Electrochemical Alkaline Fe(VI) Water Purification and Remediation

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Fe(VI) is an unusual and strongly oxidizing form of iron, which provides a potentially less hazardous water-purifying agent than chlorine. A novel on-line electrochemical Fe(VI) water purification methodology is introduced. Fe(VI) addition had been a barrier to its effective use in water remediation, because solid Fe(VI) salts require complex (costly) syntheses steps and solutions of Fe(VI) decompose. On-line electrochemical Fe(VI) water purification avoids these limitations, in which Fe(VI) is directly prepared in solution from an iron anode as the FeO_4^{2-} ion, and is added to the contaminant stream. Added FeO_4^{2-} decomposes, by oxidizing a wide range of water contaminants including sulfides (demonstrated in this study) and other sulfur-containing compounds, cyanides (demonstrated in this study), arsenic (demonstrated in this study), ammonia and other nitrogen-containing compounds (previously demonstrated), a wide range of organics (phenol demonstrated in this study), algae, and viruses (each previously demonstrated).

Introduction

This study presents an alternate water purification method in the search for methodologies with the potential to be less hazardous, simpler, and cost-effective compared to chlorination. In the novel on-line electrochemical Fe(VI) water purification methodology, highly oxidizing Fe(VI) is directly and rapidly prepared in solution as the FeO_4^{2-} ion and is available to break down a wide range of water contaminants.

Fe(VI) is an unusual and strongly oxidizing form of iron, and we have introduced its use as a charge storage for new class of super-iron batteries (*1−4*). While unusual, the valence and structure of Fe(VI) species can be definitively characterized by a variety of analytical methodologies (*5, 6*). However, Fe(VI) can also be used as a less hazardous water-purifying agent than chlorine. Sharma et al. (*7−11*) have demonstrated, using the Fe(VI) salt, K_2FeO_4, the removal from water of ammonia, cyanide, thiocyanate, and sulfide. A typical oxidation mechanism for Fe(VI) species (in this case oxidizing water) is presented in eq 1. The rapid oxidation of Fe(VI) to the environmentally benign ferric oxide product has been the basis for the suggestion of using Fe(VI) as a safer alternative to the chlorination purification of water

$$4FeO_4^{2-} + 2H_2O \rightarrow 4FeO_2^- + 3O_2 + 4OH^- \quad (1)$$

Luca et al. (*12*) used K_2FeO_4 to remove inorganic and organic compounds and to generally diminish the offensive odor of these compounds in water. Murshed et al. (*13*) have also used K_2FeO_4 to remove sulfide, and Lee et al. (*14*) have used it to oxidize and remove arsenic. F. Kazama demonstrated viral inactivation by K_2FeO_4 (*15*). Ma and Liu (*16*) have used Fe(VI) to remove algae, while Deininger et al. (*17*) have used an alkaline earth ferrate salt to treat transuranic elements in radioactive wastewater. In each of these processes, a solution of Fe(VI) ions is prepared from an alkali or alkaline earth ferrate salt, which is then used as the water treatment agent. The solution of Fe(VI) ions may also be prepared electrochemically, and Sylvester et al. (*18*) shook such a solution for 24 h with a radioactive sludge solution to remove chromium.

Challenges had existed to the implementation of Fe(VI) water purification using either prepared Fe(VI) solutions or solid Fe(VI) salts. Prepared solutions of Fe(VI) are unstable, and Fe(VI) solid salts require complex synthesis. Fe(VI) solutions are generally unstable, and decomposition by reduction to Fe(III) species occurs rapidly, often only on the order of a few hours at room temperature. Whereas this solution-phase instability is useful, to the extent that the Fe(VI) oxidant will not persist in the environment, it impedes their use for water remediation processes. The instability may be retarded but not stopped at low temperatures or with careful control of solution concentrations (*1, 19*). Hence, without steps to refrigerate or highly purify the solution, the solutions cannot be stored for use in water purification. Licht et al. (*19−23*) have described the synthesis of a variety of Fe(VI) solid salts including K_2FeO_4, Li_2FeO_4, Na_2FeO_4, Rb_2FeO_4, Cs_2FeO_4, and the alkali earth salts $BaFeO_4$ and $SrFeO_4$. The preparation of Fe(VI) salts by chemical means is a multistep procedure, which generally includes a hypochlorite oxidation step of Fe(III) or precipitation from another Fe(VI) salt.

Solid salts such as K_2FeO_4 can be highly stable (*5*), but the lengthy chemical synthesis consumes multiple reagents. Solution-phase Fe(VI) and recently solid-phase Fe(VI) salts can also be synthesized electrochemically by oxidation of an iron anode (*24, 25*). Direct electrochemical synthesis of solid Fe(VI) salts avoids the need to add a chemical oxidant and substantially decreases the synthesis time. Similarly, electrochemical Fe(VI) formation as a direct part of the water remediation process can circumvent the limitations of Fe(VI) water purification. In 2001, we introduced an on-line electrochemical formation of Fe(VI) for water treatment (*26*), and this study probes this methodology. Fe(VI) is directly and rapidly prepared in solution as the FeO_4^{2-} ion, and is immediately available at high purity to break down a range of water contaminants, as exemplified by the oxidation of sulfide, cyanide, and arsenic, and is similarly useful for other inorganic compounds as well as organics, algae, and viruses.

Experimental Methods

Analyses. The absorption of solution-phase Fe(VI) at 505 nm varies linearly over a wide range of FeO_4^{2-} concentrations and is highly independent of the alkali hydroxide cation or hydroxide concentration in solution (*1, 5*). The FeO_4^{2-} concentration was determined with a Hewlett-Packard 8453 UV/vis photodiode array spectrophotometer by the 1070 M^{-1} cm^{-1} molar absorptivity at $\lambda = 505$ nm with a 385 nm baseline correction and with dilution as required, as further detailed and previously described (*5*). The sulfide concentration was analyzed with a model 27504-28 Cole-Parmer silver/sulfide electrode and cyanide with a model number 27504-12 Cole-Parmer cyanide electrode, both using an Orion Research expandable ion analyzer EA 920, measured as a function of time using LabView data acquisition. Cyclic voltammetry analysis of arsenic is described in the Results and Discussion section.

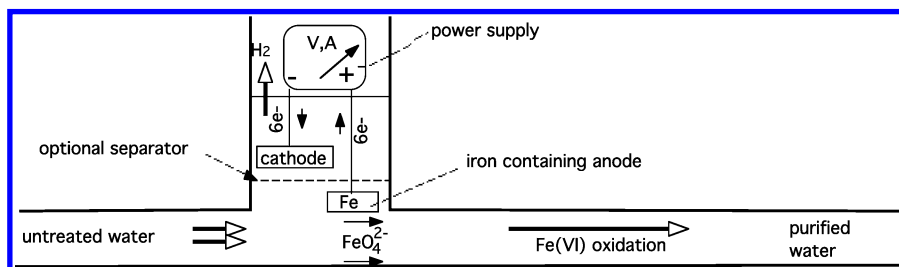* Corresponding author phone: (617)287-6130; fax:(617)287-6030; e-mail: stuart.licht@umb.edu.

FIGURE 1. Schematic of in-line electrochemical Fe(VI) water purification.

Remediation Configuration. All Fe(VI) formation electrolytes were prepared from analytical grade NaOH and triply deionized water. Solution-phase FeO_4^{2-} was electrochemically prepared with an electrolysis cell configured with a high surface area iron anode, which to ensure isolation of the generated Fe(VI) was separated from the cathode by a Nafion 350 alkali-resistant, anion-impermeable membrane. The anode may consist of an iron sheet, but a higher surface area iron anode (27) increases the rate per volume of Fe(VI) formed in solution. We have used a small diameter folded iron wire, and these high surface area iron anodes were prepared from Fluka (0.1% Cu, 0.1% Ni, and 0.7% Mn) iron wire, $d = 0.2$ mm in diameter, $L = 128$ m coiled length, with surface area $A = L\pi d = 800$ cm^2. Electrode pretreatment included 3 min of sonication in 1:3 HCl (concentrated HCl/water), followed by triply deionized water washing (Nanopure water system) to pH = 7. The Fe(VI) formation solution may consist of a 5 M or less concentrated hydroxide solution, but a more concentrated alkaline solution provides higher rates of Fe(VI) formation at a lower overpotential (25). In this study, Fe(VI) was formed with a coiled iron wire anode immersed in 40 mL of 10 M NaOH at a constant oxidative current applied by Pine AFRDE5 bipotentiostat. At a high, constant current of 1.6 A, the cell reached a steady-state Fe(VI) concentration in approximately 0.5 h; specifically, anodic oxidations of 10, 20, 30, or 60 min, respectively, generated concentrations of 21, 33, 38, and 39 mM FeO_4^{2-}, respectively (as measured by 505 nm absorption spectroscopy). We simulate effluents by preparing solutions with precise concentrations of added known impurities. All (simulated) effluents were prepared from NaOH, analytical grade reagents, and triply deionized water. The flow rate of effluent to be treated as well as the flow of generated Fe(VI) solution were separately controlled with two Control Company variable flow minipumps, model number 3385, using 2.4 mm in diameter tubing. In all measurements, the effluent and Fe(VI) streams each flow at a rate of 1.5 mL/min. Increase of the flow rate or concentration of the impurity may be compensated by current density increase generating additional Fe(VI). For greater than 100 mM FeO_4^{2-} in NaOH, the current efficiency of ferrate generation diminishes (25), and then it is preferable to also increase the flow rate of the ferrate stream. Fe(VI) was added in an on/off stepwise manner to the effluent, by turning on and off the anodic oxidation current. Specifically, the current was either 0 or a fixed oxidative current (as necessary to form the desired steady-state concentration of FeO_4^{2-}, as measured by 505 nm absorption spectroscopy).
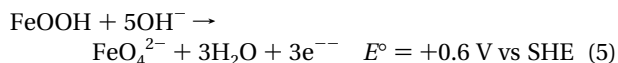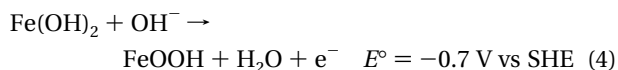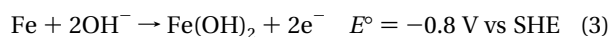
Theoretical Basis

Fe(VI) Formation Fundamentals. The water purification methodology probed in this study is based on a novel on-line electrochemical formation and addition of Fe(VI) to oxidize and treat contaminants. Fe(VI) is added in the form of FeO_4^{2-} ion. Electrochemical formation of the FeO_4^{2-} is accomplished at a positively biased iron anode in contact with an aqueous solution. Alternately, ferric or ferrous salts such as Fe_2O_3 or $Fe(OH)_2$ may be used for the anode but are observed to be less effective due to their high resistivity. High pH acts to enhance the rate of formation of the Fe(VI) species, favoring utilization of concentrated hydroxide electrolyes; similarly high surface area anodes, such as wound iron wire, favor rapid FeO_4^{2-} formation (25). At sufficiently anodic potentials in alkaline media, an iron anode is directly oxidized to the Fe(VI) species, FeO_4^{2-}. This process is qualitatively observed by a purple coloration of the solution and quantitatively by an absorption increase at $\lambda = 505$ nm, in accord with the oxidation reaction

$$Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e^- \qquad (2)$$
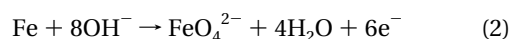
The process occurs at potentials > 0.6 V versus the standard hydrogen electrode (SHE), consistent with the alkaline rest potentials related to the formation of Fe(II), Fe(III), and Fe(VI) from Fe(0)

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^- \quad E^\circ = -0.8 \text{ V vs SHE} \quad (3)$$

$$Fe(OH)_2 + OH^- \rightarrow$$
$$FeOOH + H_2O + e^- \quad E^\circ = -0.7 \text{ V vs SHE} \quad (4)$$

$$FeOOH + 5OH^- \rightarrow$$
$$FeO_4^{2-} + 3H_2O + 3e^{--} \quad E^\circ = +0.6 \text{ V vs SHE} \quad (5)$$

Isolation of Fe(VI) away from the cathode minimizes losses due to the cathodic back-reduction of the synthesized Fe(VI), eq 6, and instead favors the cathodic evolution of hydrogen, eq 7

$$FeO_4^{2-} + 3H_2O + 3e^- \rightarrow FeOOH + 5OH^- \qquad (6)$$

$$6H_2O + 6e^- \rightarrow 6OH^- + 3H_2 \qquad (7)$$
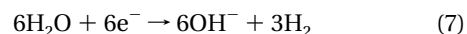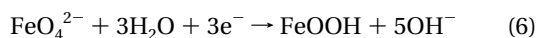
With 6 F of charge transfer through the anode and cathode per equivalent of Fe, eqs 2 and 7 combined yield the net Fe(VI) solution-phase alkaline synthesis reaction

$$Fe + 2OH^- + 2H_2O \rightarrow FeO_4^{2-} + 3H_2 \qquad (8)$$
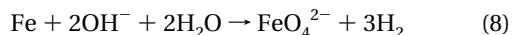
Fe(VI) Water Remediation Configuration. Fe(VI) may be electrochemically generated from a metal iron anode in a variety of aqueous alkali media (25). In a remediation configuration presented in Figure 1, which we term, *in*-line electrochemical Fe(VI) water purification, the water to be purified is in contact with and flows over the FeO_4^{2-}-generating anode. However, with this in-line configuration, the iron electrode is exposed to the untreated water and vulnerable to fouling. As an alternative, with on-line electrochemical Fe(VI) water purification, as shown in Figure 2, the water to be purified and the FeO_4^{2-} electrochemically formed in solution at the anode each have separate flows, which are brought together as a single flow downstream of the anode. In either configuration, electrochemical oxidation of the iron anode is achieved via positive electrical bias by the power supply. The second configuration eliminates electrode fouling by the untreated water, permits optimization of a separate electrolyte used to generate FeO_4^{2-}, and
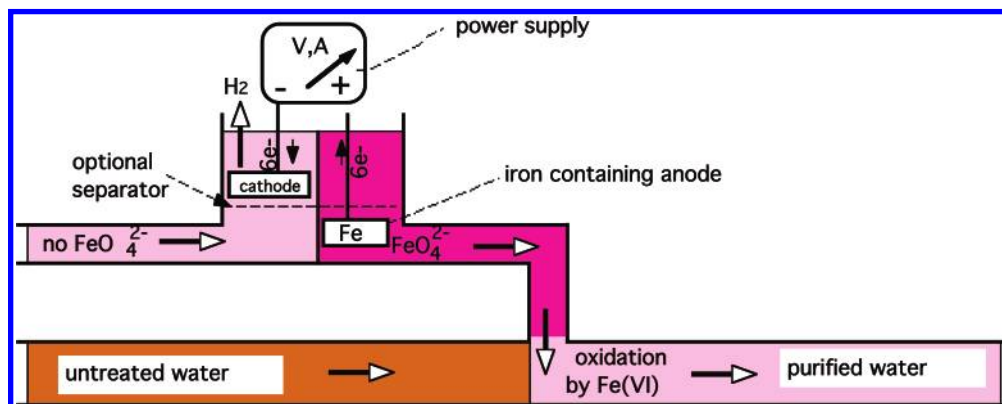
FIGURE 2. Schematic of on-line electrochemical Fe(VI) water purification.

facilitates controlled rates of formation. Whereas in-line purification utilizes the water to be treated as an electrolyte for the electrochemical formation of Fe(VI) species, on-line purification can optimize Fe(VI) formation by using an alkaline electrolyte, such as an aqueous solution of NaOH.

The cathode in the on-line Fe(VI) remediation is limited to materials that are stable when immersed in an alkaline, reductive environment and that accomplish eq 7 at low polarization losses. Cathodes used have included nickel and nickel oxide, platinum, gold, graphite, carbon black, iridium oxide, or ruthenium oxide. Nickel sheet was used in this study. As seen in Figure 2, the Fe(VI) formation compartment may have an optional separator between the cathode and the anode. When the anode is downstream of the cathode, the separator is generally not required. If the anode were in proximity of the cathode, then a portion of the anodically formed FeO_4^{2-} could be lost at the cathode via eq 6. When used, a separator between the iron anode and the cathode can be either a nonconductive separator configured with open channels, grids, or pores, such as a ceramic frit, or a membrane to impede FeO_4^{2-} transfer, such as a cation-selective membrane. The water to be purified and the solution containing electrochemically synthesized FeO_4^{2-} are brought together by means of a pump.

Results and Discussion

Fe(VI) may be readily formed on-line as the FeO_4^{2-} species in an aqueous solution and was added to an effluent to be treated in accord with the scheme presented in Figure 2 and as described in the Experimental Methods section. Fe(VI) was added in a stepwise manner to a purposely prepared effluent, by turning on and off the anodic oxidation current as described in the Experimental Methods section. The contaminant concentration was measured downstream of the Fe(VI) addition, after the combined effluent and Fe(VI) streams had intermingled for 3 min.

Sulfide was the first contaminant studied. Aqueous sulfide and sulfur (polysulfide) chemistry is complex. In all but the most alkaline solutions, sulfide solutions predominantly contain the (hydrosulfide) HS^- rather than the S^{2-} species, and partial oxidation of the sulfide solution generates a mix of polysulfides, S_x^{2-}, and thiosulfate, $S_2O_3^{2-}$, whose speciation varies with sulfide concentration and pH (28−33). H_2S is fully oxidized by excess ferrate to sulfate, SO_4^{2-}, whereas at high pH sulfite and thiosulfate products can also can occur (9) and the latter can predominate (28). Theoretically, oxidative removal of sulfide to thiosulfate, $S_2O_3^{2-}$, requires a 4:3 molar ratio consistent with eq 1, when treated by Fe(VI) as

$$4FeO_4^{2-} + 3S^{2-} + {}^{23}/_2H_2O \rightarrow$$
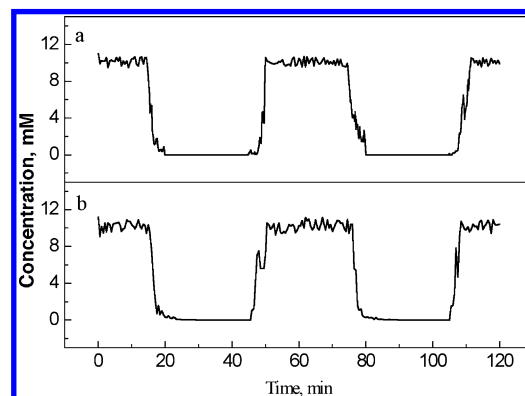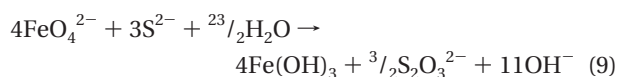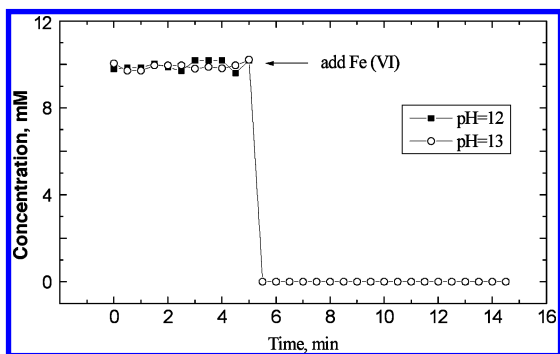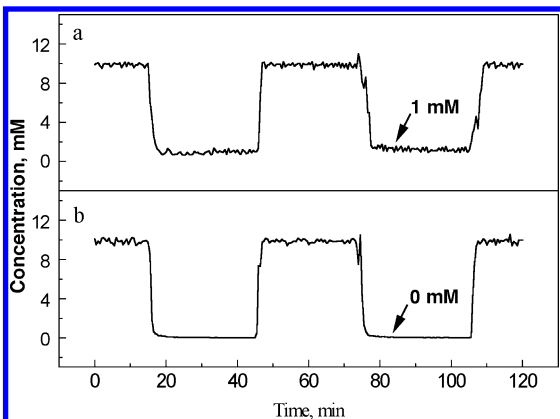$$4Fe(OH)_3 + {}^3/_2S_2O_3^{2-} + 11OH^- \quad (9)$$

FIGURE 3. (a) Remediation of sulfide by on-line Fe(VI) treatment. The variation of sulfide concentration upon FeO_4^{2-} addition to sulfide effluent flow is shown. The iron anode is alternately cycled from 0 current to constant oxidation current mode, as described in the text. (b) Sulfide concentration measurement and calibration, exposing the downstream sulfide-ion-selective electrode to the 1 M NaOH flowing solution alternately with and without 0.01 M Na_2S.

We observe that the oxidation product is thiosulfate (i) via thiosulfate's characteristic Fourier transform IR absorption peak at 996 cm^{-1} and (ii) the stoichiometric ratio of Fe(VI) required to fully remove sulfide, as measured by the sulfide-ion-selective electrode. By this latter technique, a molar ratio ≥1.4: 1 of FeO_4^{2-} to Na_2S is observed to remove all sulfide from 0.01 M Na_2S in 1 M NaOH (while a 1.3:1 molar left trace sulfide). In accord with the stoichiometric ratio of eq 9, the current-controlled concentration of added FeO_4^{2-} was four-thirds that of the sulfide concentration. The variation of sulfide concentration in time, of on-line electrochemical Fe(VI) treated 0.01 M Na_2S in 1 M NaOH, was measured using sulfide-selective-electrode analysis. This was calibrated using the same experimental configuration, but periodically interrupting the sulfide solution flow and, instead of the Fe-(VI) solution, flowing a sulfide-free (and Fe(VI)-free) solution. The sulfide calibration is presented in the bottom section of Figure 3. Figure 3 also presents the on-line electrochemical treatment of sulfide by Fe(VI), with or without anode-controlled FeO_4^{2-} addition. As seen in the top section of the figure, the sulfide is completely removed by the Fe(VI).

Generally in this study, the effluent studied was 1 M NaOH, at approximately pH 14 (34), containing different contaminants. However, the FeO_4^{2-} is also effective for oxidation remediation of water at a lower pH. Figure 4 summarizes sulfide removal at lower pH values by Fe(VI), in both pH 12 and 13 solutions, and again the complete removal of sulfide is observed. Water to be treated may also be at neutral pH, although the treated stream will be raised to a higher pH by addition of the alkali media used to generate the Fe(VI). For example, pH neutral water containing phenol may be treated.

FIGURE 4. Remediation of sulfide by Fe(VI) treatment at lower pH. The variation of sulfide concentration upon FeO₄²⁻ addition is shown. pH values of 12 and 13 are controlled by NaOH addition to 0.01 M Na₂S with FeO₄²⁻ added as K₂FeO₄.
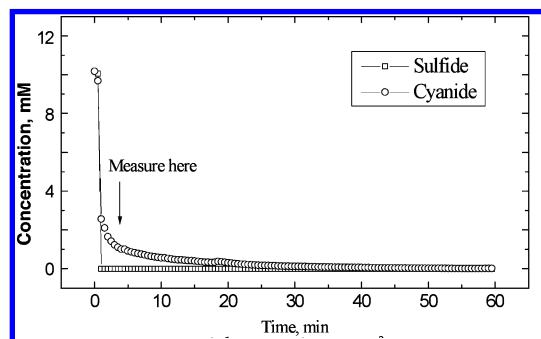

FIGURE 5. (a) Remediation of cyanide by on-line Fe(VI) treatment. The variation of cyanide concentration upon FeO₄²⁻ addition to the 0.01 M cyanide effluent flow is shown. The iron anode is alternately cycled from 0 current to constant oxidation current mode, as described in the text. (b) Cyanide concentration measurement and calibration, exposing the downstream sulfide-ion-selective electrode to the 1 M NaOH flowing solution alternately with and without 0.01 M NaCN.

Monitoring the absorption decrease at 505 nm for FeO_4^{2-} and the known 400 nm 4,4′-biphenoquinone intermediate absorption (*35*), we observe that phenol in neutral water is fully removed via oxidation by simple K₂FeO₄ addition. Additional Fe(VI) treatment of organics is beyond the scope of the present study, although we note that Fe(VI) has been applied to the oxidation of a wide variety of organics including phenol (*35*), alcohols (*36*−*40*), toluene and cycloalkanes (*36*), ketones and hydroquinones (*39*), carbohydrates (*41*), and aminobenzene (*42*).

Aqueous alkaline oxidation of cyanide generates cyanate (*43*, *44*), which will form upon Fe(VI) addition, in accord with

$$2FeO_4^{2-} + 3CN^- + 5H_2O \rightarrow$$
$$2Fe(OH)_3 + 3CNO^- + 4OH^- \quad (10)$$
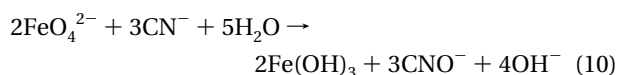
Aqueous cyanide may be treated by Fe(VI) through oxidative decomposition as described by eq 10. Calibration of the cyanide concentration, as measured by ion-selective-electrode analysis, for a 1 M NaOH solution with or without 0.01 M cyanide is presented in the bottom section of Figure 5. Removal of cyanide is in accord with the stoichiometric ratio of 2:3 for Fe(VI) to cyanide in eq 10. However, the rate of oxidation is slower than that observed for sulfide. As seen in Figure 6, whereas the Fe(VI) rate of sulfide oxidation occurs in less than 1 min, the rate of cyanide oxidation is longer. It is seen in the figure that only 90% of the initial cyanide con-


FIGURE 6. Comparison of the rate of S²⁻ and CN⁻ oxidization by FeO₄²⁻.
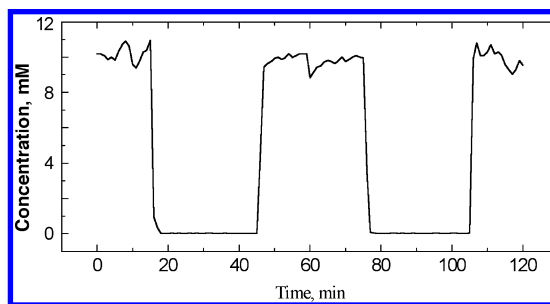
FIGURE 7. Remediation of arsenic by on-line Fe(VI) treatment. The variation of arsenic concentration upon FeO₄²⁻ addition to the 0.01 M NaAsO₂ in 1 M NaOH effluent flow. The iron anode is alternately cycled from 0 current to constant oxidation current mode, as described in the text.

centration is removed in the first 3 min. This also occurs for on-line Fe(VI) remediation of cyanide, when the effluent and Fe(VI) streams are permitted to intermix for only 3 min prior to downstream analysis. As seen in the top section of Figure 5, approximately 90% of the cyanide, to 1 mM, is removed by the Fe(VI) addition during this time. In accord with Figure 6, the fraction of cyanide removed increases with the increasing mixing time of the cyanide effluent and Fe(VI) streams.

For the arsenic contaminant, arsenite, As(III) (for example, as added NaAsO₂), the oxidation product upon Fe(VI) addition is arsenate, As(V), with the overall reaction given by

$$FeO_4^{2-} + {}^3/_2AsO_2^- + OH^- + H_2O \rightarrow$$
$$Fe(OH)_3 + {}^3/_2AsO_4^{3-} \quad (11)$$
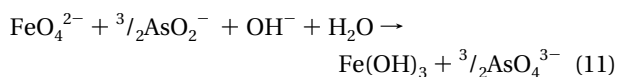
Hence, the $^2/_3$ of a mol of FeO_4^{2-} is required to oxidize 1 mol of AsO_3^{3-}. Unlike sulfide and cyanide, ion-selective analysis was not available for arsenic determination. Instead arsenic concentration was determined by three-electrode cyclic voltammetry on a 0.5 mm² platinum electrode scanned at 50 mV/s, with a Pt counter electrode and silver/silver chloride reference electrode, accomplished by monitoring the relative decrease in the observed As(III) peak current on Pt at +0.13V, which generates a linear response of peak current over the 0.5−10 mM concentration NaAsO₂ in 1 M NaOH. Figure 7 presents the on-line electrochemical treatment of arsenic by Fe(VI) using this cyclic voltammetry to measure the variation in NaAsO₂ concentration. As seen in this figure, in a manner analogous to the sulfide treatment, the Fe(VI) removal of arsenic, as As(III) in the 0.01 NaAsO₂ M effluent, is complete.

Simultaneous treatment of multiple contaminants in an effluent flow by Fe(VI) on-line remediation was also found to be effective. Figure 8 presents the treatment, by on-line electrochemically generated Fe(VI), of a solution containing both 0.01 M sulfide and cyanide. The Fe(VI) concentration is anodically controlled in accord with the sum of eqs 9 and 10. The concentrations of sulfide and cyanide in the treated
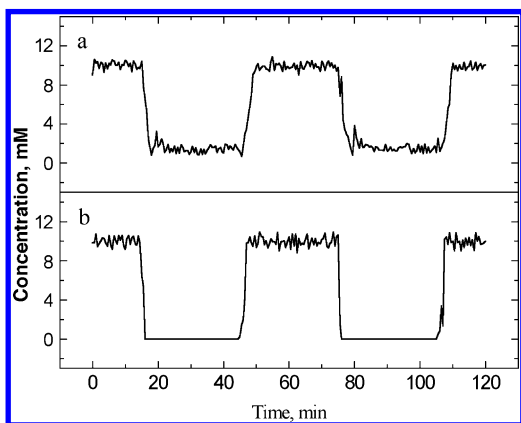
FIGURE 8. Simultaneous remediation of cyanide and sulfide by on-line Fe(VI) treatment. The effluent contains 0.01 M sulfide and cyanide. The time variation of the concentration of each ((a) cyanide and (b) sulfide), upon FeO_4^{2-} addition to the effluent flow, is shown. The iron anode is alternately cycled from 0 current to constant oxidation current mode, as described in the text.

effluent are observed to be consistent with the treatment of the individual contaminant components. Specifically, as observed in Figure 8, the sulfide removal is complete, and 90% of the initially cyanide is oxidized as limited by the (3 min) intermix time, prior to detection, of the effluent Fe(VI) and contaminant streams.

Ongoing studies include modification of the electrode and the electrolyte configuration for Fe(VI) formation. Important issues to be addressed are the treatment of lower pH wastewater and also the subsequent chemistry of the products of the redox reaction. In the on-line process, Fe(III) products are formed downstream of the Fe anode and are not observed to foul the electrode. Direct addition of 10 mM Fe(III) to untreated 10mM sulfide or cyanide is not observed to affect either species. At the level of contaminants treated (mM), Fe(III) buildup does not occur in the lines. Indeed, under certain conditions, Fe(III) products may be beneficial, acting as a coagulant for treated waste removal, and the extent of this effect needs to be studied over a range of contaminants. For example, coagulation or adsorption of arsenic can occur with Fe(III) (*14*, *25*), and this effect may lower the Fe(VI) needed to treat such solutions. While product fate is beyond the scope of the present investigation, future studies are important to evaluate the benefits of the full process. Future studies should include specific comparisons of this Fe(VI) on-line remediation process to conventional chlorination remediation as well as kinetic studies, not only of the Fe(VI) reaction rates, but also of the lifetime and fate of the Fe(III) products and the fate of the oxidized contaminants in the presence of the Fe(III) product. Fe(VI) on-line remediation can be an effective and straightforward process for water purification. Fe(VI) addition had been a barrier to its effective use in water remediation, because solid Fe(VI) salts require complex (costly) synthesis steps and solutions of Fe(VI) decompose. On-line electrochemical Fe(VI) water purification avoids these limitations, because Fe(VI) is directly prepared in solution from an iron anode as the solution-phase FeO_4^{2-} species for immediate addition to the contaminant stream. The added FeO_4^{2-} decomposes by oxidation a wide range of water contaminants including sulfides (demonstrated) and other sulfur-containing compounds, cyanides (demonstrated), arsenic (demonstrated), organics, algae, and viruses. Simultaneous remediation of multiple contaminants (a mix of sulfide and cyanide) is also demonstrated.

Acknowledgments

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