower initial arsenic concentration, and, therefore, more FeCl$_3$ is needed to achieve a desired final As(V) concentration.

7. The amount of sludge solids generated in the coagulation process was found to increase with initial arsenic concentration and with Fe/As molar ratios. However, the amount of sludge produce reaches a stable value for higher Fe/As molar ratios. For brines with initial As(V) concentration of 42.2, and 97.9 mg L^{-1}, the solids concentration stabilizes after Fe/As ratios of 2.5 and 4.2, respectively. Solid concentrations varying from 2 to 18 mg L^{-1} were found.

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