

Dynamic Adsorbents

Alumina and the Removal of Arsenic

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Arsenic cleanup is a major environmental goal. This metal is the 20th most abundant element of the earth's crust and finds its way into the soil and into the water supply all around us. There is no good reason for having arsenic absorbed by our bodies – it is toxic.

Removal of arsenic from our environment is essential for good health. Health effects are dose related and for this reason standards for acceptable exposure continue to be lowered. The goal will be the eventual removal of any detectable arsenic from the water supply.

The WHO guideline Value for arsenic in drinking water was lowered from 50 to 10 ug/Liter in 1993 and this level is enforced in the United States by the Environmental Protection Agency.

All forms of arsenic need to be removed from the water supply. Advanced water purification techniques include membrane systems, coagulation flocculation and other high technology solutions. No company does as good a job at removing arsenic as the new technology being developed by Dynamic Adsorbents. No one is able to remove all forms of arsenic in a simple single process such as the design being evaluated for commercial release like Dynamic Adsorbents. There is no simpler, more affordable and heavy duty product available on the market today.

Essentials of the Chemistry of Arsenic

A review of the chemistry of arsenic is in order.

Arsenic occurs in groundwater in two forms:

Arsenite (AsO₃³⁻)

Arsenate (AsO₄³⁻)

These two types of natural compounds leached from the earth's crust are referred to as arsenic (III) and arsenic (V) species due to the oxidation number of the central arsenic atom.

Each ion can acquire from water one or more protons, depending on the acidity of the water. They then exist as a set of chemical species:

Arsenic III series AsO₃³⁻- HAsO₃²⁻- H₂AsO₃⁻- H₃AsO₃

Arsenic V series AsO₄³⁻- HAsO₄²⁻- H₂AsO₄⁻- H₃AsO₄

At the acidity of drinking water, the dominant arsenic III species is found primarily as the neutral compound H₃AsO₃. The dominant arsenic V species are the ions HAsO₄²⁻ and H₂AsO₄⁻. However, for both the arsenic III and V species there is coexistence and rapid conversion to all of the above forms in this chemical set.

Arsenic III compounds are 10 times more toxic to the human body than Arsenic V forms. The proportion of arsenic in ground water typically ranges between 50 and 90%.

What are the commercially available technologies for the removal of arsenic from the water supply?

Oxidation reduction

This technology takes advantage of reactions that reduce (add electrons to) or oxidize (remove electrons from) chemicals, altering their chemical form. These reactions do not remove arsenic from solution, but are often used to optimize other processes utilized for the removal of arsenic from water.

Arsenic removal technologies are most effective at removing arsenic V, since arsenic III is non-charged below pH 9.2. For this reason most treatment solutions provide an oxidation step to convert arsenite to arsenate. Oxidation alone does not remove arsenic from solution, and must be coupled with other removal processes such as coagulation, adsorption or ion exchange. Commercially used oxidizing agents include gaseous chlorine, hypochlorite, ozone, potassium permanganate and hydrogen peroxide.

Precipitation

This causes dissolved arsenic to form a low solubility solid mineral such as calcium arsenate. The solid calcium arsenate can then be removed through sedimentation and filtration. When coagulants are added and form flocs, other dissolved compounds such as arsenic can become insoluble and form solids. This is known as co-precipitation. The solids formed may remain suspended, or may require removal through solid/liquid separation processes, typically coagulation and filtration.

However, coagulation is unable to lower the arsenic level to the acceptable low safety range of 10 ug/Liter. Two of the most commonly used precipitating agents are ferric chloride (FeCl_3) and alum or aluminum potassium sulfate. Ferric chloride removes around 80% of arsenic from water while alum removes 85-92%.

Adsorption and ion exchange

Various solid materials including iron and aluminum hydroxide flocs have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to sorption sites on the surfaces of these solids and effectively removed from solution. The finding that activated alumina removes arsenic from water was discovered accidentally by Bellack in 1971. The high surface area and large number of sorption sites makes activated alumina a superior adsorption agent.

The mechanism of arsenic removal is similar to that of a weak base ion exchange resin. Arsenate removal capacity is best in the narrow pH range of 5.5 to 6.0, where the alumina surfaces are protonated. Typically activated alumina has a point of zero charge (PZC) below which the surface is positively charged, and above which the surface bears a negative charge at pH 8.2 Arsenic removal capacity drops sharply as the PZC is approached and above pH 8.5 it is reduced to only 2-5% of capacity at optimal pH. For neutral and basic waters therefore pH adjustment may be necessary for effective arsenic removal.

Activated alumina also removes selenite, fluoride, sulfate and chromate which may be other undesired contaminants in the water supply.

Ion Exchange

This is a special form of adsorption involving the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Ion exchange resins are based on a cross linked polymer skeleton, called the matrix. Most commonly, this matrix is composed of polystyrene cross-linked with divinylbenzene. Charged functional groups are attached to the matrix through co-valent bonding.

What are the types of functional groups which can be attached to the polystyrene?

1. strongly acidic groups, such as sulfonate
2. weakly acidic groups, such as carboxylate
3. strongly basic groups, such as quaternary amines
4. weakly basic groups, such as tertiary amines Other forms of adsorption involves stronger bonds and are less easily reversed

Various strong base anion exchange resins are commercially available which can effectively remove arsenate from solution. Arsenite, being uncharged is not removed. Therefore, unless arsenic is present exclusively as arsenate, an oxidation step becomes a necessary precursor to arsenic removal

Role of Alumina in Arsenic Removal

During coagulation and filtration using alumina as the metal salt arsenic is removed through three main mechanisms:

1. precipitation – the formation of the insoluble compound $Al(AsO_4)$
2. co-precipitation – the incorporation of soluble arsenic species into a growing metal hydroxide phase
3. adsorption – the electrostatic binding of soluble arsenic to the external surfaces of the insoluble metal hydroxide.

All three of these mechanisms can independently contribute towards arsenic removal from source water.

Physical Exclusion

Selectively permeable synthetic membranes are commercially available allowing certain dissolved compounds to go through the membrane while excluding other compounds.. These membranes can act as a molecular filter to remove dissolved arsenic, along with many other dissolved in particulate compounds. Two classes of membrane filtration are low pressure membranes such as microfiltration and ultrafiltration and high pressure membranes such as nanofiltration and reverse osmosis. Low pressure membranes operate at 10-30 psi and have large pore sizes, while higher pressure systems run at 75 to more than 250 psi and have

smaller pore sizes with tighter membranes. Arsenic removal is independent of pH and the presence of other solutes in the source water.

What about the use of metal ions to trap arsenic?

Iron, copper, manganese, aluminum, calcium and magnesium as metal ions have been used in an attempt to trap and remove arsenic species from drinking water as their insoluble salts.

The problem is that metal salts of arsenic III and arsenic V have widely different solubilities

Arsenic V salts are less soluble than arsenic III salts – however, recall that it is the arsenic III compounds which are the more dangerous

Calcium ions and hydrogen carbonate ions are abundant in well water. When well water is exposed to air carbon dioxide is lost and calcium carbonate precipitates. Iron II ions are oxidized by oxygen forming iron III hydroxide which precipitates with calcium carbonate. Large amounts of aqueous arsenic species are adsorbed by iron III hydroxide/calcium carbonate mixtures as they precipitate. In this setting half of the arsenic III and nearly all the arsenic V are removed.

Iron and manganese can result in significant arsenic removal through coprecipitation and sorption onto ferric or manganic hydroxides. The mechanism is the same as coagulation and filtration.

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