

Arsenic removal mechanisms include adsorption, coprecipitation, ion exchange, and ion exclusion. Coagulation/filtration (C/F) involves adding ferric or aluminum salts to the water, which form a metal hydroxide floc and adsorb or coprecipitate As and other species. This is followed by removal of the floc by filtration. Modification to enhance As removal typically involves increasing the coagulant dose, which increases the average percent of total costs spent on waste disposal from 30% to 80% (Frey et al. 1998). Coagulation/microfiltration (C/MF) operates similarly, but the finer membrane used in microfiltration allows removal of smaller floc particles, enabling less coagulant to be used for equivalent As removal (Frey et al. 1998). Arsenic removal for both coagulation methods is sensitive to solution pH (Chwirka et al. 2004). Ferric coagulants typically achieve better As(III) removal (20–80%) than do aluminum coagulants (<20%) (Hering et al. 1996; Hering et al. 1997; Meng et al. 2000).

Activated alumina (AA), a mixture of amorphous and crystalline phase aluminum oxide, removes As(V) by adsorption but has little effect on As(III) (Chwirka et al. 2000). In contrast, granular ferric hydroxide (GFH) and other iron-based, disposable media adsorb both As(III) and As(V) onto poorly crystallized iron oxyhydroxides. Both technologies are pH sensitive: AA operates optimally below pH 6 whereas GFH adsorbs most effectively below pH 8. High phosphate and silica concentrations also decrease efficiency of As removal by GFH.

Ion exchange (IE) uses polystyrene resins to exchange anions in the source water for other, less undesirable anions (typically chloride). HAsO_4^{2-} is removed strongly and H_2AsO_4^- less so, but As(III), present in most waters as H_3AsO_3 , is not exchanged

(Chwirka et al. 2000). The process is not highly sensitive to pH, but sulfate causes significant interference (Kim et al. 2003).

Lime softening (LS) involves adding lime (Ca(OH)_2 or CaO) to precipitate CaCO_3 and Mg(OH)_2 . Below pH 10.5, when only CaCO_3 has precipitated, As removal can be less than 10%, but above pH 10.5 removal of As(V) is generally greater than 90% (US EPA 2000). LS is unlikely to be of great utility in small systems due to large residuals production (residuals handling and disposal contribute 85% of total treatment costs (Frey et al. 1998)) and pH adjustments required after treatment.

Reverse osmosis (RO) and electrodialysis reversal (EDR) both employ ion exchange membrane technologies to separate dissolved ions from water. RO achieves separation using a pressure gradient, whereas EDR applies an electric potential to drive ions through separation membranes. RO is applied at some small facilities and in point-of-use devices, but EDR is typically used only for brackish water treatment or desalination due to its higher cost (Morin 1994; US EPA 2000).

Oxidation/filtration (O/F), which is primarily used for source waters high in iron and manganese, uses KMnO_4 or Mn-based solid media to oxidize influent solution, followed by precipitation and separation of Fe(III) and Mn(IV) solids. Manganese has little effect on As removal, so iron levels must be sufficiently high for this to serve as an adequate As removal technique.

6.1.2 Need for pre-oxidation

With the exception of GFH, all the technologies discussed above remove As(III) less efficiently than As(V), yet As(III) comprises a third of all As found in U.S.

groundwater (Chen et al. 1999). Therefore, many facilities will require a pre-oxidation step to convert As(III) to As(V). Several oxidation technologies currently in use are appropriate for As(III) oxidation. Both chlorine (added as NaOCl) and permanganate were shown to oxidize more than 95% of 50 $\mu\text{g L}^{-1}$ As(III) in less than one minute when used at 0.48 mg L^{-1} NaOCl and 0.53 mg L^{-1} KMnO₄, even in the presence of up to 2.0 mg L^{-1} Fe(II), 0.2 mg L^{-1} Mn(II), 2.0 mg L^{-1} S(-II), or 6.9 mg L^{-1} total organic carbon (TOC) (Ghurye and Clifford 2001). In water treatment applications, 5 mg L^{-1} Cl(I) is typically used to oxidize organic and inorganic matter that cause offensive tastes or odors, whereas 1.5 mg L^{-1} Cl(I) is sufficient for disinfection. Ozone and MnO₂-based solid media have also been demonstrated to be effective As(III) oxidizers (Ghurye and Clifford 2001).

6.1.3 Current options for pre-oxidation

Chlorination is the dominant oxidant used by small systems in the United States. Depending on their specific size category, 72–82% of small systems use chlorination as a disinfectant with no other treatment, and an additional fraction (7%) employ chlorination prior to sedimentation or filtration. 1–5% of small systems use KMnO₄ as a preoxidant (US EPA 2002a), and use of ozone, chlorine dioxide, and chloramines are negligible in small systems. The latter two reactants are not effective at oxidizing As(III) (Ghurye and Clifford 2001).

Systems using chlorination prior to other treatment are not expected to require changes beyond possible optimization steps to enhance As removal. However, facilities that currently use only chlorination must install both an As(V) removal technology as well as a second point of chlorine addition so that chlorine can perform both as a

preoxidant and as a disinfectant. No additional treatment may occur after the disinfection process.

Facilities using KMnO_4 oxidation usually require no additional As removal because KMnO_4 addition is typically followed by removal of precipitated iron and manganese oxides, and As(V) is removed by adsorption or coprecipitation. However, because of the expense (3–7 times the cost of chlorination) and difficulty of working with KMnO_4 (US EPA 2000; US EPA 2003a), it is unlikely to be used by water distribution systems as a new treatment method unless source waters are also high in iron or manganese. In these cases, oxidation by KMnO_4 causes Fe(III) and Mn(IV) hydroxides to precipitate out, generating fresh sorption sites for As(V) and requiring only filtration of the precipitated solids.

Solid, manganese dioxide-based oxidant systems are also available. These are typically marketed for iron, hydrogen sulfide, and manganese removal, but they also effectively oxidize As(III) (Filox-R media (Ghurye and Clifford 2001)). However, they are commercially available only for smaller water treatment volumes: the largest reactor sizes available treat less than 0.05 MGD (1999; 2003), which is sufficient for serving populations less than 200. Systems serving up to 500 people could operated 2 or 3 of these units in parallel, but at higher volumes such parallel operation would become unmanageable (e.g., a system serving 3300 people would require 13–17 units in parallel operation). In addition, frequent backwashing (daily to once a week) at high flow rates is required, and the presence of interfering reductants under low dissolved oxygen conditions significantly slows As(III) oxidation (Ghurye and Clifford 2001).

6.1.4 As removal for systems with no existing treatment technology

If no treatment technology is currently in place, the specific source water quality and site characteristics must be considered to determine which treatment option is best suited to the system's needs. There is currently only one full-scale treatment plant built specifically for As removal in operation in the United States (Gibbs and Scanlan 1995), but more are expected to come online as the revised As MCL takes effect.

6.2 Costs of Treatment Options

For systems that currently have no form of treatment in place, GFH or other iron-based sorbents may be the best treatment alternative. Twenty year life cycle cost evaluations for GFH and other iron-based sorbents range from \$0.42–\$1.01 kgal⁻¹ depending on the source water quality (Reiber 2001; Chang 2002; Hill 2004; Kommineni 2004; Witter 2004). This is typically 30–50% higher than costs for conventional treatment methods like AA and C/F, but costs are likely to decrease with increased usage. Regardless, it is usually less expensive to install and maintain compared to adding both a pre-oxidation step and a conventional treatment method, particularly if As removal is the only goal of treatment.

In cases where a pre-oxidation step is needed upstream of an already operational As treatment technology such as C/F, AA, or IE, we must consider how costs for chlorination, the dominant choice for pre-oxidation, compare to potential costs for TiO₂ photocatalysis. Since no estimates are available for the latter, UV disinfection is used as a proxy for lamp and electricity costs generated by TiO₂/UV treatment (Table 6.2). It is