

ARSENIC REMOVAL FROM DRINKING WATER DURING COAGULATION

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ABSTRACT: The efficiency of arsenic removal from source waters and artificial freshwaters during coagulation with ferric chloride and alum was examined in bench-scale studies. Arsenic(V) removal by either ferric chloride or alum was relatively insensitive to variations in source water composition below pH 8. At pH 8 and 9, the efficiency of arsenic(V) removal by ferric chloride was decreased in the presence of natural organic matter. The pH range for arsenic(V) removal with alum was more restricted than with ferric chloride. For source waters spiked with 20 µg/L arsenic(V), final dissolved arsenic(V) concentrations in the product water of less than 2 µg/L were achieved with both coagulants at neutral pH. Removal of arsenic(III) from source waters by ferric chloride was both less efficient and more strongly influenced by source water composition than removal of arsenic(V). The presence of sulfate (at pH 4 and 5) and natural organic matter (at pH 4 through 9) adversely affected the efficiency of arsenic(III) removal by ferric chloride. Arsenic(III) could not be removed from source waters by coagulation with alum.

INTRODUCTION

Arsenic concentrations in drinking waters have been regulated for the protection of public health in the United States since 1942. The standard of 50 µg/L set over 50 years ago remains in force today as the maximum contaminant level (MCL) for arsenic. Epidemiological evidence of arsenic carcinogenicity suggests, however, that this standard may not be sufficiently protective of human health to achieve excess cancer risk levels below 10^{-4} (Tseng et al. 1968; Smith et al. 1992; Bates et al. 1992). U.S. Environmental Protection Agency (USEPA) calculations indicate that this risk level corresponds to arsenic concentrations in drinking water of 2 µg/L; the agency is evaluating a new standard for arsenic in drinking water in the range of 2–20 µg/L (Pontius 1994, 1995). In 1993, the World Health Organization recommended a provisional guideline value for arsenic of 10 µg/L based on both potential health risks and the practical quantitation limit (WHO 1993).

At the present time, only a few smaller communities in the United States, such as Hanford, Calif., and Fallon, Nev., use source waters with arsenic concentrations at the level of the current MCL (Reid 1994). Some larger communities, including Los Angeles and Albuquerque, N.M., use source waters that exceed the WHO provisional guideline values for arsenic (Reid 1994; Davis et al. 1994; Ramberg et al. 1995). At the lower bound of the range under consideration for the revised arsenic MCL, arsenic removal would become an issue for water utilities throughout the United States (Reid 1994; Davis et al. 1994).

Recent studies of arsenic removal in demonstration- and full-scale treatment plants (Cheng et al. 1994; Scott et al. 1995; McNeill and Edwards 1995, 1997) have shown that arsenic in the +V oxidation state, As(V), can be efficiently removed during coagulation with ferric chloride and alum

even when present at low concentrations in influent waters. Previous bench-scale studies have demonstrated that arsenic removal from both drinking water and wastewaters, at least to the level of the current MCL, can be achieved by addition of hydrolyzing metal salts as coagulants (Buswell et al. 1943; Shen 1973; Gullidge and O'Connor 1973; Sorg and Logsdon 1978). Coagulation has also been studied as a method for removing elevated concentrations of arsenic from wastewaters (Harper and Kingham 1992; Brewster 1992). Recent bench- and pilot-scale studies of drinking water treatment have focused on the possibility of meeting the range of anticipated (more stringent) arsenic standards (Chang 1994; Chang et al. 1994; Cheng et al. 1994; Edwards 1994; Ramberg et al. 1995; Hering et al. 1996).

Prior bench-scale studies in this laboratory examined the effects of arsenic oxidation state and the presence of co-occurring inorganic solutes on the efficiency of arsenic removal from synthetic freshwaters by ferric chloride (Hering et al. 1996). In the present work, arsenic removal from actual source waters and synthetic freshwaters is compared in bench-scale tests to identify those constituents of source waters that have the most pronounced effect on the efficiency of arsenic removal. The effectiveness of the coagulants ferric chloride and alum for arsenic removal is also compared.

MATERIALS AND METHODS

Reagents and Stock Solutions

All chemicals used were reagent-grade or better and were used without additional purification. All solutions were prepared with deionized (DI) water, pretreated by reverse osmosis and deionized using a Barnstead Nanopure system (Barnstead, Dubuque, Iowa). Glass- and plastic-ware were acid-washed before use. All low-concentration (secondary standard) stock solutions (for both arsenic and iron) were freshly prepared for each experiment from concentrated, primary stock solutions. Primary stock solutions for arsenite, 1.0 g/L As(III), were prepared from American Chemical Society (ACS) primary standard grade arsenic trioxide, As₂O₃ (Aldrich, Milwaukee) dissolved in 0.18 M trace metal grade HCl (Fisher, Pittsburgh), for arsenate, 1.0 g/L As(V), from the sodium salt heptahydrate, Na₂HAsO₄ · 7H₂O (Sigma, St. Louis) dissolved in DI water, for ferric chloride, 405.5 g/L FeCl₃ or 2.5 M Fe, from FeCl₃ · 6H₂O (Fisher), and for alum, 199.8 g/L Al₂(SO₄)₃ · 18H₂O or 0.6 M Al, from Al₂(SO₄)₃ · 18H₂O (Fisher). Alum stock solutions were used without intermediate dilution, since irreproducible results have been observed with dilute and aged alum samples (Ching 1994). Background electrolyte solutions were prepared from reagent grade salts NaNO₃ (Fisher), to fix ionic strength,

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and NaHCO₃ (Fisher), to provide alkalinity. The background electrolyte solutions were amended by addition of representative inorganic solutes in natural waters, specifically calcium, sulfate, and/or phosphate stock solutions prepared from the salts Ca(NO₃)₂·4H₂O, Na₂SO₄·10H₂O, and NaH₂PO₄·H₂O (Fisher). Natural organic matter (NOM) was obtained in freeze-dried form and was originally isolated from Suwannee River water by reverse osmosis and purified by cation exchange (Serkiz and Perdue 1990).

Source water samples were collected at the Metropolitan Water District of Southern California (MWDSC) Weymouth Filtration Plant in La Verne, Calif. Samples were collected in acid-washed low-density polyethylene carboys and stored at 4°C until use. Source water pH and turbidity were recorded upon collection. Chemical composition of the source waters (reported in Table 1) was determined in the MWDSC Water Quality Laboratory.

For arsenic analysis, ultrapure 0.14 M potassium iodide (Alfa, Ward Hill, Mass.) was used as a pre-reductant for As(V). Hydride generation was accomplished using analytical grade 4% (w/v) sodium borohydride (NaBH₄) pellets (Alfa) dissolved in 1% (w/v) sodium hydroxide (Fisher). Acetylene (Liquid air, Walnut Creek, Calif.) was used as the fuel for the spectrometer furnace and 99.999% nitrogen (Liquid carbonic, Oak Bridge, Ill.) as the purge gas for the hydride generator.

Analytcs

Arsenic was measured by hydride-generation-flame atomic absorption spectrometry using a Perkin-Elmer Model 3300 atomic absorption spectrometer (AAS) with an electrodeless discharge lamp (EDL) coupled to a Perkin-Elmer MHS-10 hydride generation system (Andreae 1983; "Standard" 1992; Hering et al. 1996; Wilkie and Hering 1996). Analyses were conducted with 20 mL samples, which were pre-reduced by addition of 2 mL 0.14 M KI (10% w/v) and 5 mL of concentrated trace metal grade HCl (Fisher) with at least a 1 h reaction time for the determination of total arsenic, the sum of As(III) and As(V). After pre-reduction, samples were transferred to the MHS-10 hydride generation system. Arsine gas was generated by continuous addition of basic sodium borohydride solution at a rate of 22–25 mL/min until the maximum absorbance was obtained (i.e., approximately 6–8 s). The reaction vessel and quartz cell were continuously purged with nitrogen gas. Absorbance at 193.7 nm was measured as peak height.

Measurements of pH were made with a pH electrode and meter (Model 15, Fisher) calibrated with three buffer solutions at pH 4, 7, and 10 (Fisher).

Coagulation Experiments

Coagulation experiments were conducted with either source water samples or a background electrolyte of 0.01 M NaNO₃ and 0.001 M NaHCO₃ (pH before adjustment was 8.3 ± 0.1). Test solutions were contained in 1 L cylindrical beakers and mixed using a variable-speed, flat-paddle stirrer (Phipps and Bird, Richmond, Va.). Before coagulant addition, the pH of 1 L of the source water sample or background electrolyte was pre-adjusted to the desired value (±0.1 pH unit) by addition of 0.1 M HCl or 0.1 M NaOH. Solutions were amended for the specific experiment (e.g., with sulfate or NOM) and spiked with As(III) or As(V) to the desired concentration. Predetermined concentrations of 0.1 M NaOH (to maintain the target pH) were added simultaneously with the coagulant (ferric chloride or alum) under rapid-mix conditions. Mixing conditions during coagulation were: 1 min rapid-mix at 100 rpm ($G = 160 \text{ s}^{-1}$), 30 min slow mix at 45 rpm ($G = 48 \text{ s}^{-1}$), and 15 min quiescent settling. After the settling period, about 100 mL

TABLE 1. Chemical Composition^a of Raw Source Waters^b

Constituent (1)	CONCENTRATION OF CONSTITUENTS IN					
	100% SPW ^c		100% SPW ^d		70% CRW ^e	
	mg/L (2)	mM (3)	mg/L (4)	mM (5)	mg/L (6)	mM (7)
Calcium	22	0.55	22	0.55	65	1.6
Sodium	49	2.1	46	2.0	93	4.0
Magnesium	11.5	0.47	11	0.45	26.5	1.1
Sulfate	60	0.6	59	0.6	234	2.4
Chloride	52	1.5	50	1.4	87	2.5
Phosphate	0.24	2.6 μM	0.15	1.6 μM	0.06	0.6 μM
Arsenic	2.4 μg/L	32 nM	2.0 μg/L	27 nM	2.6 μg/L	35 nM
TOC ^f	3.2	—	3.3	—	2.6	—
Total alkalinity ^g	—	—	67	—	111	—
pH (pH units)	8.22	—	8.24	—	8.31	—
Turbidity (NTU)	3.1	—	0.71	—	0.93	—

^aChemical composition data provided by MWDSC Water Quality Laboratory (except for pH and turbidity measured at time of collection and arsenic measured at UCLA).

^bWater samples collected at the MWDSC Weymouth Filtration Plant, La Verne, Calif.

^cState project water collected 23 May 1995.

^dState project water collected 6 June 1995.

^e70:30 blend of CRW and SPW collected 6 June 1995.

^fTotal Organic Carbon (mg C/L).

^gAs mg/L CaCO₃ (sampled 5 June 1995).

of solution was collected using a 20 mL disposable syringe from 2 cm below the liquid surface and filtered through a 0.1 μm pore size cellulose nitrate membrane filter (Sartorius, Edgewood, N.Y.) using a vacuum filter flask assembly. The filter flask assembly was rinsed with deionized water between samples; filters were not reused. Samples were acidified to approximately pH 1 for storage and analyzed within 1 week.

Adsorption Experiments

Adsorption experiments were conducted with preformed hydrous metal oxides that were freshly prepared for each experiment. Hydrous ferric oxide (HFO) and hydrous aluminum oxide (HAO) were prepared by slow addition of 0.5 or 1.0 M NaOH to solutions of 0.05 M Fe(NO₃)₃ or 0.1 M Al(NO₃)₃, respectively. Precipitated HFO or HAO solids were separated by centrifugation, washed four times with DI water, and aged for 2 h in media with the same pH and major ion composition as the subsequent adsorption experiment before use. For adsorption experiments (run in triplicate), 50 mL of source water samples or pH-adjusted 0.01 M NaNO₃ solutions amended as appropriate (e.g., with sulfate or natural organic matter) in 85 mL polycarbonate centrifuge tubes were spiked with As(III) or As(V) and then with aliquots of aged HFO or HAO suspensions. The pH of the arsenic stock solution and of the oxide stock suspension were adjusted to the pH of the adsorption experiment before their addition to the reaction vessel. Samples were equilibrated for 2 h with mixing on a wrist action shaker. At the end of the equilibration period, the final pH was recorded and samples were filtered through 0.1 μm cellulose nitrate membrane filters (Sartorius). Filtrates were analyzed for arsenic the same day or acidified to approximately pH 1 and stored for analysis, which was performed within 1 week.

RESULTS AND ANALYSIS

Two source waters, state project water (SPW) and a 70:30 blend of Colorado River water with SPW (70% CRW), were obtained from the MWDSC Weymouth Filtration Plant for this study. Arsenic removal from source waters and from artificial freshwaters (i.e., background electrolyte amended with various solutes) during coagulation was compared to identify those

constituents with the greatest effect on removal efficiencies. The effectiveness of ferric chloride and alum for arsenic removal was also compared.

Meeting Anticipated Arsenic MCL by Treatment with Coagulants

Both the arsenic concentration in the raw water and the efficiency of arsenic removal determine whether a particular value for the MCL can be met by a specific treatment technology. The range of values under consideration by USEPA for the arsenic MCL is from 2 to 20 $\mu\text{g/L}$. Since the source waters used for this study are naturally low in arsenic (with ambient arsenic concentrations between 2 and 3 $\mu\text{g/L}$), water samples were spiked with 20 $\mu\text{g/L}$ As(V) for preliminary tests.

As shown in Fig. 1(a), removal efficiencies close to or above 80% were achieved with both SPW and 70% CRW over the pH ranges 4–8 with ferric chloride (4.9 mg/L FeCl_3) and 6–8 with alum [40 mg/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$]. Correspondingly, final dissolved As(V) concentrations in the treated source waters ranged from less than 0.5 to slightly above 5 $\mu\text{g/L}$ [Fig. 1(b)]. Thus, the lower bound (2 $\mu\text{g/L}$) of the range for the anticipated arsenic MCL was met by treatment with 40 mg/L alum for both SPW and 70% CRW at pH 6 and 7 and with 4.9 mg/L FeCl_3 for 70% CRW from pH 5–7 and for SPW at pH 5. The pH range for efficient As(V) removal is more restricted for alum than for ferric chloride but, as discussed in more detail in the following, at optimal pH conditions there is less variation in As(V) removal from the two source waters with alum than with ferric chloride.

The difference in the pH ranges for application of alum and ferric chloride for As(V) removal corresponds to the greater solubility of the amorphous hydroxide solid of aluminum as compared with iron(III). In contrast to turbidity removal, which can be accomplished by charge neutralization, arsenic removal requires precipitation of the amorphous metal hydroxide solid as a substrate for arsenic adsorption. At coagulant concentrations typical of water treatment processes, the pH range over which the amorphous hydroxide solid is stable is much narrower for aluminum than for iron(III). Consequently, the possible application of alum for arsenic removal is restricted to a narrower pH range than the corresponding application of ferric chloride (Amirtharajah and O'Melia 1990; Edwards 1994; McNeill and Edwards 1995). The pH range over which As(V) is efficiently removed during coagulation with alum corresponds well with the pH range over which the added aluminum is retained by 0.1 μm filters (Hering and Elimelech 1996).

Even with ferric chloride, the efficiency of As(V) removal is markedly decreased at higher pH values (particularly at pH 9). As(V) removal efficiencies may be improved by pH adjustment for source waters with ambient pH values above 8. In previous studies, the efficiency of As(V) removal was also observed to decrease at and above pH 8; this effect of pH was more pronounced with alum than with ferric chloride (Gulledge and O'Connor 1973; Sorg and Logsdon 1978; Cheng et al. 1994). Below pH 8, however, there appears to be little opportunity to optimize As(V) removal by pH adjustment.

The observed efficiencies of As(V) removal by ferric chloride and alum and the final dissolved As(V) concentrations levels achieved in these preliminary tests are consistent with previous observations in tests from bench to full scale (Gulledge and O'Connor 1973; Chang 1994; Chang et al. 1994; Cheng et al. 1994; Scott et al. 1995; McNeill and Edwards 1995). Better As(V) removal was observed in the present study than in previous jar tests with the same source waters under comparable conditions (Cheng et al. 1994). This difference is attributable to the more efficient filtration (with 0.1 μm filters) in the present study compared with the small sand filters used

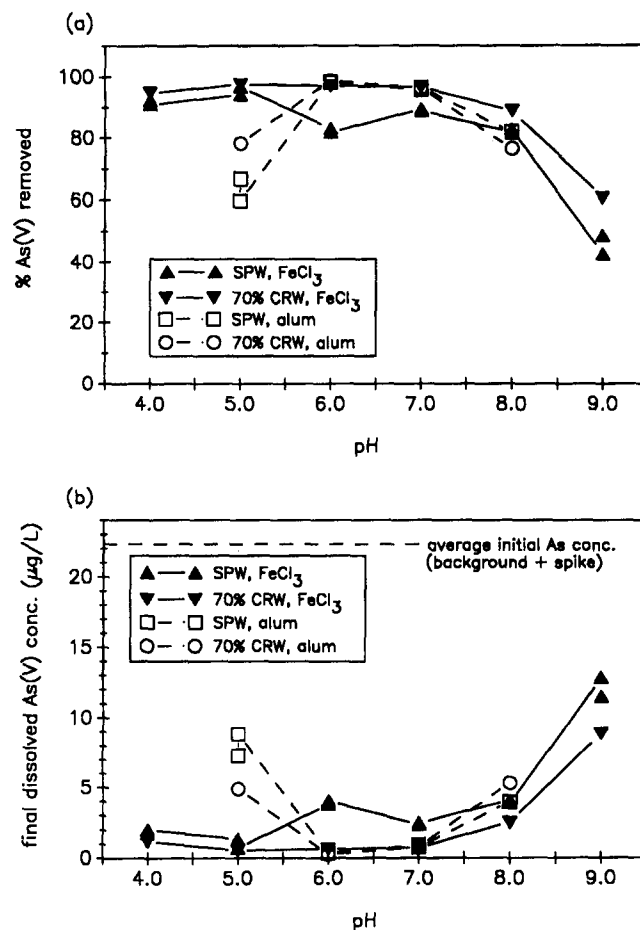


FIG. 1. As(V) (a) Removal; and (b) Final Dissolved Concentrations Achieved in Source Waters [SPW and 70% CRW Spiked with 20 $\mu\text{g/L}$ As(V)] during Coagulation with 4.9 mg/L Ferric Chloride or 40 mg/L Alum

in the previous study with a modified jar test apparatus (Cheng et al. 1994). The importance of efficient filtration to arsenic removal is confirmed by the observation of Cheng et al. (1994) that arsenic removal was improved by addition of cationic polymer.

Although final, dissolved As(V) concentrations ≤ 2 $\mu\text{g/L}$ were not achieved for all pH values in the preliminary tests; the As(V) spike (20 $\mu\text{g/L}$) used in these tests is higher than the typical arsenic concentrations in U.S. source waters (Reid 1994). In recent USEPA estimates, arsenic concentrations of 10 $\mu\text{g/L}$ were exceeded in less than 3% of public drinking water supplies (Reid 1994). With lower concentrations in raw waters and with the As(V) removal efficiencies observed in these preliminary tests, final dissolved As(V) concentrations ≤ 2 $\mu\text{g/L}$ could be easily achieved by addition of coagulants. This, of course, presupposes that removal efficiencies do not decline significantly at lower initial arsenic concentrations.

Effect of Initial Arsenic Concentration and Oxidation State

The effects of initial arsenic concentration and oxidation state on the efficiency of arsenic removal during coagulation with 4.9 mg/L FeCl_3 were examined at pH 7 by spiking both source waters with either As(V) or As(III); concentrations of the As spike ranged from 2 to 100 $\mu\text{g/L}$. Arsenic adsorption onto preformed HFO was examined at pH 7 under similar conditions (with 50 μM total iron corresponding to an equivalent coagulant dose of 8.1 mg/L FeCl_3). The ambient arsenic (about 2–3 $\mu\text{g/L}$) occurs in the +V oxidation state (Scott, personal communication, 1994) and was therefore assumed to

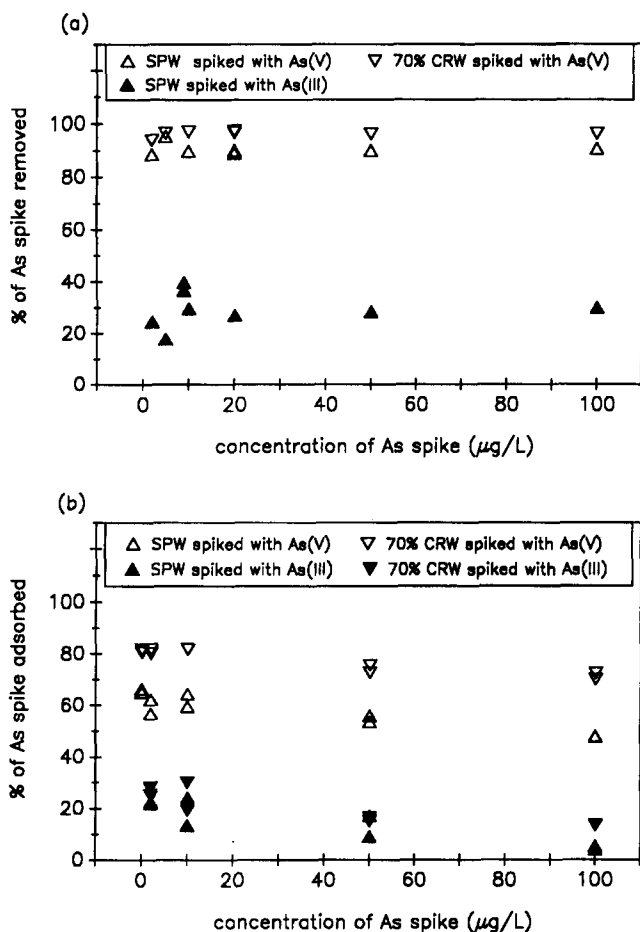


FIG. 2. Efficiency of (a) Arsenic Removal by Ferric Chloride; and (b) Adsorption onto Preformed HFO from Source Waters (at pH 7) as Function of Concentration of As(III) or As(V) Added to Source Waters

be removed with the same efficiency as the As(V) added as a spike to the source waters. Thus, for samples spiked with As(V), total arsenic removal could be examined but, for samples spiked with As(III), the difference in the efficiency of removal of the ambient As(V) and the added As(III) had to be accounted for.

Over the initial arsenic concentration range examined, removal efficiencies during coagulation with FeCl_3 were independent of initial arsenic concentration for both As(V) and As(III) [Fig. 2(a)]. This result is consistent with previous observations of As(V) removal from source waters by both ferric chloride and alum in modified jar tests (Cheng et al. 1994) and with previous studies of As(V) and As(III) removal from synthetic freshwaters by ferric chloride (Hering et al. 1996). The lack of dependence of arsenic removal efficiency on initial arsenic concentration is consistent with the expected adsorption behavior of arsenic when the surface of the freshly precipitated amorphous metal hydroxide formed upon coagulant addition is not saturated; this behavior is discussed in detail by Hering et al. (1996).

As shown in Fig. 2(a), As(V) was much more efficiently removed than As(III) during coagulation with ferric chloride. As(V) removal efficiencies of 90% or higher were achieved for both SPW and 70% CRW over the range of initial As(V) concentrations studied. Final dissolved As(V) concentrations less than $5 \mu\text{g/L}$ were achieved for initial As(V) concentrations up to $50 \mu\text{g/L}$. In contrast, only about 30% of the As(III) added as a spike to SPW was removed during coagulation with ferric chloride and final dissolved As(III) concentrations de-

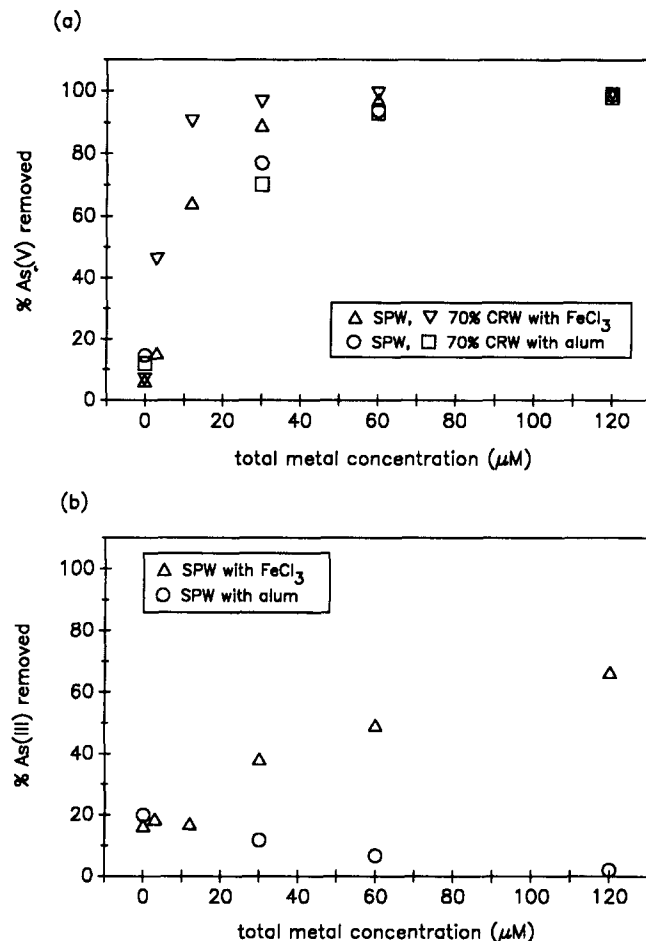


FIG. 3. Efficiency of (a) As(V); and (b) As(III) Removal from Source Waters [Spiked with $20 \mu\text{g/L}$ As(V) or $9 \mu\text{g/L}$ As(III)] by Ferric Chloride and Alum at pH 7 as Function of Total Iron(III) or Aluminum Concentration

pended strongly on the initial As(III) concentration even for low initial As(III) concentrations.

Similar results were obtained in adsorption studies [Fig. 2(b)]. The extent of arsenic adsorption was relatively independent of initial arsenic concentration for both As(V) and As(III) and significantly greater for As(V) than for As(III). A slight decrease in the percent of arsenic adsorbed was observed at higher As(V) or As(III) concentrations. Similar behavior was observed in studies of arsenic adsorption onto HFO in simple background electrolyte (0.01 M NaNO_3), consistent with preferential adsorption at high affinity sites on a heterogeneous surface (Wilkie and Hering 1996). At comparable initial arsenic concentrations, both As(V) and As(III) were more efficiently removed from solution in the coagulation tests than by adsorption onto preformed HFO despite the higher total iron concentrations in the adsorption studies (as discussed in more detail in the following).

In both coagulation and adsorption studies, As(V) was more efficiently removed from 70% CRW than for SPW. This effect of source water composition (discussed later) was more pronounced in the adsorption studies than in coagulation studies. The extent of As(III) adsorption was also greater with 70% CRW than with SPW but the source waters were not compared in coagulation tests.

Effects of Coagulant Type and Dose, and Adsorbent Type and Concentration

The effects of increasing coagulant dose on arsenic removal were examined at pH 7 for SPW and 70% CRW spiked with

either As(V) (at 20 $\mu\text{g/L}$) or As(III) (at 9 $\mu\text{g/L}$). Concentrations of total metal added as coagulant ranged from 3 to 120 μM for iron(III) (corresponding to 0.5–19.5 mg/L FeCl_3) and 30–120 μM for aluminum (corresponding to 10–40 mg/L alum). For both source waters and with both coagulants, the efficiency of As(V) removal could be improved by increasing coagulant dose; better than 98% removal of As(V) (to a final dissolved concentration $\leq 0.4 \mu\text{g/L}$) could be achieved at higher doses of either ferric chloride or alum [Fig. 3(a)]. Comparable efficiencies of As(V) removal by ferric chloride and alum (on a molar basis) have been observed in previous bench- and pilot-scale studies (Chang et al. 1994; Cheng et al. 1994; Edwards 1994). At full scale, however, As(V) removal by alum was significantly less effective than ferric chloride (comparing coagulant additions on a molar basis) (Scott et al. 1995). This difference may be attributable to incomplete precipitation of added aluminum as the amorphous hydroxide solid (McNeill and Edwards 1997).

In the present study, differences in the efficiency of As(V) removal by ferric chloride were observed when SPW and 70% CRW were compared; these effects were most pronounced at lower coagulant doses. Although only slight differences between the two source waters could be observed with alum, lower alum doses were not tested because of the solubility of amorphous aluminum hydroxide at these total aluminum concentrations.

As previously noted, As(III) was less efficiently removed by ferric chloride than As(V). Although As(III) removal by ferric chloride was improved by increasing coagulant dose, complete removal of As(III) was not achieved within the range of coagulant doses tested [Fig. 3(b)]. In contrast to As(V), As(III) removal with alum was negligible and was not increased even at higher alum doses. The apparent decrease in As(III) removal at higher alum doses is unexpected but was not further investigated in light of the obvious inability of alum addition to accomplish As(III) removal. The lack of As(III) removal by alum was consistent with previous observations of negligible As(III) adsorption onto HAO (Hering and Elimelech 1996). Previous coagulation studies have also demonstrated more efficient removal of As(V) than As(III) during coagulation with ferric chloride and particularly with alum (Sorg and Logsdon 1978). Pretreatment with oxidants, which would oxidize ambient As(III) to As(V), has been shown to improve the efficiency of arsenic removal during coagulation (Shen 1973; Sorg and Logsdon 1978).

Similar trends were observed in adsorption and coagulation experiments. Adsorption and coagulation data for source waters at pH 7 are shown together in Fig. 4 with the total iron(III) concentrations in the adsorption experiments reported as equivalent coagulant dose. Adsorption studies were conducted with SPW and 70% CRW spiked with 10 $\mu\text{g/L}$ of either As(V) or As(III); in coagulation studies, SPW was spiked with either As(V) (at 20 $\mu\text{g/L}$) or As(III) (at 9 $\mu\text{g/L}$) and 70% CRW with 20 $\mu\text{g/L}$ As(V). The results obtained under these conditions can be directly compared despite the differences in initial arsenic concentrations since removal efficiency was shown to be independent of this parameter (as discussed earlier). The observed increase in extent of adsorption with adsorbent concentration (or equivalent coagulant dose) is consistent with the expected linear increase in surface area and the concentration of surface sites for adsorption (Stumm 1992; Hering et al. 1996). The similar trends in the coagulation and adsorption experiments indicate that adsorption onto freshly precipitated amorphous metal hydroxides is an important mechanism for removal of arsenic from solution during coagulation. Arsenic removal during coagulation with ferric chloride is, however, noticeably more efficient than arsenic adsorption onto preformed HFO for both source waters and for both As(V) and

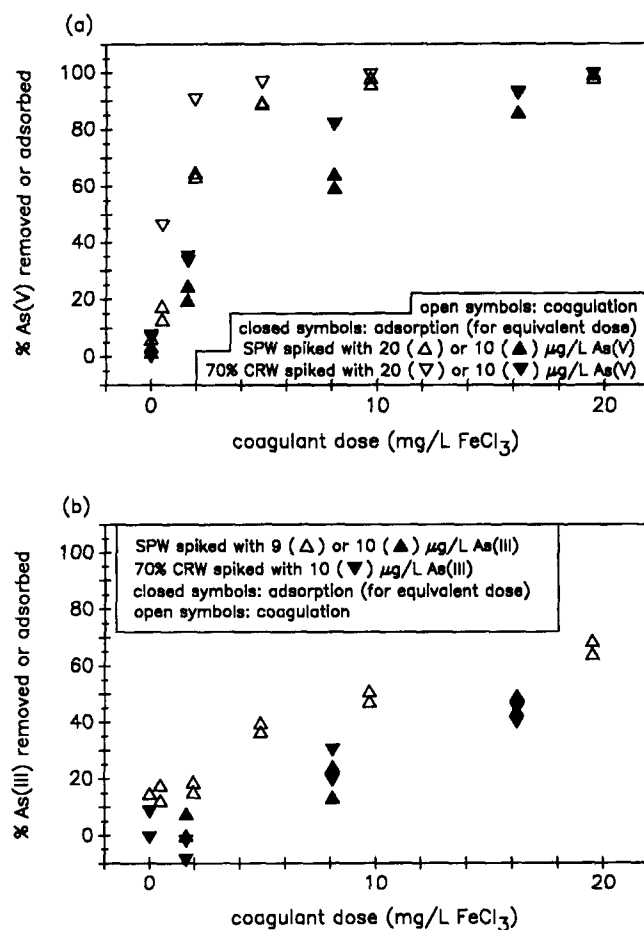


FIG. 4. Comparison of (a) As(V); and (b) As(III) Removal and Adsorption from Source Waters at pH 7; Removal by Ferric Chloride and Adsorption onto HFO Shown as Function of Coagulant Dose (or Equivalent Coagulant Dose for Adsorption)

As(III). Comparison with previous studies suggests that differences between the efficiency of arsenic removal during coagulation and arsenic adsorption become increasingly significant at arsenic-to-iron ratios higher than those examined in the present study (or pertinent to water treatment) (Fuller et al. 1993; Edwards 1994). These differences may be due to effects of sorption kinetics since, in adsorption experiments, the preformed HFO is exposed to the constituents of the source waters before addition of the arsenic spike while, in coagulation experiments, the source waters are spiked with arsenic before coagulant addition and precipitation of the amorphous iron(III) hydroxide. It is also possible, however, that the properties of the amorphous iron(III) hydroxide (e.g., surface area) are influenced by the chemical composition of the source water in which it is precipitated (Cornell et al. 1989; Chowdhury et al. 1991).

The effect of the type of adsorbent (HFO compared with HAO) on the extent of As(V) adsorption (shown in Fig. 5) was more pronounced than the corresponding effect of coagulant type (ferric chloride compared with alum) when the adsorbents or coagulants are compared on a molar basis (cf. Fig. 3). The adsorption data shown in Fig. 5 clearly indicate a significant competitive effect that results in reduced As(V) adsorption in source waters as compared with a simple background electrolyte (0.01 M NaNO₃). This effect is greater with HAO than with HFO. Comparison of the two source waters indicates that As(V) adsorption onto HFO is depressed to a greater extent in SPW than in 70% CRW, whereas the effects of the source waters are reversed with HAO. These observations are indicative of the complex effects of source water

composition on arsenic removal, which are discussed in the following section.

Effects of Source Water Composition

The effects of source water composition were examined by comparing the efficiency of arsenic removal from source waters and from artificial freshwaters (i.e., background electrolyte amended with various inorganic and organic constituents). Both source waters and artificial freshwaters were spiked with either As(V) (at 20 $\mu\text{g/L}$) or As(III) (at 9 $\mu\text{g/L}$) and adjusted to target pH values (from pH 4 to 9) before addition of coagulant (4.9 mg/L FeCl_3). As shown in Fig. 6(a), As(V) re-

moval from SPW and 70% CRW was less efficient than removal from the pH-adjusted background electrolyte (0.01 M NaNO_3 , 0.001 M NaHCO_3) at higher pH values (at pH 9 and, to a lesser extent, at pH 8). As(V) removal efficiencies comparable to those observed for the source waters at pH 8 and 9 were obtained when the background electrolyte was amended with 4 mg/L Suwannee River NOM. Addition of sulfate (at 40 mg/L SO_4 or 0.42 mM for pH 4–8 and 250 mg/L SO_4 or 2.6 mM at pH 9) to the background electrolyte had no effect on As(V) removal over the pH range examined.

A striking decrease in As(V) removal efficiency was observed in coagulation experiments with NOM-amended solutions at pH 6 (Fig. 7). This effect, however, was eliminated by the addition of calcium and is thus unlikely to be significant in natural waters. The addition of NOM at pH 6 also had little effect on As(V) adsorption. This suggests that the effect of NOM observed at pH 6 in the coagulation experiments results from changes in the precipitation of amorphous iron(III) hydroxide (i.e., either the extent of precipitation or the surface properties of the precipitated solid) rather than from competitive adsorption effects. In practical terms, this effect corresponds to an increased coagulant dose in the presence of NOM. In previous jar tests with ground-water samples, As(V) removal at pH 6 by low doses of either ferric chloride or alum was decreased at higher total organic carbon (TOC) concentrations (Chang 1994; Chang et al. 1994). Since major ion compositions for these tests solutions were not reported, comparison with the results of the present study is difficult. It is interesting to speculate, however, that the lower efficiency of As(V) removal (at pH 6) ferric chloride from SPW as compared with 70% CRW corresponds to the combination of slightly higher TOC and significantly lower calcium in SPW (cf. Table 1). Variation in the composition of the organic mat-

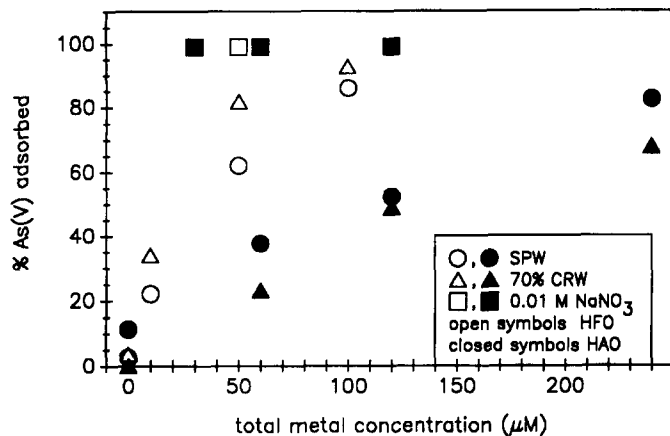


FIG. 5. Comparison of As(V) Adsorption onto HFO and HAO from Source Waters at pH 7 and from 0.01 M NaNO_3 at pH 6 as Function of Total Iron(III) or Aluminum Concentration [All Solutions Spiked with 10 $\mu\text{g/L}$ As(V)]

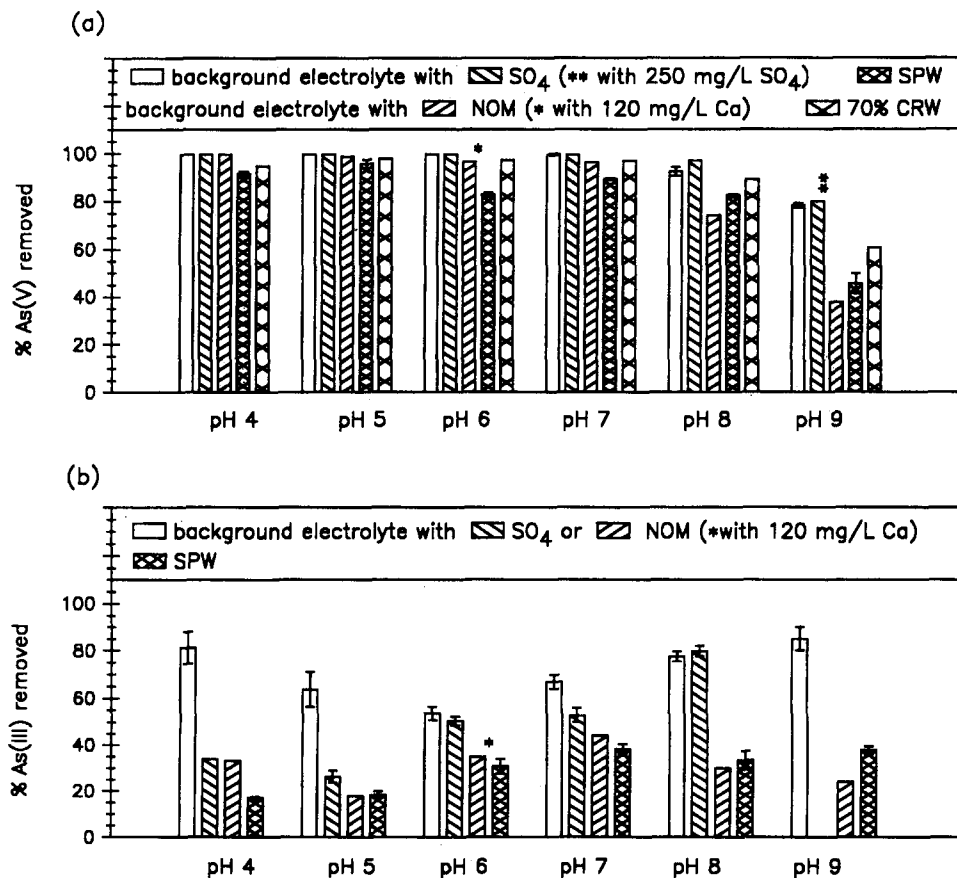


FIG. 6. Comparison of Arsenic Removal by Ferric Chloride (4.9 mg/L) from Source Waters and from Background Electrolyte (0.01 M NaNO_3 , 0.001 M NaHCO_3) Amended with Sulfate (40 mg/L) and NOM (4 mg/L) over pH Range 4–9; Both Source Waters and Electrolyte Spiked with (a) 20 $\mu\text{g/L}$ As(V); (b) 9 $\mu\text{g/L}$ As(III)

ter in the two source waters may also affect arsenic removal; dissolved organic matter in SPW has more humic character (as indicated by a higher ratio of UV absorbance to TOC) than that in 70% CRW (Ching 1994).

With As(III), the discrepancies between arsenic removal from source waters and from pH-adjusted background electrolyte were much more dramatic than for As(V) [Fig. 6(b)]. Correspondingly, additions of inorganic and organic solutes to the background electrolyte had pronounced effects on the efficiency of As(III) removal by ferric chloride over the entire pH range examined. Addition of sulfate (at 40 mg/L SO_4 or 0.42 mM) significantly depressed As(III) removal at pH 4 and 5 but had no effect at higher pH values, consistent with competitive adsorption of sulfate and As(III) as discussed by Wilkie and Hering (1996) and Hering et al. (1996). Addition of 4 mg/L NOM significantly decreased the efficiency of As(III) removal at all pH values tested. Comparison of As(III) removal at pH 4 from sulfate- and NOM-amended electrolyte solutions and from SPW suggests some additive effects of sulfate and NOM, which are both present in SPW (at concentrations of 60 mg/L SO_4 and 3.3 mg/L TOC or about 6.6 mg/L NOM). Additive effects in coagulation experiments are not, however, apparent at pH 5.

In adsorption experiments with As(III), significantly less adsorption of As(III) onto HFO was observed with pH-adjusted source waters than with sulfate- or NOM-amended electrolyte solutions (Fig. 8). Additive effects of NOM and sulfate might account for this discrepancy at pH 5 and 6 but appear to be insufficient to account for the weak As(III) adsorption from SPW and 70% CRW observed at pH 7.

Comparison of the results shown in Fig. 6 clearly shows that source water composition has a much greater effect on arsenic removal by coagulation with ferric chloride when arsenic is present in the +III oxidation state. Thus, not only is As(III) generally removed with less efficiency than As(V), but As(III) removal is likely to be subject to greater variability (i.e., with seasonal or spatial variations in source water composition). Sulfate and NOM appear to be the constituents adversely affecting the efficiency of arsenic removal from SPW and 70% CRW. With As(III), these effects are most significant for sulfate at pH 4 and 5 and for NOM from pH 4–9 and, with As(V), for NOM at pH 8 and 9.

The contrasting pH ranges over which the effects of NOM are observed on As(III) and As(V) removal suggest that competitive adsorption of NOM is important for As(III) but not for As(V). Competitive adsorption effects should be strongest at pH 4 and 5, where As(V) removal is unaffected by NOM. NOM sorption onto iron oxides is strongest in the pH range from 4 to 6 and decreases significantly above pH 7 (Tipping 1981). Competitive adsorption of phosphate and NOM on iron(III) and aluminum oxides has been observed from pH 4 to 6 but not at higher pH (Sibanda and Young 1986). The effects of NOM on As(V) removal at high pH are thus more probably due to changes in the extent or surface properties of precipitated amorphous iron(III) hydroxide.

In the absence of NOM, As(III) and As(V) removal by coagulation with ferric chloride can, to some extent, be described by surface complexation modeling; this approach assumes adsorption of inorganic ions onto HFO stoichiometrically precipitated upon coagulant addition as discussed in detail by Hering et al. (1996) and Hering and Elimelech (1996). This modeling approach relies on the extensive data set for the adsorption of inorganic ions on HFO compiled by Dzombak and Morel (1990). A comparable data set is not available for HAO (which would allow predictions for coagulation with alum) nor does the data set for HFO include NOM. Arsenic removal from source waters (containing NOM) can be described by an empirical model based on adsorption as the process governing

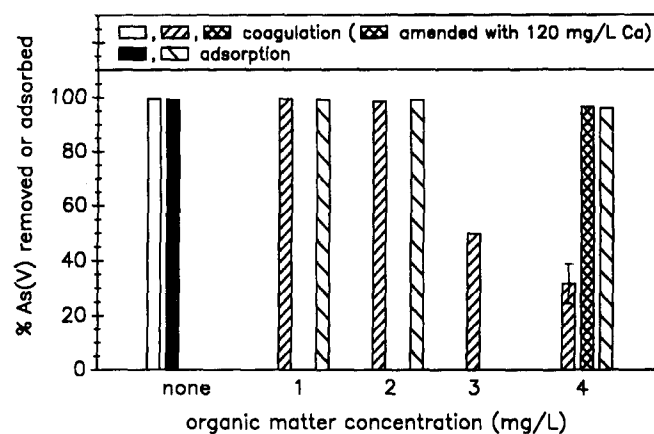


FIG. 7. Effects of NOM (and Calcium) on As(V) Removal by Ferric Chloride (4.9 mg/L FeCl_3 or 30 μM Total Fe) and As(V) Adsorption onto HFO (50 μM Total Fe) at pH 6 [Solutions Spiked with 20 $\mu\text{g/L}$ As(V) for Coagulation and 10 $\mu\text{g/L}$ As(V) for Adsorption Experiments]

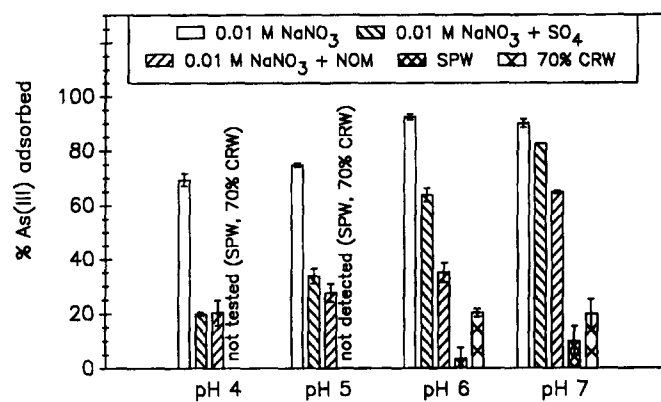


FIG. 8. Effects of Sulfate (250 mg/L) and NOM (4 mg/L) on Adsorption of As(III) [Initial Concentration 10 $\mu\text{g/L}$] onto HFO (50 μM total Fe) at pH 4–7]

removal (McNeill and Edwards 1997), but this approach cannot account predictively for the effects of variations in source water composition.

CONCLUDING REMARKS

The anticipated downward revision of the arsenic MCL to a value in the range of 2–20 $\mu\text{g/L}$ will have significant consequences for water utilities, particularly if the new MCL falls at the lower bound of this range. In this and previous studies, coagulation has been shown to be a technology capable of achieving final dissolved As(V) concentrations $\leq 2 \mu\text{g/L}$ for the range of influent As(V) concentrations found in U.S. source waters. Both alum and ferric chloride can be used to achieve efficient As(V) removal. The suitable pH ranges and minimum coagulant doses for treatment are governed by the solubility of the amorphous metal hydroxide solids; thus, the pH range is narrower and the minimum coagulant dose higher for alum than for ferric chloride. The efficiency of As(V) removal can be increased by increasing coagulant dose. Comparable trends observed in studies of As(V) adsorption onto preformed hydrous metal oxides confirm that adsorption is an important (though not the sole) process governing As(V) removal during coagulation. As(V) removal efficiencies were minimally affected by variations in source water composition except at high pH. As(V) was poorly removed from source waters by ferric chloride at pH 9; comparison with artificial freshwaters suggested that the decreased removal efficiency was due to the presence of NOM.

As(III) removal from source waters by ferric chloride was

much less efficient and more strongly influenced by source water composition than was As(V) removal. The presence of sulfate (at pH 4 and 5) and NOM (at pH 4–9) significantly decreased the efficiency of As(III) removal by ferric chloride. Removal of As(III) from source waters could not be accomplished by coagulation with alum. For source waters containing As(III), preoxidation would be necessary to achieve efficient removal by alum and advisable to ensure efficient removal by ferric chloride.

Even under optimal coagulation conditions for arsenic removal, the overall effectiveness of this process will depend on the efficiency of the subsequent solid-liquid separation process. Efficient filter performance (i.e., low effluent turbidity) is crucial to prevent breakthrough of fine colloidal particles to which arsenic may be adsorbed. Such breakthrough could result in increased total arsenic concentrations (i.e., dissolved plus colloidal arsenic) in product water.

Although this study focuses primarily on the final dissolved arsenic concentrations achievable by coagulation, other issues must also be considered in evaluating the applicability of this treatment technology for arsenic removal. While modification of existing conventional treatment plants may be an attractive option to meet a more stringent arsenic MCL, some facilities (such as direct filtration plants) lack the flexibility required to optimize processes for arsenic removal. Disposal of arsenic-contaminated coagulant sludges also poses considerable problems; the possible necessity of disposing of such sludges as hazardous waste would add significantly to treatment costs. Clearly such issues must be considered in evaluating the feasibility and cost of meeting a more stringent arsenic standard.

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