Abstract

Bench-scale experiments were conducted to test the effectiveness of a direct coprecipitation filtration (DCF) process for removal of arsenate [As(V)] and arsenite [As(III)]. The process involved injection of small amounts of ferric chloride solution into a sand filter. Arsenic was removed by ferric hydroxide formed in the filter through coprecipitation and adsorption. As(V) concentration was reduced from 90 µg/L to less than 4 µg/L by the DCF process at an iron dosage 1 mg/L and a filtration rate of 3 gal/min•ft². In general, greater than 95% of As(V) removal was achieved when influent As(V) concentration was less than 200 µg/L. The DCF process was more effective than batch coprecipitation for As(V) removal. Since effluent arsenic concentration increased only slightly during the filtration, headloss was the determining factor for backwash regeneration of the filters. As(III) was removed effectively by concurrent injection of NaOCl and FeCl₃ solution into the filter. Full-scale DCF systems have been successfully implemented for the removal of arsenic from groundwater.

Introduction

Ferric chloride is commonly applied in coagulation treatment for the removal of arsenic in water since ferric hydroxide precipitate has a high adsorptive capacity for As(V) and moderate adsorptive capacity for As(III)¹-⁷ The precipitation of ferric hydroxide includes formation of iron oxyhydroxyl monomers and dimers, Fe-O-Fe polymerization, and precipitation of a solid phase.⁸,⁹ The primary particles, ranging from 10 to 40 Å in size, form large flocs through aggregation. As(V) and As(III) are adsorbed on ferric hydroxide through the formation of inner sphere surface complexes.⁹-¹¹ Conventional coagulation treatment typically consists of rapid mixing, flocculation, sedimentation, and filtration stages. Several innovative processes have been tested which utilize ferric
hydroxide for arsenic removal while eliminating the flocculation and sedimentation stages. Ferric hydroxide coating formed on sand and granular activated carbon have been used as filter media for heavy metal removal.\textsuperscript{12-14} Granular ferric hydroxide adsorbents with a high adsorptive capacity for As(V) have been prepared by a high pressure process.\textsuperscript{15} These absorbents can treat 30,000-40,000 bed volumes of water containing 100-180 \(\mu\)g/L As(V) before arsenic concentration in the filtrate exceeds 10 \(\mu\)g/L. In a microfiltration process, heavy metals are coprecipitated by ferric hydroxide and the precipitates are removed directly with a membrane filter.\textsuperscript{16}

In the present work, a direct coprecipitation filtration process was investigated for arsenic removal. In this process, coprecipitation, adsorption, and particulate removal occurred simultaneously in the sand filter. The effects of ferric dosages, arsenic oxidation states and concentrations, and filtration rate on arsenic removal were evaluated. Preliminary filtration results obtained with the DCF process have been presented elsewhere.\textsuperscript{17} Based on the experimental results obtained from this work, full-scale filtration systems have been installed and used for the removal of arsenic from groundwater. Since the process can be fully automated, it is particularly suitable for small water treatment facilities with low turbidity water.

Experimental procedures

Three types of experiments were conducted in this study, namely, direct coprecipitation filtration, batch coprecipitation, and batch adsorption. The bench-scale DCF system consisted of a sand column, the chemical injection pumps, and a water pump. The sand column was fabricated using an acrylic pipe with an inside diameter of 3.0 inches (7.6 cm). The column was packed with approximately 20 inches (51 cm) of sand with effective size of 0.35-0.60 mm and a uniformity
coefficient of 1.2-1.6 (Rici Bros. Sand Co. Inc. Port Norris, New Jersey). Reagent grade FeCl₃, As₂O₅, and NaAsO₂ were used to prepare the stock solutions. Tap water was spiked with As(V) or As(III) solutions and used in the filtration experiments. To eliminate oxidation of As(III) by residual chlorine in the tap water, 2.5 mg/L of Na₂SO₃ was added to the tap water to react with the free chlorine for 1 hour prior to the addition of As(III). Speciation analysis with disposable As-cartridges indicated that 81-87% of the As(III) in the water remained in As(III) form. In order to evaluate the effectiveness of the filtration process in removing arsenic from source water, groundwater samples containing 70 µg/L arsenic were collected and treated by a bench-scale DCF unit. Approximately 98% of the arsenic in the groundwater sample were in As(V) form.

The sand filters were operated in a constant filtration rate mode at rates of 1, 3 and 5 gal/min·ft². During filtration, an acidified FeCl₃ solution containing 3-9 mM ferric ions was directly pumped into the sand column. In order to determine the effects of flocculation, a number of filtration tests were conducted where the ferric solution was pre-mixed with water in an in-line container prior to filtration. The pre-mixing container provided a hydraulic detention time of 7 minutes. In conventional direct filtration processes using aluminum sulfate coagulant, detention time in the flocculation tank prior to filtration is usually longer than 7 minutes. The hydraulic detention time in the sand column was approximately 2.5 minutes. Effluent samples were collected at the bottom of the sand column and analyzed for total arsenic and iron concentrations, pH, and turbidity.

In selected filtration runs, water samples were taken from the sampling ports located at different depths of the sand bed. Total and soluble arsenic and iron concentrations were determined by analyzing the water samples before and after membrane filtration. Polycarbonate membranes of 0.4 or 0.1 µm pore size were used to filter the water samples. During membrane filtration, the first 10 mL of filtrate
was used to rinse the sample tubes. Then approximately 20 mL of filtrate was collected in sample tubes and analyzed for the metals of interest. The concentrations of arsenic and iron were measured using a Graphite Furnace Atomic Absorption Spectrometer (Varian SpectrAA-400). The method detection limit for arsenic was 0.7 µg/L. A pressure gauge located on the top of the sand column was used to monitor the filter pressure. After each filtration run, the column was backwashed with tap water at a flow rate of approximately 24 gal/min ft² (gpm/ft²) for approximately 3 minutes.

Coprecipitation experiments were conducted using a jar test mixer (Phipps & Bird, Inc., Richmond, VA) and 1-L glass beakers. An acidified FeCl₃ solution (0.036 M Fe) was added to As-spiked tap water in the beakers during mixing. The suspension was mixed rapidly at a rotating speed of 120 rpm for 1 minute. After rapid mixing, the suspension was mixed at a rotating speed of 40 rpm. Samples were taken at different times and filtered through 0.4 or 0.1 µm pore size membranes to separate the solution from the solid for analysis of arsenic and Fe.

In the batch adsorption tests, ferric hydroxide precipitate was formed by adding 0.5 mL of the 0.036 M FeCl₃ solution to 1 L of tap water to reach an iron concentration of 1 mg/L. The suspension was rapidly mixed for 1 minute followed by slowly mixing at a rotating speed of 40 rpm for 4 minutes. During mixing, As(V) solution was added to the iron hydroxide suspension to initiate As(V) adsorption. At specified mixing times, samples were withdrawn, filtered, and analyzed for soluble arsenic and iron.

Results and discussion

The rate of arsenic coprecipitation with ferric chloride may significantly affect the removal of arsenic by the DCF process since hydraulic retention time of the DCF column is less than 3 minutes. The results of
the batch experiments presented in Figure 1 show the removal of As(V) and iron as a function of coprecipitation and adsorption time. Ferric hydroxide precipitate was formed rapidly in the water. After 1 minute of coprecipitation, the iron concentration was reduced from 1000 to 50 \( \mu \text{g/L} \) in the water sample filtered through a 0.1 \( \mu \text{m} \) membrane, corresponding to 95\% removal. More than 98\% of the iron formed flocs with particulate size greater than 0.1 \( \mu \text{m} \) after 2.5 minutes. In contrast, iron concentration in the water sample filtered through a 0.4 \( \mu \text{m} \) membrane was 243 \( \mu \text{g/L} \) after 2 minutes of mixing, thus resulting in 76\% iron removal. It took approximately 5 minutes for 96\% of the iron to form flocs with sizes larger than 0.4 \( \mu \text{m} \). As expected, the formation of larger flocs required longer reaction time.

The kinetics of As(V) removal by batch coprecipitation followed similar trends to that of iron (Figure 1). After 5 minutes of mixing, As(V) concentration was reduced from 50 to less than 4 \( \mu \text{g/L} \) in the sample filtered through a 0.4 \( \mu \text{m} \) membrane. Water samples collected after 1 minute of coprecipitation and filtered through the 0.1 \( \mu \text{m} \) membrane exhibited an As(V) concentration of 3.3 \( \mu \text{g/L} \). These results suggest that As(V) adsorption reaches equilibrium at the early stages of ferric hydroxide nucleation. Therefore, removal of As(V) by filtration appears to be limited by the growth rate of the ferric hydroxide flocs.

In the batch adsorption tests, ferric hydroxide precipitates had been aged for 5 minutes prior to the addition of the As(V) solution. It is clearly demonstrated by the arsenic concentration profiles shown in Figure 1 that the amount of As(V) removed by adsorption was less than the amount removed by coprecipitation. This is probably due to fact that only the external surface sites of the ferric hydroxide flocs were readily available to As(V). It is expected that the rate of As(V) removal will also be influenced by the size of the flocs. In the As(V) adsorption process, it took approximately 2 minutes to
reach a near-equilibrium condition. On the other hand, most of the As(V) was removed by filtration through 0.1 μm membrane in the coprecipitation test within 1 minute. The longer time required for adsorption to reach equilibrium may be attributed to the diffusion of the As(V) to the inner surface sites of the flocs.

The effectiveness and capacity of the sand filters for iron and arsenic removal are determined by the depth of the sand bed, the floc strength, sizes of iron hydroxide particles, surface potential of the particles, and the filtration rate. Water chemistry such as pH and concentrations of specific ions and organic matter also influence the removal efficiency of the filters. The effects of the sand filter depth on iron and arsenic removal were evaluated by analyzing water samples taken at different depths below the top of the sand bed. The samples were taken after 85 bed volumes of water were passed through the filter. When iron was directly injected into the sand column, the total iron concentration decreased from 1000 to 493 μg/L in the top 5 inches of the sand bed (Figure 2). At this depth, soluble (<0.4 μm) iron concentration was 120 μg/L. At the depth of 10 inches approximately 94% of the iron was removed. The total and soluble iron concentrations in the effluent of the column (i.e. 20 inches sand bed) were 26 and 21 μg/L, respectively, corresponding to 97% iron removal. The results indicate that the sand column removes iron effectively and that precipitation, aggregation, and removal of the particles occurred simultaneously in the sand bed. Since the particles tend to penetrate deep in the sand bed, in field applications it may be necessary to increase the depth of the sand bed to prolong the duration of the filtration runs.

When ferric chloride was pre-mixed with water for 7 minutes prior to filtration, the total iron concentration was reduced to 172 μg/L (i.e. 83% removal of the iron) by the top 5 inches of
the sand bed (Figure 2). This increase in iron removal, compared to direct iron injection, was
due to the formation of larger flocs, which reduced the penetration depth of the particles. The
effluent iron concentration showed that pre-mixing slightly improved iron removal.

The concentration profiles of As(V), for the direct iron injection runs, along the filter
depth were similar to that of iron (Figure 3). At a depth of 1.3 inches, the total and soluble
As(V) concentrations were 37.5 and 5.9 μg/L, respectively. The results indicate that 84% of the
As(V) at this depth was associated with particles larger than 0.4 μm. Approximately 93% of the
As(V) were removed by the top 10 inches of the sand bed. Total As(V) concentration in the
effluent was 2.4 μg/L. Experiments conducted with iron pre-mixing (data not shown) did not
improve As(V) removal, therefore, the pre-mixing step was eliminated in subsequent filtration
tests.

The percents of As(V) removal versus iron removal by the batch coprecipitation and the DCF
process is illustrated in Figure 4. The solid line represents equal As(V) and iron removal. The batch
coprecipitation data were slightly below the solid line, indicating that the percent of As(V) removed was
slightly less than the percent of iron removed. For example, after 50 seconds of coprecipitation 64% of
the As(V) was removed along with 66% of the iron by filtration with a 0.4 μm membrane. In the DCF
process, 20% of the As(V) and 8% of the iron were removed by the top 1.3 inches of the sand bed. At
a depth of 5 inches the amounts of As(V) and iron removed were 75% and 51%, respectively. The
results indicate that the As(V) content in ferric hydroxide was higher in the upper portion of the sand
bed than in the lower portion.

Filtration rate is an important physical parameter for the removal of arsenic in the DCF process.
Increasing filtration rate may result in high effluent arsenic concentration due to shorter detention times
and increased shear forces that cause floc break-up and reduced particle capture. Effluent As(V) concentrations obtained at different filtration rates are plotted in Figure 5 as a function of effluent bed volumes. At all filtration rates tested, arsenic concentrations decreased significantly during the filtration of the first 10 bed volumes, which corresponds to a ripening period of less than 1 hour for a filtration rate of 3 gpm/ft². After the ripening period and at a filtration rate of 1 gpm/ft², arsenic concentration was reduced from 16 μg/L in the influent to approximately 1 μg/L in the effluent. When the filtration rate was increased to 3 gpm/ft², no significant increase in effluent arsenic concentration was observed. Effluent arsenic concentration was increased to approximately 2 μg/L when the filtration rate was increased to 5 gpm/ft². These results indicate that the DCF filters can be operated at filtration rates similar to those of conventional sand filters (2-6 gpm/ft²), and achieve high arsenic removal efficiencies.

The effect of iron dosages on arsenic removal was tested by passing the tap water spiked with 16 μg/L As(V) through the column at a filtration rate of 3 gpm/ft². When iron dosage was 0.5 mg/L, effluent As(V) concentration was approximately 1.8 μg/L. Effluent As(V) concentration was decreased to approximately 1 μg/L when iron dosage was increased to 1 mg/L. No apparent decrease in effluent As(V) concentration was observed when iron dosage was increased to 3 mg/L. At high iron dosages, more iron hydroxide sludge will be generated thus reducing the duration of the filtration runs. It is, therefore, critical to determine the optimal iron dosages required for a specific water treatment application.

The results in Figure 7 demonstrate the effect of influent As(V) concentrations on the removal efficiency of the DCF process at an iron dosage of 1 mg/L. When the influent As(V) concentration was increased from 16 to 90 μg/L, the effluent As(V) concentration was increased from approximately 1
to 3 μg/L. At an influent As(V) concentration 180 μg/L, the effluent As(V) concentration was very high during the initial ripening period, which lasted for approximately 2 hours. However, after 20 bed volumes of filtrate the DCF process reached a pseudo-steady state at an effluent arsenic concentration of approximately 8 μg/L. As(V) removal from the groundwater sample was similar to the removal from the spiked tap water. The As(V) concentration in groundwater sample was reduced from 70 μg/L to less than 3 μg/L after 9 bed volumes of water were passed through the DCF column.

After selection of the optimal conditions, tests were conducted at longer filtration times to evaluate the performance of the DCF process. The results in Figure 8 were obtained from a 50-hour continuous filtration test. The effluent arsenic concentration increased slightly from approximately 1 to 2.5 μg/L by the end of the filtration run. Effluent iron concentration increased to approximately 200 μg/L after 466 bed volumes of water were filtered. Effluent turbidity increased from approximately 0.2 to 0.4 NTU due to the leakage of trace amount of ferric hydroxide particles at the end of the filtration. Filter pressure was increased to 9 psi after 600 bed volumes of water were filtered. The headloss through the filter bed was the determining factor for termination of the filtration runs. After each filtration run, the filters were regenerated by backwash with tap water at a flow rate of approximately 24 gpm/ft² for approximately 3 minutes. When longer backwash time was used, the ripening time was shortened.

Similar filtration performance was observed in pilot- and full-scale filtration tests of the DCF process for the treatment of water containing 200-300 μg/L of As(V). The pilot-scale filtration results indicate that the duration of the filtration runs increases significantly when dual-medium (i.e. anthracite-sand) filters are used. It was also found during pilot-testing, that the removal of arsenic and iron can be improved by the addition of organic polymers in the DCF process. However, the filter pressure
increases more rapidly in the presence of organic polymers because the large flocs are retained in the top layer of the sand bed.

The results in Figure 9 show the removal of As(III) by the DCF process and the effect of sodium hypochlorite (NaOCl) on the As(III) removal. When the tap water spiked with 90 \( \mu \text{g}/\text{L} \) of As(III) was passed through the DCF system, arsenic concentration was only reduced to 31-70 \( \mu \text{g}/\text{L} \) (Figure 9). This is because ferric hydroxide precipitate has much lower adsorption capacity for As(III) than As(V). The adsorption capacity of ferric hydroxide for As(V) and As(III) was 645 and 87 \( \mu \text{mol}/\text{mmol Fe} \), respectively. The capacity values were determined with coprecipitation experiments in 0.04 M KNO\(_3\) solution at pH 6.8. When NaOCl solution was pumped concurrently with ferric chloride into the column, the effluent arsenic concentration was effectively reduced to less than 5 \( \mu \text{g}/\text{L} \) after 20 bed volumes of water were filtered. In this case, both oxidation of As(III) and coprecipitation occurred in the filter.

A comparison of the effectiveness of arsenic removal by the DCF and the batch coprecipitation processes is presented in Figure 10. The total ferric concentration was 1 mg/L and equilibrium pH was approximately 6.7 in both filtration and batch coprecipitation tests. In the batch coprecipitation tests, the residual arsenic concentrations were determined by analyzing arsenic in the samples filtered through 0.4 \( \mu \text{m} \) membranes after 30 minutes of coprecipitation and flocculation. The residual concentrations for the DCF process are average values of the total arsenic concentrations in the effluent. The residual arsenic concentrations increased gradually when the initial arsenic concentration was between 16 and 100 \( \mu \text{g}/\text{L} \). However, the residual arsenic concentration increased dramatically when the initial arsenic concentration exceeded 100 \( \mu \text{g}/\text{L} \). These results indicate that higher iron dosages should be used to treat water with arsenic concentration greater than 100 \( \mu \text{g}/\text{L} \).
The results in Figure 10 show that the DCF process was more effective than the batch coprecipitation for As(V) removal. When initial As(V) concentration was 50 \( \mu \text{g/L} \), the residual arsenic concentrations in the water treated with the DCF and batch coprecipitation were 2.2 and 3.3 \( \mu \text{g/L} \), respectively. The ratio of the residual arsenic concentrations for the two processes was 66.7\%. When the initial As(V) concentration was increased to 600 \( \mu \text{g/L} \), the ratio was decreased to 42\%. The higher arsenic removal efficiency observed in the DCF process is probably due to the lower arsenic content of the ferric hydroxide particles in the lower portion of the sand bed and the removal of fine particles by the sand column. It has been reported that fine particles ranging from the sub-colloidal (less than 0.01 \( \mu \text{m} \)) up to 100 \( \mu \text{m} \) can be removed by granular filters.\(^{21}\)

Conclusions

Bench-scale filtration results demonstrated that the DCF process can be used to remove As(V) effectively at filtration rates similar to those of conventional sand filters. Since the removal of As(V) by coprecipitation with ferric hydroxide occurred rapidly and the coprecipitates can be removed directly by the sand filter, no flocculation period is needed prior to filtration. During the filtration, no arsenic breakthrough occurs. The spent filter loaded with the coprecipitates can be regenerated by backwashing with water when headloss through the filter reaches a preset limit. The DCF process is more effective than batch coprecipitation for As(V) removal. As(III) can be effectively removed by concurrent injection of NaOCl and ferric chloride into the DCF filter.

Reference


Figure Captions

Figure 1. Removal of As(V) and iron by coprecipitation and adsorption with ferric chloride, equilibrium pH=6.7±0.1; As(V) = 50 μg/L or 0.67 μM in spiked tap water; Fe(III) = 1000 μg/L or 17.8 μM.

Figure 2. Effect of sand bed depth on iron removal without and with 7 minutes flocculation time. Filtration rate=3 gal/min.ft²; influent As(V)=50 μg/L; Fe(III)=1 mg/L; pH=6.7±0.2.

Figure 3. Effect of sand bed depth on arsenic removal without flocculation. Filtration rate=3 gal/min.ft²; influent As(V)=50 μg/L in spiked tap water; Fe(III)=1 mg/L; pH=6.7±0.2.

Figure 4. Correlation between the amounts of iron and arsenic removed. Influent As(V)=50 μg/L; Fe(III)=1 mg/L; pH=6.7±0.2.

Figure 5. Effect of filtration rates on the effluent arsenic concentration. Influent As(V)=16 μg/L; Fe(III)=1 mg/L; pH=6.7±0.2.

Figure 6. Effect of iron dosages on effluent arsenic concentration. Filtration rate=3 gal/min.ft²; influent As(V)=16 μg/L; pH=6.7±0.2.

Figure 7. Arsenic removal from tap water spiked with different amounts of As(V) and from a groundwater sample. Filtration rate=3 gal/min.ft²; Fe(III)=1 mg/L; pH=6.7±0.2.

Figure 8. Performance of the DCF process in a long filtration run. Influent As(V)=16 μg/L; filtration rate=3 gal/min.ft²; Fe(III)=1 mg/L.

Figure 9. Effect of hypochlorite on As(III) removal. Influent As(III)=90 μg/L; filtration rate=3 gal/min.ft²; Fe(III)=1 mg/L; initial Cl₂ = 0.5 mg/L in NaOCl treated water.

Figure 10. Comparison of As(V) removal by DCF and batch coprecipitation. Fe(III)=1 mg/L; pH=6.7±0.2; filtration rate=3 gal/min.ft²; coagulation time=30 minutes.
Figure 1

![Soluble As & Fe (g/L) vs Mix Time (min)](image1)

- Fe copre. 0.4 micron
- Fe copre. 0.1 micron
- As copre. 0.4 micron
- As copre. 0.1 micron
- As ads. 0.4 micron

Figure 2

![Residual Fe (µg/L) vs Sample Position (in. below sand surface)](image2)

- no pre-mix, total
- no pre-mix, soluble
- pre-mix, total
- pre-mix, soluble
Figure 3

Figure 4
Figure 5

Figure 6
Figure 7

Figure 8
Figure 9

Figure 10
Precipitation processes, including coagulation/filtration, direct filtration, coagulation assisted microfiltration, enhanced coagulation, lime softening, and enhanced lime softening. Adsorptive processes, including adsorption onto activated alumina, activated carbon and iron/manganese oxide based or coated filter media. Fe-Mn Oxidation Conventional iron and manganese removal can result in significant arsenic removal, through coprecipitation and sorption onto ferric or manganic hydroxides (Johnston, R. and Heijnen, H., 2001). Most low-cost methods for arsenic and manganese removal rely on aeration and filtration through porous media such as sand and gravel. In the case of arsenic removal, direct precipitation has not been shown to play an important role. However, coprecipitation and adsorption are both active arsenic removal mechanisms. Numerous studies have shown that filtration is an important step to ensure efficient arsenic removal. After coagulation and simple sedimentation, HAO and HFO along with their sorbed arsenic load can remain suspended in colloidal form. Hering and others showed that coagulation and sedimentation without filtration achieved arsenate removal efficiencies of 30%; after filtration through a 1.0 micron filter, effici