

Oxidizing Arsenic III to Arsenic V for Better Removal

On June 22, 2000, the U.S. Environmental Protection Agency (EPA) proposed lowering the maximum contaminant level (MCL) for arsenic from 50 down to 5 micrograms/L (Federal Register, 2000). Their proposal followed the recommendation of the National Academy of Sciences report, which concluded that the current 50 ppb standard was not sufficiently protective of public health, and should be lowered as soon as possible (NAS, 1999). EPA estimated that the proposed 5 ppb standard would provide additional protection for 22.5 million Americans from cancer and other health problems. Because of anticipated objections from both environmentalists and water suppliers, MCLs of 3, 10 and 20 ppb also were being considered for the final MCL, which was announced at 10 ppb in late January. The 10 ppb MCL will affect 10.7 million Americans, and approximately 3,000 community water systems will be subjected to additional treatment for arsenic removal.

III. When examining all these treatment possibilities, it is apparent that As III, when present, must be oxidized to As V for efficient removal.

In addition to arsenic concentration and speciation, it is important to know the pH and the concentration of background contaminants in order to design an effective arsenic treatment system. For example, high sulfate concentration negatively affects the ion exchange process while silica, phosphate and fluoride lower the arsenic capacity of activated alumina and iron-oxide-based adsorbents.

POU/POE Devices for Arsenic Removal

According to the 1996 amendments to the Safe Drinking Water Act, point-of-use/point-of-entry (POU/POE) systems may be used for MCL compliance providing that the systems are under the control of the water utility either directly or by contract. Although anion exchange cartridges, pour-through devices and

Clifford, 2000) examined the effectiveness of seven oxidants for converting As III to As V. These were chlorine, permanganate, ozone, chlorine dioxide, monochloramine, ultraviolet (UV) irradiation and Filox, a manganese-oxide-based solid media. The chemical oxidants were dosed at three- and 10-times the required stoichiometric amount based on the As III to As V conversion. This study, which used initial As III concentrations in the range of 50 to 1,000 ppb, also examined the influence of pH in the range of 6.3 to 8.3 and the potential influence of reducing contaminants such as Fe II, Mn II and sulfide. The following is a summary of the results.

- **Chlorine** successfully oxidized As III to As V under all the conditions tested. Iron (0.3 and 3 mg/L) and manganese (0.2 mg/L) had little, if any, effect on As III oxidation. Although sulfide (1.0 and 2.0 mg/L) slowed As III oxidation by chlorine, complete oxidation still was obtained in less than one minute.
- **Permanganate** was as successful as chlorine in oxidizing As III to As V under all the conditions tested. In fact, it was as fast as chlorine in the absence of any interfering reductants and slightly faster than chlorine when reductants were present.
- **Ozone** was extremely effective at As III oxidation; complete oxidation was achieved in less than 15 seconds. No adverse effect was observed in the presence of either dissolved manganese or dissolved iron, but sulfide slowed As III oxidation considerably.
- **Surprisingly, chlorine dioxide** was not effective for As III oxidation. A three-fold stoichiometric dose of chlorine dioxide produced only 20 to 30 percent oxidation in 21 seconds and none thereafter. Even a 100-times stoichiometric dose produced only 76 percent oxidation in five minutes.
- **Preformed monochloramine** was ineffective as an oxidant for As III, confirming the findings from earlier research.
- **Filox solid media** was effective for As III oxidation under most of the conditions tested. In the absence of interfering reductants, greater than 95 percent oxidation was achieved in both low (0.1 mg/L)- and high (8.2 mg/L)- dissolved-oxygen (DO) waters at

empty-bed contact times as short as 0.75 min. As III oxidation by Filox was slowed considerably in the presence of all the interfering reductants tested in low-DO water at a contact time of 1.5 min. with sulfide exhibiting the greatest effect. The effects of interfering reductants were eliminated either by increasing the contact time to six min. or increasing the DO to 8.2 mg/L.

- **UV irradiation** alone was not effective for As III oxidation unless an extremely high UV dose (7,000 times the UV dose required for *E. Coli* inactivation) was used. Even with such a high UV dose, only 73 percent As III oxidation was observed. The presence of sulfite, however, provided for the rapid and quantitative oxidation of As III.

Summary

The new arsenic MCL will require the addition of arsenic treatment technologies to many community water supplies. All the currently known technologies suitable for POU, POE and small community treatment systems do a far better job of removing As V compared with As III, which is the natural form of arsenic in many water supplies. Oxidation of As III to As V can be achieved readily by chlorine, permanganate, ozone and manganese-oxide-based solid media. Chlorine dioxide, UV and monochloramine showed little, if any, effectiveness for As III oxidation. All the oxidation processes can be negatively affected by the presence of reductants such as Fe II, Mn II and sulfide.

About the Authors

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Arsenic Speciation, Treatment

Arsenic contamination primarily is a groundwater problem although some surface waters also are affected. In groundwaters, only inorganic arsenic species in the form of arsenite (As III) and arsenate (As V) are significant. At pH 6.5 to 8.5, As III is present as unchanged arsenous acid, H_3AsO_3 , under reducing conditions, whereas As V is present in the form of singly and doubly charged $H_2AsO_4^-$ and $HAsO_4^{2-}$ anions in oxidizing waters. Thus, processes that remove anions (e.g., anion exchange and activated alumina adsorption) are suitable for removing As V but not As III. Other small system processes that are suitable for removing As V anions are iron coagulation followed by multimedia filtration or microfiltration. Iron-oxide-based adsorbents such as granular ferric hydroxide (GFH) and iron-doped filtration as well as adsorption media also are effective. Reverse osmosis does a better job of removing As V compared with As III, and electro dialysis will remove As V but will not remove any As

distillation units are capable of effective arsenic removal, they are as of now not considered as acceptable, centrally managed POU/POE options for compliance with the arsenic MCL. The EPA has listed only POU reverse osmosis, POU activated alumina and POE activated alumina as best available treatment (BAT) technologies. Additional technologies may be considered as BAT when more data are accumulated on their performance.

Potential Oxidants for As III in Water

It often has been observed during field determination of arsenic species that As III converts to As V during sampling and storage, thus it is reasonable to consider aeration for arsenite oxidation. However, aeration, which is effective for iron II oxidation in groundwaters, was shown to be ineffective for As III oxidation during a field study at three locations in the United States (Lowry, 2000).

A recently completed study at the University of Houston (Ghurye and

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