1 **Enhanced Arsenite Removal through Surface-catalyzed Oxidative Coagulation Treatment**

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Abstract

Arsenic being a naturally-occurring groundwater contaminant is subject to stringent water quality regulations. Coagulation and adsorption are widely used methods to treat arsenic-contaminated water, however, these treatments have been reported to be less efficient for the removal of arsenite (As(III)) than arsenate (As(V)). In this study, the feasibility of *in situ* oxidation of As(III) during coagulation was investigated in two systems: Fe(II) or H₂O₂-assisted oxidative coagulation treatment using ferric chloride as the coagulant. This setup exploits the catalytic property of the fresh formed Fe(III) hydroxide colloids in coagulation suspension to mediate the production of reactive oxidants capable of As(III) oxidation. Fe(II)-assisted coagulation brought about small improvements in As(III) removal compared to treatment with Fe(III) coagulant alone, however, its arsenic removal efficiency is strongly dependent on pH (observed optimal pH = 7-9). Addition of H₂O₂ together with ferric chloride led to a significant enhancement in arsenic retention at pH 6 - 8, with final arsenic concentrations well below the U.S.EPA regulatory limit (10 µg/L). H₂O₂-assisted oxidative coagulation can attain reliable As(III) removal over a broad pH range of 4 to 9. Radical quenching experiments with 2-propanol and benzoquinone reveal the participation of superoxide radical in As(III) removal in the oxidative coagulation systems. Phosphate (at > 0.1 mM) strongly suppresses As(III) removal efficiency, whereas carbonate and humic acid pose a minor impact. Overall, the results suggest that a low dose addition of H₂O₂ along with ferric coagulant is a feasible method for the existing water treatment facilities to achieve improved As(III) removal efficiency.

Keywords: arsenite, drinking water treatment, coagulation, Fe(III) hydroxide, surface-mediated oxidation

44

45 **Introduction**

46 Arsenic is a contaminant of wide-spread occurrence in groundwater at diverse geological
47 locations, and the increasing dependence of global drinking water supply on groundwater has
48 resulted in major epidemics of arsenic poisoning in the past few decades (Khandaker et al., 2009;
49 Smedley and Kinniburgh, 2002). Although the use of arsenic as agricultural chemicals (*e.g.*,
50 insecticides and wood preservatives) has been banned in many countries (Vaughan, 2006),
51 natural processes such as mineral weathering contribute a major source of arsenic in groundwater.
52 In some cases, the release of arsenic from mineral deposits is aggravated by anthropogenic
53 activities that can lead to substantial changes in subsurface biogeochemical conditions (Neumann
54 et al., 2010; Dittmar et al., 2010).

55 The dominant forms of arsenic found in groundwater are arsenite (As(III), as H_3AsO_3 at neutral
56 pH) and arsenate (As(V), as HAsO_4^{2-} at neutral pH) (Johnston and Singer, 2007; Bang et al.,
57 2005). While As(III) is considered more toxic than As(V), the health risk associated with arsenic
58 exposure also depends on the mobility of different arsenic species (Vaughan, 2006). The
59 adsorption behavior of As(III) and As(V) onto various forms of amorphous or crystalline iron
60 oxides has been investigated under a broad range of aqueous conditions, and iron minerals are
61 also widely applied as adsorbents for treating arsenic-contaminated water (Mohan and Pittman,
62 2007; Bissen and Frimmel, 2003). With an environmentally relevant pH range (pH 4 – 10), the
63 adsorption edge of arsenite onto common iron oxides (*e.g.*, goethite and ferrihydrite) exhibit
64 maximum absorption over a broad pH, whereas that of arsenate declines substantially with
65 increasing pH (Goldberg and Johnston, 2001; Dixit and Hering, 2003; Raven et al., 1998). In
66 addition, the capacity of arsenic uptake is affected by the initial arsenic concentration, the As to

67 Fe ratio, and the composition of background solutes (Goldberg and Johnston, 2001; Dixit and
68 Hering, 2003). Common background anions such as phosphate, sulfate, and carbonate pose
69 competition against arsenic species for the surface sites of iron oxides, as a result, their presence
70 can severely impact the efficiency of arsenic adsorbents (Dixit and Hering, 2003; Su and Puls,
71 2001; Hug et al., 2008).

72 Many studies have examined the removal of arsenic from water during the conventional
73 coagulation process. Coagulation is an essential process in a drinking water treatment system for
74 the removal of turbidity. The treatment typically entails the addition of ferric or aluminum salts
75 (*i.e.*, the coagulants) into feed water during a rapid mixing step, followed by a period of slow
76 agitation to induce flocculation of colloidal particles into large aggregates due to either charge
77 neutralization by hydrolyzed ferric or aluminum complexes or enmeshment of small particles in
78 polymerized floc network (Edzwald, 1993). It is considered that arsenic can be sequestered from
79 aqueous phase during conventional coagulation via adsorption onto the floc surface and/or co-
80 precipitating with the coagulants (Edwards, 1994; Hering et al., 1996; Meng et al., 2000). It has
81 been shown that As(V) is more effectively removed than As(III) at neutral pH due to the
82 sensitivity of As(III) removal to the type of coagulant used and the background constituents
83 (Hering et al., 1996; Hering et al., 1997). Attempts have been made, therefore, to incorporate an
84 oxidation step prior to arsenic removal by coagulation or adsorption. Accordingly, oxidative
85 pretreatment using chlorine (Pio et al., 2015), permanganate (Sen et al., 2010; Bordoloi et al.,
86 2013), or ferrate (Lee et al., 2003) have been proposed. These techniques require the addition of
87 strong oxidants to drive homogeneous oxidation of As(III) in the aqueous phase. As(III)
88 oxidation catalyzed by solid surfaces may present an alternative and potentially more efficient
89 route of As(III) oxidation. Surface-mediated oxidation has been shown for various iron-

containing minerals including magnetite, goethite and ferrihydrite (Ona-Nguema et al., 2010; Voegelin and Hug, 2003; Amstaetter et al., 2010; Bhandari et al., 2011). In the case of solids containing only Fe(III), it entails the addition of Fe(II) (Ona-Nguema et al., 2010; Amstaetter et al., 2010) or H₂O₂ (Voegelin and Hug, 2003) or exposure to sunlight irradiation (Bhandari et al., 2011, Bhandari et al., 2012) to generate reactive oxidants capable of As(V) formation. Moreover, As(III) oxidation in Fe(II) or H₂O₂-Fe(III) systems was not significantly affected by hydroxyl radical quenching agents at neutral pH (Hug and Leupin, 2003), suggesting the oxidants arising in these systems are fairly selective towards As(III). Considering this and the high affinity of As(III) for iron oxides, surface-catalyzed oxidation may be more advantageous for arsenite sequestration than solution-phase oxidation methods. Indeed, the concept of catalytic As(III) oxidation in the presence of iron-containing solids has been explored in recent studies in the form of photo-reduction of Fe(III) (Hug et al., 2001), electro-coagulation (Lakshmanan et al., 2010; Kumar et al., 2004), or chemically enhanced As(III) oxidation (via addition of H₂O₂) (Hug and Leupin, 2003). However, these studies are mostly catered to point-of-use treatment systems, and the feasibility of utilizing solids generated during conventional coagulation treatment as heterogeneous catalysts for enhanced arsenic removal is a concept not explored to date. Importantly, coagulation generates a vast amount of Fe(III) hydroxide colloids and the process operates with ample hydraulic residence time, rendering coagulation basin an interesting arena to explore the reactivity of interfacial redox reactions for contaminant abatement. The objective of this study is to evaluate the performance of two oxidative coagulation systems in treating As(III)-contaminated water. In reference to conventional coagulation using ferric chloride as the coagulant, oxidative coagulation entails the addition of a small dose of Fe(II) or H₂O₂ in addition to the coagulant to promote the formation of reactive oxidants. The effects of

chemical dose, pH, and background solutes on the total arsenic removal (initially present as As(III) in the feed water) were systematically assessed. The role of As(III) oxidation in assisting its removal from the aqueous phase was investigated through comparison of the kinetics and final arsenic retention in the oxidative coagulation treatments against those in conventional coagulation as well as analysis of arsenic speciation in the solid residues of coagulation using X-ray photoelectron spectroscopy (XPS). In addition, radical quenching experiments were conducted to understand the nature of the oxidants responsible for As(III) oxidation. Finally, the performance of the proposed oxidative coagulation treatment in source water of complex composition was evaluated by examining the effects of individual solutes.

Materials and Methods

Reagents

All aqueous solutions used in this study were prepared with Milli-Q purified water (18 MΩ·cm). Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), bentonite (sodium form), sodium bicarbonate (NaHCO_3), hydrogen peroxide (H_2O_2 , 3% w/w) and 2-propanol (HPLC grade) were purchased from Fisher Scientific. Aluminum sulfate, commonly referred to as alum, ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{--}18 \text{H}_2\text{O}$) was from MCB Reagents. Sodium (meta)arsenite (NaAsO_2 , 98%) and humic acid sodium salt (technical grade) were from Sigma-Aldrich. Potassium phosphate (monobasic, KH_2PO_4) and 1,4-benzoquinone were from Acros Organics. All chemicals are of ACS reagent grade or higher unless otherwise noted. FeCl_3 stock (4 g/L) was prepared daily immediately before the experiments. Arsenite stock (1000 mg/L) was also prepared fresh before each experiment.

Coagulation Experiments

Conventional coagulation tests. All coagulation tests were performed with a 6-station floc tester (Orbeco Hellige ET750, NovaTech). The jars were 1000-mL HDPE graduated receptacles (Capitol Scientific). Synthetic feed water containing 2 mM NaHCO₃ and 0.1 g/L of bentonite to mimic turbidity in natural water was used throughout this study. Other background constituents (*e.g.*, phosphate and humic acid) were not amended except for those experiments investigating the effect of background solutes on the coagulation performance. The feed water was stirred thoroughly and allowed to settle overnight (for approx. 16 h) prior to the experiments. Only the top portion of the feed water with turbidity of approximately 20 NTU was used. The initial pH of the feed water was adjusted to 8.0 using dilute HCl or NaOH, except for a subset of experiments evaluating the effect of pH.. Immediately before the test, the feed water was spiked with arsenite stock solution to reach an As(III) concentration of 100 µg/L. At the onset of rapid mixing, a small aliquot of the coagulant stock solution was added to each jar of synthetic water. A typical coagulation experiment consists of rapid mixing for 5 min at a mixing speed of 90 rpm, followed by slow mixing for 30 min at 20 rpm, and a settling period of up to 40 min. At the end of the settling period, 5-mL samples were withdrawn at about 2 cm below the solution surface. A portion of the sample was immediately analyzed for turbidity and the remaining was filtered through a disposable syringe filter with 0.2 µm hydrophilic PTFE membrane (SLLG025SS, Millipore) for the analysis of dissolved arsenic. Samples for dissolved arsenic analysis were acidified with 2% nitric acid and analyzed within one week after collection. During some experiments, additional samples were collected periodically during coagulation for arsenic analysis.

Oxidative coagulation tests. The experimental procedure of oxidative coagulation is identical to that of the conventional coagulation except that immediately after the addition of the coagulant, the solution was spiked with a small aliquot of FeSO_4 or H_2O_2 stock solution to reach pre-determined Fe(II) or H_2O_2 concentration. In order to probe the nature of the oxidants produced during the oxidative coagulation process, radical scavenging tests were performed by adding appropriate amounts (2 – 20 mM) of 2-propanol or benzoquinone to the synthetic feed water after arsenite spiking but before the addition of coagulants.

Analytical Methods

Turbidity measurement was performed at the end of coagulation tests with a spectrophotometer (Hach DR2000). pH of the solution was measured with a portable pH meter (Hach HQ40d) equipped with a PHC 705 pH probe, and the pH probe was calibrated on a daily basis with a 3-point calibration. Total arsenic was determined using graphite furnace atomic absorption spectrometry (GF-AAS) performed on a Perkin-Elmer AAnalyst 800 spectrometer equipped with a transversely-heated graphite furnace. The absorption of As was measured at 193.7 nm using an As EDL lamp. As standards were prepared from commercial As standard (NIST traceable, Inorganic Ventures) in 2% (v/v) HNO_3 matrix. The detection limit of this method is 1 $\mu\text{g/L}$ and a linear calibration curve ($R^2 > 0.999$) is attained at up to 100 $\mu\text{g/L}$.

Arsenic speciation on the solid phase was investigated using high-resolution X-ray photoelectron spectroscopy (HR-XPS). Due to detection limit, the coagulation tests subject to XPS investigations were conducted at an initial As(III) of 1000 $\mu\text{g/L}$. The solid residues settling out from the solution at the end of coagulation tests were collected by vacuum filtration and were dried in a N_2 glove box for 48 h. HR-XPS spectra were acquired of the solid samples on a PHI 5000 Versa Probe System using a radiation source of monochromated $\text{AlK}\alpha$ line. High-

resolution spectra at As3d transition were collected at a 45° take-off angle and a pass energy of 23.5 eV. The binding energy of the spectra was calibrated against that of adventitious carbon in the C1s region (284.8 eV). Curve-fitting was performed using the CasaXPS package (version 2.3.17) as described in previous studies (Yan et al., 2012; Yan et al., 2010).

Results and discussion

As(III) removal via conventional coagulation

As mentioned in the Materials and Methods, the synthetic feed water was amended with 0.1 g/L of bentonite to imitate the natural turbidity of surface water. It was found that the addition of bentonite had no significant impact on arsenic removal, and replacing the bentonite with silica particles resulted in similar extents of arsenic removal (Figure S1), indicating that the background colloids present in the feed water have a minor effect on the arsenic sequestration efficiency. Except for experiments that investigated the effect of pH on coagulation, the solutions of all experiments were maintained within a pH range of 6 – 8 due to the buffering capacity of bicarbonate ions in the feed water. The initial and final pHs of all experiments are listed in Table S1. The concentration of bicarbonate used in this study (2 mM) is within the range of its typical occurrence in surface or ground water (Snoeyink and Jenkins, 1980; Benjamin, 2014).

Figure 1 shows the arsenic removal with conventional coagulation process using ferric chloride as the coagulant. Increasing the coagulant dose in the range of 89 to 357 µM (14 to 58 mg/L as FeCl₃) resulted in up to 91% of arsenite removal. Further increasing the coagulant dose to as high as 714 µM (116 mg/L as FeCl₃) did not lead to appreciable improvement in arsenite retention. Note that at the highest Fe(III) dose, the final turbidity of the solution was greater than

200 NTU, suggesting overdosing the coagulant had caused re-stabilization of particles in the feed water and formation of suspended Fe(III) hydroxide precipitates.

A typical coagulation-flocculation process comprises of three phases, namely, rapid-mixing, slow-mixing, and settling, and the duration of each phase is indicated in Figure 1. The data shows that the majority of arsenite was taken up during the course of rapid-mixing and the early stage of slow-mixing, when the formation of ferric hydroxide floc was clearly visible. The effects of initial As(III) concentration and pH on conventional coagulation were also tested (Figure 2). The final arsenic concentration increases in a linear trend with an increasing As(III) initial concentration, thus keeping arsenic concentration below the regulatory limit (denoted as As MCL in Figure 2a) is difficult using Fe(III) alone when the source water has a relatively high As(III) content. Figure 2b shows that conventional coagulation treatment exhibits a significant pH dependence. The maximum As(III) removal was obtained at the highest pH (~ 9.1). Decreasing the pH led to a general decline in As(III) removal efficiency, with the effect being most severe when pH was below 5. Previous studies of As(III) adsorption on ferric (hydr)oxides reported a broad pH envelope (pH 5 – 10) of optimal adsorption (Raven et al., 1998, Dixit and Hering, 2003). Compared to its adsorption by Fe(III) minerals, As(III) removal with conventional coagulation is more sensitive to solution pH, which we attribute to limited (and slower) formation of ferric hydroxide precipitates as pH decreases. Overall, these results indicate that conventional coagulation alone can retain a fair amount of arsenite in water, but the efficiency is greatly influenced by pH.

As(III) removal via Fe(II)-assisted oxidative coagulation

Fe(II) was amended to the coagulation system to promote oxidation of As(III). Reaction of Fe(II) and dissolved O₂ produces superoxide anion radical (O₂^{•-}), which may react with another Fe²⁺ to

produce H₂O₂. The above reactions may take place in the solution phase involving dissolved Fe(II) (Eqs. (1) and (2)) or be mediated by the surface of ferric hydroxide formed *in situ* from Fe(III) coagulant (Eqs. (3) and (4)). Previous Fe(II) oxygenation studies indicate that the surface-catalyzed pathway is kinetically more important at circumneutral pH (Tamura H. et al., 1980; Sung and Morgan, 1980).

Alternatively, H₂O₂ may be produced via dismutation of superoxide radicals (Eq. (5)), but in a dilute Fe(II) solution at a near neutral pH, this reaction is generally considered unimportant (Hug and Leupin, 2003).

The H₂O₂ formed proceeds to react with dissolved or surface Fe(II) species to produce reactive oxidants such as HO· (Eqs. (6) and (7)). It has been suggested that the reaction of H₂O₂ with surface iron species may produce ferryl species (>Fe^{IV}=O) instead of HO· at near neutral pH (Hug and Leupin, 2003; Leupin and Hug, 2005). Both species are able to convert As(III) to As(V) (Hug and Leupin, 2003, Pang et al., 2011), thus the nature of the oxidant cannot be resolved unequivocally in this study.

246 The kinetics of As(III) sequestration during Fe(II)-assisted oxidative coagulation is shown in
247 Figure 3. Compared to conventional coagulation, the amendment of 31 to 124 μM of Fe(II) in
248 addition to 178 μM of Fe(III) resulted in 8 to 10% increase in As(III) removal. Furthermore, this
249 additional arsenic uptake occurred predominantly during the slow-mixing phase. In spite of this
250 enhancement effect, varying the dose of Fe(II) within the range studied did not seem lead to a
251 substantial increase in the final arsenic concentration. The lowest final arsenic concentration
252 obtained with Fe(II)-assisted oxidative coagulation was approximately 5 $\mu\text{g/L}$. To further
253 investigate the effect of iron dose, Fe(III) and Fe(II) concentrations were varied independently
254 and the results were plotted in Figure 4. As shown in the main plot, the increase in arsenite
255 removal brought about by Fe(II) addition is more obvious when the coagulant (*i.e.*, Fe(III)) was
256 applied at low doses. To understand whether the enhancement associated with Fe(II) amendment
257 is primarily due to increased flocs formation since oxidation of Fe(II) will contribute to a higher
258 level of Fe(III) in the solution, or assisted by As(III) oxidation during Fe(II) oxygenation, arsenic
259 removal was plotted with respect to the total dose of Fe in the system (inset of Figure 4).
260 Although the lines appear more clustered than those in the main plot, small yet evident
261 improvements in arsenite sequestration can be discerned in systems with Fe(II) amendments,
262 suggesting As(III) oxidation by reactive oxidative species (ROS) generated during Fe(II)
263 oxygenation is partially accountable for the enhanced arsenic sequestration. Regardless of the
264 dose of Fe(II), arsenite removal in all Fe(II)-assisted oxidative coagulation tests plateaus at
265 around 95%. We hypothesize that this is due to the relatively slow rate of As(III) oxidation and
266 the limited time allowed during slow-mixing (30 min). Hug and Leupin evaluated the kinetics of
267 As(III) oxidation in the presence of Fe(II) and dissolved oxygen (Hug and Leupin, 2003). At an
268 initial As(III) concentration of 500 $\mu\text{g/L}$, around 30% of As(III) was oxidized in approximately

one hour in the presence of 90 μM Fe(II) at pH 7.0, and kinetic modeling suggests the formation of As(V) was primarily controlled by the rate of Fe(II) reacting with O_2 (*i.e.*, Eqs. (1) and (3)). Similar rates of As(V) formation were reported by Johnston and Singer at comparable Fe(II) concentration and pH (Johnston and Singer, 2007). Since the enhancement in As(III) sequestration took place mainly during the slow-mixing phase where there was negligible fluid agitation, As(III) oxidation in the current system is expected to be slower than the reported rates. However, the mild agitation during slow-mixing is necessary for the optimal removal of turbidity (Metcalf, 2003). The kinetic limitation in As(III) oxidation during Fe(II) oxygenation may explain the relatively small improvements in arsenic removal efficiency with Fe(II)-assisted coagulation.

Along this discussion, we evaluated the effect of the time point of Fe(II) amendment. Specifically, in addition to the default procedure with Fe(II) amendment at the beginning of rapid mixing, experiments were performed with Fe(II) dosed immediately before slow-mixing (*i.e.*, 5 min after the start of rapid-mixing), 10 min into slow-mixing, and 20 min into slow-mixing. The results are illustrated in Figure S2. The most effective arsenic removal was achieved by injecting Fe(II) together with Fe(III) at the beginning of rapid-mixing. Furthermore, the same observation was made when Fe(II) was used at different doses. The results support our previous inference that As(III) oxidation is kinetically slow compared to the time frame of the coagulation treatment. Adding Fe(II) at a later stage would delay As(III) oxidation and forfeit the opportunity to achieve more complete arsenic removal through As(III) to As(V) conversion.

The effects of initial As(III) concentration and pH on Fe(II)-assisted oxidative coagulation were examined (Figure 2). The addition of Fe(II) results in a noticeable improvement in arsenic removal (Figure 2a), yet a strong increasing trend with the initial As(III) concentration implies

the Fe(II) system has a limited capacity in accommodating a large increase in the initial As(III) concentration. Similar to conventional coagulation, As(III) retention efficiency appears to increase sharply when pH rises from 4 to 7 (Figure 2b). This strong pH dependence is due to the increased solubility of iron species in acidic environment, which undermines effective flocculation. Another reason for the inefficient arsenic removal at a low pH is thought to be the slow kinetics of Fe(II) oxygenation in acidic solutions. The model proposed by Sung and Morgan (Sung and Morgan, 1980) considers the rate of homogeneous Fe(II) oxygenation to depend on the square of OH^- concentration. The rate of heterogeneous Fe(II) oxygenation is proportional to the amount of solid surface present, which is largely contributed by the flocs formed. Both processes are critically dependent on the solution pH, therefore, Fe(II) oxygenation is considerably slow at $\text{pH} < 5$ (Sung and Morgan, 1980; Tamura H. et al., 1980; Jones et al., 2014).

Finally, the effect of adding alum as a co-coagulant to the Fe(II)-Fe(III) system was investigated (Figure S3), based on the consideration that alum is another common coagulant other than ferric salts and As(III) oxidation on aluminum oxide surface in the presence of H_2O_2 has been reported (Önnby et al., 2014). In this series of experiments, the concentration of Fe(III) varied while the doses of alum and Fe(II) were kept constant. As can be seen from the figure, addition of 10 mg/L alum suppressed arsenic removal, and the effect appears to be more severe when Fe(III) was used at a low dose. This can be rationalized on the basis that the surface of alumina hydroxide is less affinitive for As(III) compared to ferric hydroxide particles (Goldberg and Johnston, 2001; Manning and Goldberg, 1997; Hering et al., 1997), therefore, adding alum together with Fe(III) as a coagulant mixture may decrease the available Fe(III) sites for As(III) uptake. Furthermore, the flocs of aluminum hydroxide are possibly of lower catalytic activity than ferric hydroxide

particles for the oxygenation of Fe(II). These factors may explain the observed negative effect of alum addition on As(III) removal.

As(III) removal via H₂O₂-assisted oxidative coagulation

An alternatively setup involves the injection of H₂O₂ during coagulation treatment. In this system, Fe(III) serves not only as a coagulant, but also a precursor of iron catalysts that facilitate the decomposition of H₂O₂ to form reactive oxidants capable of oxidizing As(III) (Eq. (8)). Note that in Eq. (8), As(III) is written in a surface attached form, and it is possible that oxidation of As(III) may also occur in the solution phase.

The kinetics of H₂O₂-assisted oxidative coagulation is shown in Figure 5. H₂O₂ was added to the coagulation vessels at 1, 8, 20, and 50 mg/L, respectively. The enhancement in arsenite removal is evident at all doses of H₂O₂. The final arsenic concentration was 5 µg/L with 1 mg/L of H₂O₂, 2 µg/L with 8 mg/L of H₂O₂, and below the detection limit (1 µg/L) at higher H₂O₂ doses. We attribute the increased arsenic uptake to efficient As(III) oxidation in the presence of H₂O₂, considering that the As(V) formed is more amenable to sequestration via coagulation treatment (Elimelech et al., 1996). Different from Fe(II)-assisted coagulation, where the incremental arsenite retention was observed mainly during the slow-mixing step, there were significant improvements in arsenic retention during the rapid-mixing phase with H₂O₂ amendments, suggesting rapid production of reactive oxidants in the presence of H₂O₂ and Fe(III) that enabled efficient As(III) conversion.

More data showing the effect of H₂O₂ dose at varying coagulant concentration is included in Figure 6. The final arsenic removal was plotted with respect to Fe(III) dose in the system.

338 Substantial enhancements in arsenic removal were noticed across all doses of coagulants.
339 Notably, even with the lowest dose of H_2O_2 (1 mg/L), the final arsenic concentration is well
340 within the regulatory limit (10 $\mu\text{g/L}$) as long as the Fe(III) coagulant was applied at above 100
341 μM . This indicates that H_2O_2 can deliver a high oxidant yield in the presence of a suitable
342 amount of catalysts, and As(III) oxidation is more competitive than other side-reactions that
343 could consume the oxidants. The loss of H_2O_2 during coagulation treatment was measured for an
344 initial H_2O_2 dose of 20 mg/L and 50 mg/L, respectively (Figure S4). Limited consumption of
345 H_2O_2 was observed, which occurred mainly during the rapid and slow-mixing phases. The initial
346 concentration of As(III) does not have a significant effect on the consumption of H_2O_2 .
347 Another way to compare the performance of arsenite removal between the conventional and
348 H_2O_2 -assisted oxidative coagulation is to examine the amount of arsenic retained per unit amount
349 of iron floc generated. This quantity is represented in Figure 7 as As/Fe molar ratio in the solid
350 residue, which was computed from the moles of arsenic removed from the aqueous solution at
351 the completion of coagulation normalized by the moles of Fe(III) coagulant introduced at the
352 beginning of the coagulation. Since dissolved iron concentration in the effluent is negligible
353 compared to the initial Fe(III) dose, we consider that all Fe(III) added was converted to sludge in
354 the above calculations. Although plotting As/Fe ratio in the solid residue against the final
355 concentration of arsenic in the aqueous solution sets up a graph that resembles the classical
356 adsorption isotherms, we note that the processes responsible for arsenite removal in the
357 conventional or oxidative coagulation are more complex than adsorption alone. Oxidation of
358 As(III) and adsorption and co-precipitation of As(V) are expected to occur concurrently with
359 As(III) adsorption by ferric hydroxide particles. In spite of the complex mechanisms involved, a
360 salient feature in Figure 7 is the initial slope of the isotherms. A steeper slope suggests that the

treatment has a greater capability in attaining a final As concentration below the target level of 10 µg/L. It is apparent from Figure 7 that the addition of H₂O₂ results in more favorable capturing of arsenic from the aqueous phase, and this capability is more prominent with increasing H₂O₂ dose.

It was observed that the addition of 20 mg/L H₂O₂ during Fe(III) coagulation was able to attain a high efficiency of arsenic sequestration across a broad range of the initial As(III) concentration (Figure 2a). Furthermore, in contrast to the strong pH dependence observed with conventional coagulation and Fe(II)-assisted oxidative coagulation, As(III) sequestration performance was largely unaffected by pH in H₂O₂-assisted coagulation (Figure 2b). Unlike Fe(II) oxygenation reactions that are strongly influenced by pH, efficient activation of H₂O₂ by Fe(III) catalysts can be achieved across a broad range of pH, although the nature of the reactive oxidants formed (*e.g.*, free OH• vs. surface bound OH• or ferryl species) may vary (Pignatello et al., 1999; Pang et al., 2011; Pham et al., 2009). The lack of strong dependence on pH for As(III) oxidation observed here may therefore serve as indirect evidence that the reaction does not require an exclusive form of oxidant. It has been shown that As(V) adsorbs favorably to iron oxides and other mineral colloids, and the maximum adsorption density is attained in the lower pH range (pH < 5) (Goldberg and Johnston, 2001; Dixit and Hering, 2003). Greater As(V) adsorption at lower pH is therefore able to counteract the effect of diminishing flocs formation, giving rise to stable arsenic retention performance across a broad range of pH. From operation control point of view, this attribute of H₂O₂-assisted oxidative coagulation is highly desirable.

Effect of Background Solutes

The effect of background solutes on the performance of H₂O₂-assisted oxidative coagulation was assessed by amending the feed water with an appropriate concentration of carbonate (as HCO₃⁻), phosphate (as H₂PO₄⁻ / HPO₄²⁻), or humic acid before the addition of coagulant and H₂O₂. The results are presented in Figure 8. Carbonate ion has an insignificant effect on arsenic removal at up to 10 mM (Figure 8a). Carbonate species may affect As-Fe interaction in several ways. The presence of carbonate as a major anion in groundwater can pose a significant quenching effect on the hydroxyl radical to form carbonate radical (CO₃^{•-}) (Grebel et al., 2010). Carbonate radical is less reactive than hydroxyl radical but more selective towards As(III) (rate constant 1.1 x 10⁸ M⁻¹s⁻¹ at neutral pH) (Hug and Leupin, 2003). In addition, carbonate-As(III) complexes have been suggested to be more amenable to oxidation (Kim et al., 2006), although other studies have seen less uptake of As(III) or As(V) in the presence of carbonate ions due to competition for surface adsorption sites on iron oxides (Appelo et al., 2002; Su and Puls, 2001). Our observation of a negligible impact caused by carbonate ions suggests these counteracting effects of carbonate may offset each other during H₂O₂-assisted oxidative coagulation treatment. We would like to note that the absence of a strong impact of carbonate offers a practical convenience as addition of carbonate salts is often required in typical coagulation operations to maintain an optimal pH. It is evident in Figure 8b that phosphate ion strongly affects As(III) retention efficiency. Even at the lowest concentration evaluated (0.1 mM), phosphate is able to suppress As(III) removal by 60%. This strong interference of phosphate is attributed to its high affinity for the surface of iron hydroxides (Dixit and Hering, 2003; Su and Puls, 2001). It has been proposed by other groups that arsenic sequestration in the presence of significant phosphate competition can be mitigated through increased amendment of Fe(II) or Fe(III) chemicals (Roberts et al., 2004; Hug et al., 2008). Humic acid has a moderate influence on arsenic removal (Figure 8c). The adverse effect

406 amounts to a 10% decrease in arsenic sequestration when humic acid is present at a high
407 concentration (25 mg/L). Dissolved organic matter (NOM) may affect As(III) oxidation by
408 scavenging reactive radicals (Pignatello et al., 2006) and interfere with the formation of iron
409 oxide precipitates (Hering et al., 1997). The relatively mild impact cast by humic acid in this
410 study seems to point to an efficient role played by surface-mediated As(III) oxidation in H₂O₂-
411 assisted oxidative coagulation.

412

Nature of oxidants during oxidative coagulation

Two radical scavengers were applied to identify the reactive oxygen species (ROS) involved in As(III) oxidation and total arsenic removal during H₂O₂-assisted oxidative coagulation. 2-propanol is able to scavenge hydroxyl radical (OH·) (Hug and Leupin, 2003; Keenan and Sedlak, 2008), while 1,4-benzoquinone is known as a scavenger for superoxide radical (O₂^{·-}) (Yin et al., 2009). For H₂O₂-assisted coagulation, arsenic removal was not affected when 2-propanol was added into the feed water at up to 20 mM (Figure 9). In comparison, a small reduction in arsenic retention was discerned when benzoquinone was amended. This indicates the participation of superoxide, but not hydroxyl radical, during oxidative coagulation with H₂O₂. In Fe(II)-assisted coagulation treatment, the addition of 2-propanol or benzoquinone caused a moderate loss of arsenic removal efficiency, which suggests the involvement of both hydroxyl radical and superoxide in arsenic uptake during Fe(II)-assisted oxidative coagulation. Overall, the relatively small effect of OH· scavenger observed here is in agreement with the earlier findings of iron-catalyzed As(III) oxidation at pH > 5 (Hug and Leupin, 2003). We postulate that reactive oxidants other than free OH· are responsible for the oxidation of arsenite, and such species may possibly be surface-bound hydroxyl radicals, ferryl species, or carbonate radicals (Pignatello et al., 2006; Pang et al., 2011).

As speciation with XPS analysis

Figure 10 shows As3d HR-XPS scans of solid residues collected at the end of three coagulation tests. Spectra were fitted based on the known energy split and intensity ratio of As3d_{5/2} and As3d_{3/2} components of the As3d doublet peaks (Yan et al., 2012), and the assignment of peaks is indicated in the figure. Approximately 55% of arsenic was immobilized as As(III) via conventional coagulation. The balance (45%) was as As(V). The results, therefore, imply that

nearly half of the As(III) in the solution was oxidized in conventional coagulation. As(III) oxidation on Fe(III) surface may occur in the presence of visible light irradiation (Bhandari et al., 2011) or be catalyzed by a small amount of Fe(II) present in the bentonite structure. With Fe(II) amendment, 47% of the arsenic retained on the surface was in the state of As(V). Considering the uncertainty of the analysis due to the low signal intensity, the distribution of arsenic in these two systems is similar. In comparison, the spectrum of H₂O₂-assisted coagulation exhibits a substantially increased As(V) doublet (67% of total As), indicating that the addition of H₂O₂ has significantly boosted the extent of As(V) formation. Relating this result to arsenic removal data of the coagulation experiments, we consider that H₂O₂ amendment is a more effective method to achieve enhanced arsenic removal via oxidative As(III) conversion.

Conclusion

Experiments were performed with As(III)-laden synthetic feed water to investigate the performance of two oxidative coagulation treatment systems on arsenic removal. The two systems involve the addition of Fe(II) or H₂O₂ in addition to Fe(III) coagulant, based on the consideration that the *in situ* formed ferric hydroxide particles in a coagulation tank may serve as active catalysts to enable the generation of reactive oxidants capable of As(III) oxidation in the presence of the externally amended Fe(II) or H₂O₂. Both oxidative coagulation treatments brought about enhanced arsenic removal compared to the conventional coagulation process. However, the increases in arsenic uptake caused by Fe(II)-assisted oxidative coagulation were relatively small due to Fe(II) oxygenation and reactive oxidant production being kinetically slow within the typical time frame of coagulation treatment. Moreover, Fe(II)-assisted oxidative coagulation is susceptible to pH change and is inefficient at low pH (< 5) due to decreases in

Fe(II) oxygenation rate and ferric hydroxide precipitation rate with lower pH. H₂O₂-assisted oxidative coagulation is able to achieve a significant increase in arsenic retention at a H₂O₂ loading of 1 mg/L or more. The performance of H₂O₂-amended coagulation is less influenced by pH within a pH range of 3-9. The results of this study inform that the addition of a small dose of H₂O₂ with Fe(III) coagulant may create significant synergy for the production of reactive oxidants to form As(V), an arsenic species more amenable to removal by coagulation. Consistent with observations reported in prior studies, the sequestration of As(III) is strongly affected by phosphate ion and to a less degree, carbonate ion. More investigation is required to extend this current study to real water of diverse composition.

Acknowledgement

The authors acknowledge funding from the U.S. National Science Foundation (CHE-1308726) that has supported this study.

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Figure 1. As(III) removal by conventional coagulation process. The coagulant, Fe(III) (from FeCl_3), was added at different doses at the onset of the rapid mixing phase ($t = 0$ min). Inset shows final turbidity obtained at each coagulant dose. The initial As(III) concentration was $100 \mu\text{g/L}$. R/M and S/M represent the rapid mixing and slow mixing phases, respectively.

Figure 2. Effects of initial arsenite concentration (a) and pH (b) on As(III) removal by conventional coagulation (Fe(III) only) and Fe(II)-assisted or H₂O₂-assisted oxidative coagulation treatments. The initial As(III) concentration was 100 µg/L in (b). The dose of Fe(III) was 185 µM in all treatments in (a) and was 178 µM in all treatments in (b). The dose of Fe(II) or H₂O₂ in oxidative coagulation was 62 µM and 20 mg/L, respectively.

Figure 3. Kinetics of As(III) removal during Fe(II)-assisted oxidative coagulation treatment. All chemicals were introduced at the onset of rapid mixing. The initial As(III) concentration was 100 $\mu\text{g/L}$. The dose of Fe(III) in all treatments was 178 μM . The dose of Fe(II) varies as indicated in the legend.

Figure 4. Effect of Fe(III) and Fe(II) doses on As(III) removal during Fe(II)-assisted oxidative coagulation. The main plot shows arsenic removal as a function of the coagulant (i.e., Fe(III)) added. The removal efficiency with respect to the total Fe amendment is shown in the inset. The initial As(III) concentration was 100 μg/L.

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637 **Figure 5.** Kinetics of As(III) removal during H₂O₂-assisted oxidative coagulation process. All
 638 chemicals were introduced at the onset of rapid mixing. The initial As(III) concentration was 100
 639 µg/L. Dashed line represents the limit of detection (LOD) of the arsenic analysis method.

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Figure 6. Effect of H₂O₂ dosage on As(III) removal by H₂O₂-assisted oxidative coagulation process. All chemicals were added at the onset of rapid mixing. The initial As(III) concentration was 100 μg/L. The limit of detection (LOD) of the arsenic analysis method is shown as a dashed line.

Figure 7. Effect of H₂O₂ concentration on arsenic retention capacity per mole of Fe(III) added. The inset shows a magnified view of the enclosed area in the main plot.

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652 **Figure 8.** Effect of (a) bicarbonate, (b) phosphate, and (c) humic acid on As(III) removal during
653 H_2O_2 -assisted oxidative coagulation process. The initial As(III) concentration was 100 $\mu\text{g/L}$.
654 Fe(III) and H_2O_2 were dosed at 185 μM and 20 mg/L, respectively.

Figure 9. Effect of radical scavengers on As(III) removal during oxidative coagulation process. Two radical scavengers, 2-propanol (IPA) and benzoquinone (BQ), were add at different concentrations prior to coagulation. The initial As(III) concentration was 100 $\mu\text{g/L}$. Open symbols represent H₂O₂-assisted oxidative coagulation process (111 μM Fe(III) and 20 mg/L H₂O₂). Closed symbols denote Fe(II)-assisted oxidative coagulation (111 μM Fe(III) and 62 μM Fe(II)).

Figure 10. As_{3d} HR-XPS spectra of solids collected from conventional coagulation (a) and those from Fe(II)-assisted (b) and H₂O₂-assisted oxidative coagulation tests. Fe(III) dose was 538 μ M. Fe(II) and H₂O₂ were added at 538 μ M and 50 mg/L in (b) and (c), respectively.

SUPPORTING INFORMATION

Enhanced Arsenite Removal through Surface-catalyzed Oxidative Coagulation Treatment

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684 **Table S1. The initial and final pH of coagulation experiments**

Experiment Description	[Fe(III)]	[Fe(II)]	[H ₂ O ₂]	Initial pH	Final pH
Conventional coagulation	89 µM	-	-	8.5	7.6 +/- 0.0
	178 µM	-	-	8.5	7.2 +/- 0.0
	357 µM	-	-	8.5	6.8 +/- 0.0
	536 µM	-	-	8.5	6.2 +/- 0.0
	714 µM	-	-	8.5	4.4 +/- 0.3
Fe(II)-assisted coagulation	18 µM	31 µM	-	8.0	7.6 +/- 0.2
	37 µM	31 µM	-	8.0	7.5 +/- 0.1
	179 µM	31 µM	-	8.0	7.0 +/- 0.0
	357 µM	31 µM	-	8.0	6.6 +/- 0.0
	536 µM	31 µM	-	8.0	6.0 +/- 0.1
	18 µM	62 µM	-	8.0	7.4 +/- 0.0
	37 µM	62 µM	-	8.0	6.9 +/- 0.5
	179 µM	62 µM	-	8.0	6.7 +/- 0.5
	259 µM	62 µM	-	8.0	6.6 +/- 0.0
	357 µM	62 µM	-	8.0	6.1 +/- 0.3
	18 µM	124 µM	-	8.0	6.8 +/- 0.8
	37 µM	124 µM	-	8.0	6.7 +/- 0.7
	148 µM	124 µM	-	8.0	7.0 +/- 0.1
	259 µM	124 µM	-	8.0	6.6 +/- 0.0
	370 µM	124 µM	-	8.0	6.4 +/- 0.0
H ₂ O ₂ -assisted coagulation	18 µM	-	1 ppm	8.0	7.8 +/- 0.3
	37 µM	-	1 ppm	8.0	7.7 +/- 0.3
	179 µM	-	1 ppm	8.0	7.1 +/- 0.3
	259 µM	-	1 ppm	8.0	6.9 +/- 0.3
	357 µM	-	1 ppm	8.0	6.6 +/- 0.5
	18 µM	-	8 ppm	8.0	7.9 +/- 0.1
	37 µM	-	8 ppm	8.0	7.8 +/- 0.1
	148 µM	-	8 ppm	8.0	7.4 +/- 0.1
	259 µM	-	8 ppm	8.0	7.0 +/- 0.1
	370 µM	-	8 ppm	8.0	6.7 +/- 0.1
	18 µM	-	20 ppm	8.0	7.7 +/- 0.2
	37 µM	-	20 ppm	8.0	7.2 +/- 0.6
	179 µM	-	20 ppm	8.0	7.1 +/- 0.1
	259 µM	-	20 ppm	8.0	6.8 +/- 0.0
	357 µM	-	20 ppm	8.0	6.6 +/- 0.1
	18 µM	-	50 ppm	8.0	7.8
	37 µM	-	50 ppm	8.0	7.6
	179 µM	-	50 ppm	8.0	7.1
	357 µM	-	50 ppm	8.0	6.8

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Figure S1. Effect of seed particle on conventional coagulation process. Seed particles, bentonite and silica aerogel were added to synthetic test water to simulate natural turbidity. Fe(III) was used at 178 μ M in all experiments.

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695 **Figure S2.** Effect of time of Fe(II) addition during Fe(II)-assisted oxidative coagulation. Fe(II)
696 was added at the beginning of rapid mixing (R/M), before slow mixing (S/M), 10 minutes into
697 S/M, and 20 minutes into S/M, respectively. The initial As(III) concentration was 100 µg/L.
698 Fe(III) was added at the onset of R/M in all cases.
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Figure S3. Effect of alum on performance of Fe(II)-assisted oxidative coagulation. All chemicals were added at the onset of rapid mixing. The initial As(III) concentration was 100 $\mu\text{g/L}$.

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708 **Figure S4.** Consumption of H_2O_2 during H_2O_2 -assisted oxidative coagulation tests. Dose of
 709 H_2O_2 was 20 mg/L in (a) and 50 mg/L in (b), respectively. Fe(III) added was 185 μM for all
 710 experiments. H_2O_2 concentration was measured using the titanium oxalate method (Kosaka et al.,
 711 1998).

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