

pH Adjustment for As Removal Systems

Simple, Value-Adding Processes for Adsorption Media



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Introduction

Arsenic removal from drinking water by adsorptive media has been a proven technology for years. In the western and southwestern United States, however, much of the As-tainted groundwater has a pH value which is high enough to significantly reduce the operating capacity of adsorptive media including the iron, alumina, and titanium-based media commercially available to municipalities. To lower the treatment cost for these higher pH waters, pH adjustment has been successfully employed to increase the capacities of all of these media. pH adjustment involves the use of an acid (an inorganic acid such as sulfuric or hydrochloric) or even gases such as carbon dioxide to depress the pH to a suitable treatment range of 6 – 7. While typically associated with larger flow rates from centralized water treatment plants, pH adjustment has also been adapted to lower flow rates from individual wells or even small community water supplies with flow rates of 50 gpm and lower. The pH adjustment systems are fully automated and require little operator maintenance or supervision.

Background

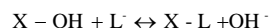
On January 22, 2001, the Environmental Protection Agency (EPA) adopted a new standard for arsenic in drinking water at 10 parts per billion (ppb) from its previous standard of 50 ppb. The revision will provide additional protection for 13 million Americans who are currently drinking water with arsenic levels greater than 10 ppb against cancer and other health problems including cardiovascular disease and diabetes, as well as neurological effects.¹ The previous standard of 50 ppb was set by the EPA in 1975 based on a Public Health Service standard originally established in 1942. The new standard, requiring compliance by public water systems beginning on January 23, 2006, will finally elevate the federal standard to that of other developed countries. In 1993, the World Health Organization (WHO) set 10 ppb as the recommended limit for arsenic in drinking water while the 15-nation European Union, confirming the science behind the WHO limit, also adopted 10 ppb as its mandatory standard for arsenic in drinking water in 1998.²

Arsenic is a common, naturally-occurring drinking water contaminant that originates from arsenic-containing rocks, minerals, and ores, and is transported to natural waters through weathering, erosion, and dissolution. While occurring in both the inorganic and organic forms, arsenic is predominantly inorganic in natural waters and is the most likely form of arsenic at concentrations that cause regulatory concern.³ Predominately found in groundwater as opposed to surface water, arsenic exists in drinking water in two primary valence forms: arsenate (As^{5+}) and arsenite (As^{3+}). The relative concentrations of each depend primarily on the geology of the surrounding rock formations and the water chemistry at each

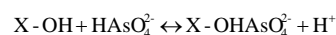
individual site. Within the two valence forms, arsenic exists in four different species for each valence state. Arsenite can exist as H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} , and AsO_3^{3-} and arsenate as H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} . The overall negative charges on the arsenic species is the inherent property that allows its removal from drinking water using adsorption, ion exchange, or co-precipitative processes.

Arsenic Adsorption on Media

The negative charge of arsenic species allows for its removal via adsorptive processes. The two predominant "sorption" processes which bind the arsenic ions to an adsorbent are ligand exchange and surface complexation, also known as inner-sphere complex formation. With the ligand exchange, the hydroxide groups on the surface of the adsorbent are replaced with the arsenic species as shown below:



With inner-sphere complex formation, the arsenic species are selectively bound to the oxide surface through the formation of inner-sphere complexes in which one or two of the arsenate's oxygen atoms bond to surface of the adsorbent as shown below:



The two attractive forces binding the arsenic to the adsorbents surface during inner-sphere complex formation are coulombic bonding and a Lewis Acid-Base attraction.

Both adsorption processes are influenced by several fundamental properties of the untreated water – most notably the pH of the water and the level of competing ligands such as hydroxide (hence the pH dependence), silica, phosphate, vanadium, and selenium. With the concentration of arsenic in the part per billion range, these competing ligands, often present in the groundwater at part per million levels, can significantly lower the arsenic capacity of any media. pH adjustment can therefore be utilized to suppress the presence of the ligand with the highest selectivity – OH^- . For most commercially-available adsorptive media, the optimal pH is < 7.5 and preferably a pH of 7 for optimal arsenic capacity.

Breakthrough column testing results (see Figure 1) completed on NSF-53 challenge water shows the dramatic impact of pH on both an activated alumina and iron-based adsorptive media. At a contact time of 1.5 minutes, the capacity of the adsorptive medias all show a dramatic increase in capacity with decreasing pH. For the iron-based media #1, the ~7,500 BV capacity at pH 8.5 increases by 100% to 15,000 by decreasing the pH to 7.5 – 7.6. A similar decrease in pH increases the modified alumina capacity by over 300%. This capacity increase is directly related to the operating cost per the following table (see Table 1).

¹ Fact Sheet: Drinking Water Standard for Arsenic, EPA 815-F-00-015, January 2001.

² Council of the European Union, "Council Directive 98/83/EC of November 1998 on the quality of water intended for human consumption," OFFICIAL JOURNAL OF THE EUROPEAN COMMUNITIES May 12, 1998, pgs. L330/32-L330/52.

³ Edwards, M., S. Patel, L. McNeil, H. Chen, M. Frey, A. D. Eaton, R. C. Antweiler, and H. E. Taylor, 1988. "Considerations in As Analysis and Speciation." J. AWWA (March): 103-113.

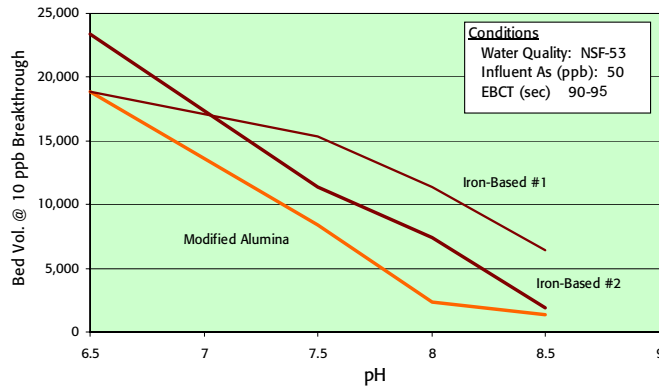
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Figure 1

pH Effect On Adsorptive Media Arsenic Capacity

Modified Alumina and Iron-Based Media. Bed Volumes @ 10 ppb



To translate the adsorptive media capacities into an operating cost, an all-inclusive (media, changeout, and disposal) costing of \$100/cu. ft. and \$170/cu. ft. for the activated alumina and

iron-based medias, respectively, for large commercial-scale systems was used. Additionally, large scale systems operate at longer contact times (typically 3 – 4 minute EBCT) and a ratio factor between the laboratory and commercial EBCT (3 minutes / 90 seconds = 2) was used to determine the capacity at full-scale operating conditions. Per Table 1, the operating costs can be effectively reduced from \$1.52/1,000 gallons to \$0.47 /1,000 gallons for the best performing iron-based media and from \$2.67/1,000 gallons to \$0.35/1,000 gallons, respectively, based on ANSI NSF-53 water quality at an inlet arsenic V concentration of 50 ppb and a pH change from 8.5 to 6.5.

pH Adjustment – Equipment and Controls

pH adjustment is a simple unit operation that can utilize a standard acid such as sulfuric or hydrochloric or a more benign option, carbon dioxide gas. As shown in Figure 2, the acid is typically stored in plastic tanks and added / injected into the raw water line, typically prior to a static mixer. The static mixer provides turbulence to ensure that the acid is fully dispersed into the raw water. Next, a pH probe measures the pH of the adjusted water to ensure that the adsorption system will be operated at the appropriate pH.

Figure 2

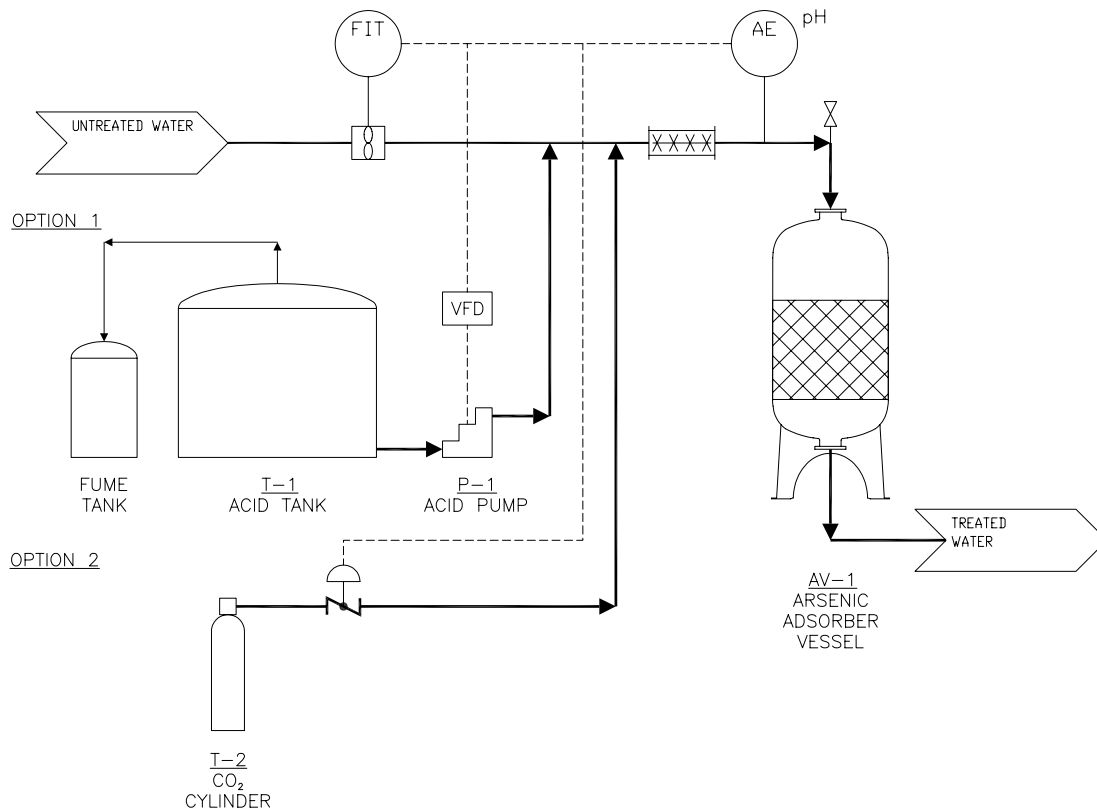


Table 1
Adsorptive Media Operating Costs

Media	pH	Capacity at 95 sec. EBCT (BV)	Est. Capacity at 3-4 min. EBCT	Media Pricing (\$/ft ³)	Operating Cost (\$/1,000 gal)
Iron Based #1	8.5	7,500	15,000	170	1.52
	7.5	17,000	34,000	170	0.67
	6.5	24,000	48,000	170	0.47
Iron Based #2	8.5	3,000	6,000	170	3.79
	7.5	12,500	25,000	170	0.91
	6.5	19,000	38,000	170	0.60
Modified Alumina	8.5	2,500	5,000	100	2.67
	7.5	8,000	16,000	100	0.84
	6.5	19,000	38,000	100	0.35

pH Adjustment Costing

The costs for pH adjustment are primarily based on the acid consumption and are laid out in detail in the referenced EPA document⁴. While the most accurate method for determining acid consumption is acid titration, a straightforward calculation can suffice when a raw water analysis is available and raw water samples are not. This method requires the pH, the total alkalinity (M as mg/L CaCO₃), and/or the free carbon dioxide (CO₂ as mg/L). In the following example, sulfuric acid was used to decrease the pH of a sample groundwater from 8.1 to 7. An acid cost of \$0.10/lb was used which includes the acid and its storage and feed systems which can be serviced by companies such as Basic Chemical Solutions, LLC. In a trial-and-error iteration, a 25 mg/L reduction in the bicarbonate level to 125 mg/L as CaCO₃ and its associated increase in free CO₂ to 24 mg/L will yield a pH 7 water with 125 mg/L bicarbonate and 24 mg/L of free CO₂.

Figure 3

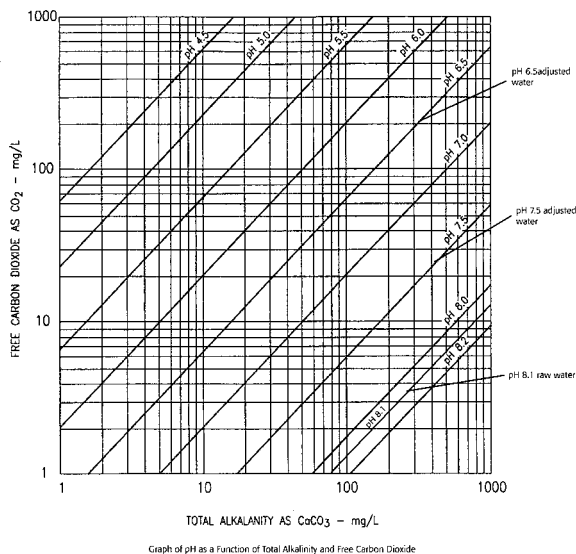


Table 2
pH Adjustment Costing

pH	8.1
Bicarbonate	150 mg/L as CaCO ₃
Free CO ₂	2 mg/L
Bicarbonate Reduction	65 mg/L as CaCO ₃
New Bicarbonate	85 mg/L as CaCO ₃
New Free CO ₂	59.2 mg/L
Adjusted pH	6.5
Requirement	1.30 meq/L
	0.0049 eq/gal
Sulfuric Acid	\$ 200/ton
	\$ 0.10/lb
Treatment Cost	\$ 0.052/1,000 gallons

As an example, a pH adjustment from pH 8.1 to 7.5, 7, or 6.5 requires a reduction in bicarbonate of 7, 25, and 65 mg/L as CaCO₃, respectively. This reduction is achieved via the acid addition at an incremental increase in operating cost of <\$0.01/1,000 gallons, \$0.02/1,000 gallons, and \$0.05/1,000, respectively.

Per Table 3, titled Adsorptive Media Operating Cost, the cost of arsenic treatment can be dramatically reduced via this pH reduction. Adding in the loaded acid costs outlined above, an arsenic treatment cost ranging from \$1.50 - \$4.00/1,000 gallon can be substantially reduced to \$0.40 - 0.70/1,000 gallon.

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Table 3
Adsorptive Media Operating Costs

Media	pH	Operating Cost (\$/1000 gal)	pH Adj. Cost (\$/1000 gal)	Total Op. Cost(\$/1000 gal)
Iron Based #1	8.5	1.52		
	7.5	0.67	0.02	0.69
	6.5	0.47	0.05	0.52
Iron Based #2	8.5	3.79		
	7.5	0.91	0.02	0.93
	6.5	0.60	0.05	0.65
Modified Alumina	8.5	2.67		
	7.5	0.84	0.02	0.86
	6.5	0.35	0.05	0.40

Implemented Technology

The Environmental Protection Agency (EPA) is currently sponsoring two rounds of demonstration projects to develop more cost-effective technologies for arsenic removal in addition to providing technical assistance and training to operators of small systems to reduce their compliance costs. The specific sites in the two rounds of demonstration projects were chosen to provide a cross-section of water qualities from several different states - of the 12 Round 1 sites, 9 states are represented and of the 29 Round 2 sites, 17 states are represented.

The projects were "bid" upon by solution providers who provided the capital and operating costs associated with their particular systems. This process, in effect, showcases the most cost-effective technologies and allows the bid selection panel to evaluate each technology on a site-by-site basis. As can be seen on Table 4, arsenic removal by adsorption was the dominant technology in both rounds of demonstration. In addition, pH adjustment was utilized in the bulk of these "small system" projects that had flow rates greater than that associated with a point-of-use application.

Table 4

	Total Projects Funded	Adsorption-Based Technology	pH > 7.5 & Flow > 5 gpm	pH Adjusted
Round 1	12	9	5	4
Round 2	29	13	8	4

Water Quality Considerations

pH adjustment of water does have the potential for negative affects on water quality if not performed properly. The most noticeable effect could be the formation of "red" water. "Red" water is commonly associated with the dissolution of previously formed scaling on the inner surface of water pipe.

By calculating the Langelier Saturation Index (LSI) of both the raw water and pH-adjusted water, one can determine the potential for "red" water. The LSI is a simple prediction of the tendency of water to precipitate, dissolve, or be in equilibrium with calcium carbonate. Expressed as the difference between the actual pH and the saturation pH, the LSI can be positive (scale can form), negative (scale will dissolve), or zero (borderline scale potential).

From the example above for NSF-53 Challenge Water, the LSI for the pH 8.1 water is 0.234. Adjusting the pH of the water to 7.5 results in an LSI of -0.943. In this example, the water shifted from "borderline scale potential" to "scale-dissolving". The water could, therefore, potentially dissolve the existing deposits on the interior of any piping and fitting and could potentially lead to an unacceptable water quality at the tap. While the addition of water stabilizers such as poly- or ortho-phosphates can remedy this problem, awareness of this potential will help minimize its impact on the end consumer.

Conclusions

pH adjustment is a fully implementable technology to substantially lower the cost of arsenic treatment. Operating costs for compliance to the EPA's 2001 National Primary Drinking Water Regulation for Arsenic can be dramatically lowered for all adsorption-based medias by using pH adjustment. pH adjustment allows all medias to operate under conditions that boost their operating capacities and therefore, lower the total operating costs for arsenic removal. Based on the individual water quality, the lowest treatment cost technology can quickly switch from one media to another and municipalities and engineering firms should thoroughly evaluate these factors prior to recommending an arsenic treatment technology. The pH adjustment technology can be applied to large-, medium- and small-scale treatment facilities with a minimum amount of effort from the operation and maintenance workforce.



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