Regeneration of iron-based adsorptive media used for removing arsenic from groundwater

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ABSTRACT

Adsorptive media technology is regarded as a simple, low cost method of removing arsenic from drinking water particularly for small systems. Currently, when the effluent of a treatment system reaches the USEPA maximum contaminant level (MCL) of 10 ug/L, the exhausted media is removed and replaced by new virgin media. Although the commonly used iron-based media products are reasonable in price, the replacement cost accounts for around 80% of the systems total operational costs. One option to media replacement is on-site regeneration and reuse of the exhausted media. To determine whether an iron based media can be successfully regenerated and reused, laboratory batch and column regeneration tests were conducted on six exhausted iron-based media products obtained from six full scale arsenic removal treatment systems. Batch tests conducted on three of the media products to evaluate the effectiveness of 1–6% caustic regenerant solutions found that arsenic desorption increased until around 4%. Using 4% caustic solutions, the columns tests on the six exhausted media products showed arsenic removals ranged from 25 to 90% with the best results obtained with the Severn Trent E33 media. Exposing the media to caustic (pH ≥ 13) and acid (pH ≤ 2) solutions found minimal media loss with the caustic solution, but significant media dissolution with a pH 2 acid solution. A six column pilot plant test at an Ohio test site with the lab regenerated media products found that the regenerated media could achieve arsenic removals somewhat similar to virgin media.

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1. Introduction

1.1. Adsorptive media process

A variety of treatment technologies exist for removing arsenic from drinking water. Commonly used techniques are (1) chemical coagulation/filtration (C/F) using aluminum or iron coagulants; (2) precipitation on oxidized naturally occurring iron; (3) adsorption (AM) onto solid media; (4) anion exchange (AE) and (5) reverse osmosis (RO). A review of these technologies have been made by a number of authors (Amy et al., 2000; Chen et al., 1999, 2002; Choong et al., 2007; Chowdhury et al., 2002; Cundy et al., 2008; Giles et al., 2011; Jain and Singh, 2012; Jekel, 1994; Kartinen and Martin, 1995; Mohan and Pittman, 2007; Mondal et al., 2013; Sorg and Logsdon, 1978; USEPA, 2003; Wang et al., 2002).

The AM technology is a simple, fixed bed process where arsenic and other anions are adsorbed onto a packed bed of media. The arsenic removal mechanism of the adsorptive media process is usually an exchange of anions, such as arsenic, for surface hydroxides of the media. The exchange process is generally called sorption or adsorption, although ligand exchange is a more appropriate term for the highly specific surface reactions involved (Clifford et al., 2011). When the arsenic concentration of the effluent from an adsorption system reaches the regulatory limit of 10 μg/L, the media is commonly replaced with new media. The simplicity and the relatively low capital cost of the technology have resulted in AM being utilized by many drinking water systems for removing arsenic, particularly small systems (Chen et al., 1999; Chang et al., 2005, 2005 Giles et al., 2011; Jain and Singh, 2012; Jeong et al., 2007b; Möller et al., 2011; Rubel Jr., 2003a; Wang et al., 2002; Wang and Chen, 2011; Xie et al., 2007; Zeng et al., 2008).

During the past several decades, a substantial amount of research has been conducted on a wide variety of adsorbent materials, both naturally occurring and commercially produced, for the removal of arsenic from drinking water sources (Amy et al., 2005; Choong et al., 2007; Daus et al., 2004; Dixit and Hering, 2003; Kolbe et al., 2011; Melitas et al., 2002.; Mohan and Pittman, 2007; Giles et al., 2011; Mahler and Person, 2013; Mamindy-Pajany et al., 2011; Aredes at el., 2012; Yadanaparthi et al., 2009; Youngran et al., 2007; Xie et al., 2007; Zeng et al., 2008; Westerhoff, 2006). The majority of the commercially available adsorbents are metal oxide/hydroxides that include iron, aluminum, zirconium and titanium (Amy et al., 2005; Chang et al., 2004; Choong et al., 2007; Bang et al., 2005; Jain and Singh, 2012; Lakshmanan et al., 2008; Rubel Jr., 2003a, 2003b). Of the commercially available adsorbents, iron and aluminum-based materials have received the most attention and evaluation for their effectiveness in removing arsenic from drinking water. And of the two metals, the iron-based adsorbents generally have been found to have the higher arsenic adsorptive capacity and efficiency (Amy et al., 2005; Chang et al., 2004; Jain and Singh, 2012; Jekel, 1994; Jeong et al., 2007a; 2007b).

Activated alumina (AA), an aluminum oxide/hydroxide media, has a relatively long history for removing arsenic from water (Bellack, 1971; Fox and Sorg, 1987; Fox, 1989; Ghosh and Gupta, 2012; Hathway and Rubel, 1987; Jain and Singh, 2012; Jekel, 1994; Rosenblum and Clifford, 1984; Rubel and Williams, 1980; Rubel Jr, 2003a; Singh et al., 2001; Stewart and Kessler, 1991; Wang et al., 2002; Lin and Wu, 2001). Because of its historical application, AA adsorption was listed by the US Environmental Protection Agency (USEPA) as a best available technology (BAT) when the USEPA revised its maximum contaminant level (MCL) for arsenic from 50 μg/L to 10 μg/L in 2001 (USEPA, 2001, 2003). None of the newer, granular iron media products were listed as BAT because they had been available and used in drinking water treatment for only a few years and thus lacked sufficient full scale system performance information required by the USEPA for them to be listed (USEPA, 2003).

Several iron media products have been introduced in the drinking water treatment market during the past 10–15 years (Choong, 2007; Clifford et al., 2011; Mohan and Pittman,

2007; Rubel Jr., 2003a; Wang and Chen, 2011). Two of the more commonly used products are granular ferric hydroxide, GFH®ʼ (GFH) and granular ferric oxide Bayoxide® E33 (E33) (Amy et al., 2005; Badruzzaman et al., 2004: Choong et al., 2007; Nguyen et al., 2011; Sperlich et al., 2005; Sperlich et al., 2008; Thirunavukkarasu. et al., 2003; Wang and Chen, 2011). GFH is produced by GEH Wasserchemie GmbH 7 Co. in Germany and has been commercially available since 1997 (Driehaus et al., 1998; Driehaus, 2002). E33, a ferric oxyhydroxide media, was developed and produced by Bayer AG in Germany in 2000 in partnership with Severn Trent Water, Fort Washington, PA (Amy et al., 2005; Choong et al., 2007; Rubel Jr, 2003a; Wang et al., 2005).

1.2.   Adsorptive media operational cost

When adsorptive media no longer has the ability to reduce the arsenic to less than the MCL, the common practice is to remove and replace the exhausted media with new virgin media. The exhausted media, that normally passes the federal toxicity characteristic leach procedure (TCLP) (USEPA, 1992), can be disposed in a sanitary landfill (Chen et al., 1999; Cornwell and Roth, 2011; Clifford et al., 2011; MacPhee et al., 2001). In California, a waste extraction test (WET) (California Code of Regulations (1985)) is required for media disposal. Frequently, the exhausted media products will failed the California WET even though they passed the federal TCLP test (Jing et al., 2005). When an exhausted media fails the WET procedure, the State of California requires that the media be disposed at a California hazardous waste designated landfill.

The operation and maintenance (O/M) cost elements of the adsorptive media process include media replacement, chemicals, electricity, and labor (Wang and Chen, 2011). In the USEPA Arsenic Demonstration Program (ADP), where capital and operating costs were collected on 15 AM systems having to undergo media replacement, the cost of media replacement (that included exhausted media disposal) averaged around 80% of the total O/M cost (Wang and Chen, 2011). In only two cases was the media replacement cost less than 50% of the total O/M cost. Some systems had to replace the media within only a few months resulting in an O/M cost as high as $20 per 1000 gal of treated water (Wang and Chen, 2011).

1.3.   Options for adsorptive media cost reduction

The cost of media replacement is a function of the cost of the media and the life of the media. Two options to reduce the O/M cost is (1) to replace the existing media with a lower cost media having the same bed life or (2) to replace the media with one of high performance (longer bed life). The ideal situation is the combination of both options: replace the media with one of lower cost and higher performance. A third option that is rarely considered is on-site regeneration and reuse of the adsorptive media.

Conventional anion exchange resins, that have low arsenic removal capacities, must be regenerated (with salt) to be a competitive arsenic removal technology (Clifford et al., 2011; Rubel Jr., 2003b). Because the AE requires frequent regeneration (1–3 days), produces a large quantity of brine waste and is more costly than AM, AE has generally been limited to treating

waters that contain arsenic and a co-contaminant such as, nitrate and/or uranium (Rubel, 2003b; Wang and Chen, 2011). Most adsorptive media products, however, are not marketed as being regenerable with the notable exception being the modified (iron) resin products (Möller et al., 2011; Sylvester et al., 2007). Although these modified resins are capable of being regenerated, the authors are not aware of any systems regenerating the exhausted resins on-site. Regeneration of this media generally requires both a caustic solution (4%) and salt solution (2%) (Möller et al., 2011: SenGupta and Cumbal, 2005).

Activated alumina (AA) media has a long history of being regenerated when used for fluoride removal because of a short bed life (400–600 bed volumes). Regeneration studies have been conducted on exhausted AA used for the removal of phosphate, dissolved organic matter and arsenic (Chen et al., 1989; Clifford et al., 2011; Hathway and Rubel, 1987; Ghosh and Gupta, 2012; Rubel Jr, 1984; Rubel Jr. and Williams, 1980; Wang et al., 2002). Pilot studies conducted on the regeneration of AA used for simultaneous fluoride and arsenic removal have found that fluoride regeneration require a 1% caustic (NaOH) solution whereas 4% is required to strip the arsenic from the AA (Hathway and Rubel, 1987; Rubel, 1984). Gosh and Gupta (2012) also reported that a 2% caustic solution is effective for the regeneration of exhausted AA used in very small arsenic removal systems in West Bengal.

1.4. Regeneration of granular iron media

Although a few studies have been conducted on the desorption of arsenic from various iron minerals (Jessen et al., 2005; Mamindy-Pajany et al., 2011; Roy et al., 2013), studies on the iron-based commercially available adsorbents have focused almost entirely on their arsenic loading capacities and the impact of competitive anions and not on regeneration (Mohan and Pittman, 2007). Regeneration of iron media is occasionally mentioned by some authors (Giles et al., 2011; Joeng et al., 2007b), but generally dismissed because of the new, inexpensive and easy to manage adsorbents and concerns for the disposal of the liquid regenerant wastewater. Some authors have even suggested that it is not possible to regenerate granular iron-based media because the process will cause particle degradation and, therefore, are only viable for sin-gle–use application (Möller and Sylvester, 2008; Mohan and Pittman, 2007; Sylvester et al., 2007). Similarities between chemistries of AA and the iron-based media products (oxides/hydroxides) suggest, however, that iron-based media can be regenerated. If an iron-based media can be regenerated and reused with little or no loss of arsenic removal capacity and no major particle degradation, regeneration offers a potential option to reduce the cost of the adsorptive media process.

The pH of the point of zero charge (pH_{pzc}) of iron-based media is generally in the 7.5 to 8.5 range with GFH reported as 7.6 to 8.0 and E33 at 8.3 (Amy et al., 2005; Guan et al., 2008). Below the pH_{pzc}, the media would have a positive surface that would attach the negatively charged arsenic anions. Above the $pH_{pzc,}$ the surface is negatively charge that repels the arsenic anion. Increasing the pH of the aqueous solution of an iron-based media should, therefore, result in arsenic being desorbed (regeneration) in the same manner as occurs with AA.

To determine the feasibility of regenerating granular iron-based media with a caustic solution, regeneration studies were conducted at the Battelle Memorial Institute, Columbus, OH on a several exhausted iron-based media products obtained from USEPA ADP sites. These studies, which are likely the first systematic, regeneration studies to be conducted on iron-based media products, consisted of batch tests followed by laboratory and pilot column studies. The overall objective of studies was to determine if select iron-based media could be effectively regenerated and, if so, develop a regeneration procedure suitable for use in the field. Specific objectives included:

- Determine an efficient regenerant (caustic) concentration for iron media regeneration.
- Evaluate the regenerability of the spent iron-based adsorptive media.
- Examine effects of the regeneration process the on structural integrity of regenerated iron media.

2. Methods and materials

2.1. Adsorptive media samples and analyses

The exhausted (arsenic) media samples for all of the laboratory batch and column studies were obtained from four USEPA ADP sites and an USEPA sponsored arsenic pilot study (Battelle) site in Ohio. For the initial batch tests to determine the optimal caustic regeneration solution, the first three media samples obtained were tested, GFH, E33-G and ARM200 (VV). For the second phase column studies, six exhausted media sample were tested: the same three from the batch studies (GFH, E33-G and ARM200(VV)) and E33-P, KemIron (CFH-0818) and a second ARM200 (LVS). A general description of the physical properties for the six media samples are shown in Table 1.

The media analyses to determine the arsenic content of the exhausted media samples were conducted by the Battelle ICP-MS Laboratory (Columbus, OH). The procedure consisted of air drying, concentrated nitric acid digestion and analysis by inductively coupled plasma-mass spectrometry (ICP-MS) of the digested media samples (Battelle, 2004). More specifically, approximately 0.5 g of a media sample was weighed on a Mettler analytical balance (Model AE 160, S/N D85618) and placed into 40-mL fluorocarbon microwave vessel. Acid digestion followed EPA Method 3051 (Microwave assisted Acid Digestion of Sediments, Sludges, and Soils). One method blank was prepared for every 20 samples. Ten mL of concentrated HNO_3 was added into each vessel. The vessel was capped and heated in the microwave unit. After cooling, the vessel contents were filtered, centrifuged or allowed to settle and then diluted to volume (typically 50-mL) with deionized water. Samples were subsequently diluted 1:10 and 1:100 via serial dilutions with 1% HNO_3. These samples were then quantitatively analyzed on an ICP-MS (Perkin Elmer-Sciex Elan 6000) following EPA Method 200.8.

Table 1 – Physical and chemical properties of exhausted adsorptive media samples.

Exhausted media samples – characteristics

Parameter	GFH	KemIron	E33-P	E33-G	ARM200 (VV)	ARM200 (LVS)
Project site	Reno, NV	Reno, NV	Anthony, NM	Rimrock, AZ	Valley Vista, AZ	OH – test site
Media source	Siemens	Kemira Water Solutions	Severn Trent	Severn Trent	Engelhard	Engelhard
Matrix	β-ferric oxyhydroxide and ferric hydroxide	Ferric oxide and ferric hydroxide	Ferric oxyhydroxide α-FeOOH	Ferric oxyhydroxide α-FeOOH	Ferric oxyhydroxide	Ferric oxyhydroxide
Physical form	Granular	Granular	Granular – Pelletized	Granular	Granular	Granular
Color	Dark-brown to black	Brown or reddish-brown	Amber	Amber	Dark-brown	Dark-brown
Bulk density (lb/ft^3)	71.8	74.9	35	28	45–50	45–50
Moisture content (%)	47	16	<15	<15	8	8
Sieve size (mesh)	NA	NA	14 x 18	10 x 35	14 x 40	14 x 40
Iron content (%)	61	44	90.1	90.1	NA	NA
pHpzc	7.6–8.0	NA	8.3	8.3	NA	NA

NA – Not available.

To obtain the dry weight of the sample, moisture content was measured separately following ASTM Method D2216. The analytical results from the wet-weight samples were adjusted using the dry weights of the samples and reported as mg/g or mg/kg of dry weight.

2.2. Chemicals, reagents and sampling materials

Caustic solutions used for regeneration were prepared using NaOH pellets and Milli-Q® purified water. For the studies requiring pH adjustment, Milli-Q® purified water adjusted with hydrochloric acid (HCl) was used.

All water samples were collected in clean plastic beakers and/or VWRbrand™ TraceClean™ HDPE bottles or I-CHEM certified 300 series high-density polyethylene (HDPE). Filtering consisted of 0.45-μm filter screwed onto a 60-mL syringe.

2.3. Chemical analyses

Laboratory pH measurements were conducted using a VWR Symphony SP90M5 Handheld Multimeter that was calibrated for pH prior to use following the procedures provided in the user's manual.

All water samples were analyzed by the Battelle ICP-MS Laboratory using ICP-MS. The analytical procedures were conducted according to an EPA approved Quality Assurance Project Plan (QAPP) (Battelle, 2004). Laboratory quality assurance/quality control (QA/QC) of all methods followed the prescribed guidelines. Data quality in terms of precision, accuracy, method detection limits (MDL), and completeness met the criteria established in the QAPP (i.e., relative percent difference [RPD] of 20%, percent recovery of 80–120%, and completeness of 80%).

2.4. Batch regeneration tests

The batch regeneration tests consisted of placing 0.20 g of each media (GFH, E33-G and ARM200) into four 250-mL Erlenmeyer flasks, each containing 100-mL of a caustic solution 1% (pH 13.4), 2% (pH 13.7), 4%, (pH 13.9) and 6% (pH 13.97) for a total of 12 individual tests. The selection of the test range of 1%–6% was based upon the regeneration of AA used for fluoride and dissolved organic matter (1% requirement) and arsenic (4% requirement) (Chen et al., 1989; Hathway and Rubel, 1987; Rubel, 1984). Each flask was sealed with Teflon tape and a screw cap and then placed on a shaker table for 24 h at approximately 20 rotations per minute (rpm). After the flasks were removed from the shaker table, approximately 80 mL of the regenerant solution in each flask was filtered with 0.45-μm screw-on filters and the filtrate was dispensed into a 125-mL plastic bottle. All 12 sample solutions were analyzed for arsenic and iron. The arsenic concentrations of these solutions were used in determining the amount of arsenic stripped from the media during the regeneration tests. The arsenic removal efficiency was calculated from the arsenic loading on the media before and after regeneration on a dry weight basis (sample weight adjusted for respective moisture content).

2.5. Column regeneration tests

Small column regeneration tests were conducted on six exhausted media samples (Table 1). The column test apparatus consisted of six, 2-in diameter × 24-in length glass columns, each loaded with 6-in of gravels and 12-in of a selected exhausted media. Each column was connected to a Fluid Metering, Inc. (FMI) "Q" Pump (either Model QG50 or QG150) via Teflon tubing. Each column was rinsed with tap water and then Milli-Q® purified water to adjust flow rates to 5.0 mL/min to achieve an empty bed contact time (EBCT) of approximately 120 min. The long regenerant exposure time of 120 min EBCT was arbitrarily selected with an objective to achieve high arsenic release and to determine the possibility of iron leaching (media dissolution). After the columns were rinsed and flow rates adjusted, a 4% NaOH solution (determined from the results of the batch tests) was pumped through each column for 8.5-hr (just over 4 bed volumes (BV)). At this point in time, the pH of the effluent of the columns level off at around pH 13 indicating that the caustic solution front had advanced through the media beds.

During a 6.5-hr period (3–4 BV), pH 2.0 DI water was pumped through each column to neutralize the media. The influent was then replaced with Milli-Q purified water with no pH adjustment. In total, the media regeneration column experiment required 36-hrs (approximately 18 BVs).

Effluent samples were collected from each column at hours 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 22, 28, and 35. The samples were collected in clean plastic beakers and then filtered (0.45-μm) into individual plastic bottles. All effluent samples were analyzed for arsenic, iron, phosphorous and only three effluents (GFH, KemIron, and E33-P) for silicon. In addition, flow rate and pH were measured during the column experiments.

After the column experiments were completed, a composite water sample from each column was produced from 13 effluent samples. From the composite sample, a filtered (0.45-μm) and unfiltered water sample were collected into separate sample bottles. These samples were analyzed for arsenic and iron.

After the regeneration test was completed, approximately 2 g of media was collected from each column at approximately 2-in below the top of the media bed. The media samples were air-dried, digested and analyzed for As, Fe, P, Si, Mn, Ba, Ca, and Mg.

2.6. Media dissolution tests

Several authors have reported that iron oxides can dissolve under strongly acidic and strongly reducing conditions (Clifford et al., 2011; Smedley and Kinniburgh, 2002). Moreover, media disintegration/dissolution was observed of the E33-G media during the acid rinse step of the media regeneration column tests. Because the regeneration process requires the media to be exposed to high pH (>13) water during the arsenic stripping step and low pH water (≤2) during the media neutralization step, media loss was evaluated under both conditions.

To determine possible media loss during caustic regeneration, the media solids in each flask of the batch regeneration tests were carefully removed with Milli-Q® purified water and

filtered though a multi-stage vacuum filtration apparatus. The media solids (along with filter paper) were placed in a drying oven at approximately 100 °C to remove moisture. The samples were systematically removed from the oven, placed in a desiccator to cool, and then weighted (media solids and filter paper) on a top-loading balance to determine its dry weight and moisture content. These measurements along with the moisture content of each spent media were used to determine the amount of media dissolution during the caustic batch tests.

An acid batch test was conducted to evaluate media dissolution under varying pH conditions. The acid batch tests consisted of placing 5 g of each spent media in three 250-mL Erlenmeyer flasks, each containing 200-mL of pH 1.8, 3.5, and 5.0 water respectively. Each flask was sealed with Teflon® tape and a screw cap and then placed on a shaker table for approximately 3-days at 20 rpm. The pH of each flask was measured periodically and adjusted to 1.8, 3.5, and 5.0 as necessary. Once removed from the shaker table, the final pH was measured to determine any deviation from the target values.

The acidic solutions with media solids were filtered though a multi-stage vacuum filtration apparatus. The final filtrate volume was recorded and a sample filtered through 0.45-mm screw-on filter (60-mL syringe) into a 125-mL plastic bottle acidified with nitric acid. The sample was analyzed for iron.

The media solids along with filter paper were placed in a drying oven at approximately 100 °C to remove moisture. The samples were then systematically removed from the oven, placed in a desiccator to cool, and then weighed on a top-loading balance. These weight measurements along with the iron concentration of the filtrate solution were used to determine the amount of media dissolution during the acid batch tests.

2.7. Pilot scale tests of regenerated media

Approximately six months after the laboratory regeneration column tests, the six columns were transported to a test site near Newark, OH. The test columns were connected up to an existing pilot apparatus to evaluate the adsorptive capacities of the regenerated media for As(V) removal over a 35-week study period.

Raw water for the column study was supplied by one well (#1) for 20 weeks and for the remaining 15 weeks by a bend of two wells (#1 and #2). The raw water that contained high iron (1.1–2.2 mg/L) and predominantly As III was pretreated with a column containing 8-in of Filox-R™ overlain with 8-in of Birm® used to remove the iron to below detectable levels (25 ug/L) and to oxidize As(III) to As(V). The pretreatment column also reduced the influent arsenic levels to the test columns by around 25%.

The flow rate to the columns was set at 116 L/min to provide an EBCT of 5-min with one exception (column C5) where a ball valve problem reduced the flow rate to only 66 mL/min resulting in an 8.8-min EBCT. Some test columns were occasionally backwashed to remove media fines to help maintain the set flow rates.

The feed water and six column effluent waters were sampled biweekly and analyzed for arsenic, iron, and
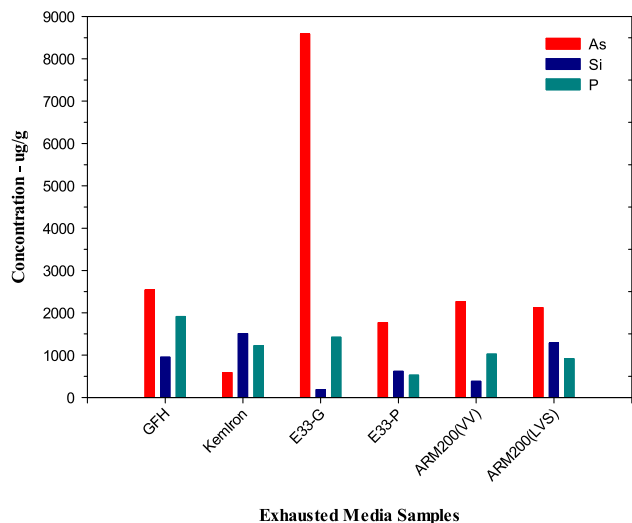
Fig. 1 – Concentrations of arsenic, silica (as Si) and phosphate (as P) of exhausted media samples.

manganese (ICP-MS). The feed water was also analyzed for pH and ORP using a VWR Symphony SP90M5 Handheld Multimeter calibrated prior to use following the procedures provided in the user's manual.

3. Results and discussion

3.1. Exhausted adsorptive media composition

An adsorptive media removing arsenic from drinking water is defined as being "exhausted" (spent) when arsenic effluent from an AM system reaches 10 μg/L. The amount of water that can be treated to this stopping point is dependent on the media (product) and source water quality. Thus, the composition of an exhausted media will vary from site to site depending on the media and source water quality.

The arsenic, phosphate and silicate concentrations of the six exhausted media samples are shown in Fig. 1. The

phosphate and silicate concentrations are provided along with the arsenic concentrations because both anions are known to be removed from water and to have an impact on the arsenic removal capacities of natural iron and iron-based media (Choong et al., 2007; Guan et al., 2009; Jeong et al., 2007a; Kolbe et al., 2011; Meng et al., 2002; Mercer and Tobiason, 2008; Möller et al., 2011; Ngygen et al., 2011; Roberts et al., 2004; Smedley and Kinniburgh, 2002; Su and Puls, 2001; Westerhoff et al., 2006; Zeng et al., 2008).

The arsenic concentration of the six exhausted media samples varied from 590 to 8590 μg/g (Fig. 1). The E33 media with the highest arsenic concentration (8590 μg/g) came from an AM system treating a ground water of pH 6.9 and with high arsenic (60 μg/L), low phosphate (as P) (0.06 μg/L) and moderate silicate (SiO_2) (26 mg/L) for 39,000 BV. The KemIron sample with the lowest arsenic concentration (590 μg/g) was from a system treating a ground water with a pH 7.3 and with very high arsenic (90 μg/L), very high phosphate (as P) (115 μg/L) and high silicate (SiO_2) (75 mg/L). With a difficult to treat water, arsenic breakthrough at 10 μg/L occurred at only 3700 BV resulting in a media with a low concentration of arsenic, but rather high phosphate and silicate as compared to the other media samples.

A more complete analysis of the five exhausted media products obtained from ADP sites can be found in individual project reports at http://epa.gov/nrmrl/wswrd/dw/arsenic/publications.html. These reports also describe the performance of the media products and the composition of the source waters being treated.

3.2. Batch regeneration tests

The arsenic recovery efficiencies of the media regeneration batch tests were based upon the dry weight of the samples whose moisture content varied with condition of the media sample received (wet/dry) (Table 2). The results of the tests to determine the optimal caustic solution concentration for spent media regeneration are shown in Table 3 and Fig. 2.

The test results indicate a maximum arsenic removal of greater than 80% for E33-G (88.1%) and ARM200(VV) (87.2%), but only 54.9% for the GFH media. The GFH had a high level of silica (i.e., 953 μg/g [as SiO_2] of media) and a low level of arsenic

Table 2 – Results of moisture content tests (triplet) on exhausted media samples.

Sample	Tray		Measured weight of sample & tray		Weight of sample		Moisture content (%)
			Wet (g)	Dry (g)	Wet (g)	Dry (g)	
GFH	1	1.00545	2.92512	2.68451	1.91967	1.67906	12.53
	2	1.00596	2.96263	2.71953	1.95667	1.71357	12.42
	3	1.00886	3.02717	2.77693	2.01831	1.76807	12.40
Average							12.45
ARM200(VV)	1	1.00294	4.80166	3.82646	3.79872	2.82352	25.67
	2	1.00244	4.89886	3.89558	3.89642	2.89314	25.75
	3	1.00428	4.84092	3.87273	3.83664	2.86845	25.24
Average							25.55
E33-G	1	1.00934	4.14395	2.75299	3.13461	1.74365	44.37
	2	1.00879	4.18604	2.77803	3.17725	1.76924	44.32
	3	1.00829	4.19162	2.78591	3.18333	1.77762	44.16
Average							44.28

Table 3 – Removal of arsenic from exhausted media by regenerant solutions.

Media ID	NaOH strength (%)	Exhausted media wet weight sample (g)	Exhausted media dry weight sample[a] (g)	Arsenic loading on exhausted media (μg/g)	Total arsenic on exhausted media (μg)	Arsenic conc. in NaOH solution[b] (μg/L)	Iron conc. In NaOH solution[b] (μg/L)	Arsenic removed from exhausted media[c] (μg)	Arsenic recovery efficiency (%)
GFH	1%	20.0	17.5	2540	44,450	162,290	<25	16,229	36.5
E33-G		20.0	11.1	8590	95,349	533,070	<25	53,307	55.9
ARM200 (VV)		20.0	14.9	2268	33,793	207,880	<25	20,788	61.5
GFH	2%	20.0	17.5	2540	44,450	244,200	<25	24,420	54.9
E33-G		20.0	11.1	8590	95,349	576,950	<25	57,695	60.5
ARM200 (VV)		20.0	14.9	2268	33,793	252,990	<25	25,299	74.9
GFH	4%	20.0	17.5	2540	44,450	232,800	<25	23,280	52.4
E33-G		20.0	11.1	8590	95,349	779,070	<25	77,907	81.7
ARM200 (VV)		20.0	14.9	2268	33,793	291,830	<25	29,183	86.4
GFH	6%	20.0	17.5	2540	44,450	229,340	<25	22,934	51.6
E33-G		20.0	11.1	8590	95,349	840,380	<25	84,038	88.1
ARM200 (VV)		20.0	14.9	2268	33,793	294,800	<25	29,480	87.2

[a] Determine by using moisture content data of Table 2.
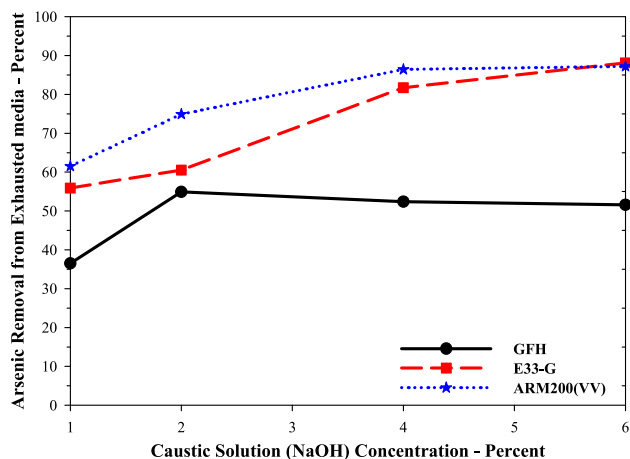[b] Arsenic/iron analyses of regenerant solutions.
[c] Total arsenic removed from media sample based on 100 mL of NaOH in each flask.

(i.e., 33.7 μg/g) on the exhausted media that might account for the lower percent of arsenic striped from the sample. In general, arsenic recoveries increased with caustic solution concentrations until approximately 4%. At 4% NaOH, the arsenic recovery efficiency effectively leveled off. Because a greater NaOH concentration would not result in additional arsenic removal, 4% was selected for the column test regeneration studies. This 4% result is consistent with the regeneration studies conducted with AA by Rubel Jr. and Williams (1980) and Hathway and Rubel Jr. (1987).
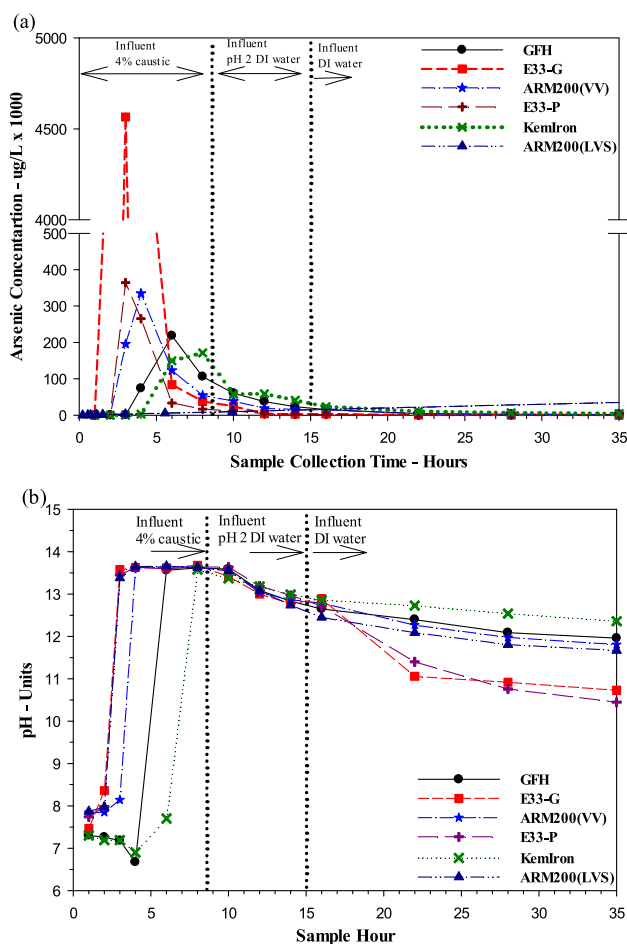
3.3. Column regeneration tests

3.3.1. Arsenic removal
The arsenic and pH of the effluent from the six columns of exhausted media over the 35-h test are shown in Fig. 3a and b. As shown in these figures, most of the arsenic and pH spikes

(a)

(b)

Fig. 3 – Effluent arsenic concentrations (a) and pH (b) from six column regeneration tests.

Fig. 2 – Batch tests results of arsenic removed from exhausted media by caustic regenerant solutions.

Table 4 – Arsenic removed during column regeneration tests based on 13 grab sample.

Column no. and media ID	Arsenic mass recovered during Regen (g)	Arsenic on exhausted media (μg/g)	Dry weight density (g/cm³)	Exhausted media volume in column (cm³)	Exhausted media mass in column (g)	Arsenic mass on exhausted media (g)	Arsenic removal efficiency (%)
C1-GFH	0.305	2540	0.79	598	472	1.198	25.5
C2-KemIron	0.306	590	1.07	598	640	0.378	80.7
C3-E33-G	2.242	8590	0.49	598	293	2.517	89.1
C4-E33-P	0.226	1767	0.54	598	323	0.571	39.9
C5-ARM200 (VV)	0.412	2268	0.77	598	461	1.046	39.4
C6-ARM200 (LVS)	0.474	2123	0.77	541	403	0.856	55.4

occurring between 2 to 8-h (1-4/5 BV). Using the 13 arsenic grab sample test results and flow rate data, the amount of arsenic stripped from the media of each column test was calculated using the following expression .

$$\sum \left[\frac{As(\mu g/L)T^1 + As(\mu g/L)T^2}{2} \right] * \left[\frac{Flowrate(mL/min)*(T^2 - T^1)}{1000} \right]$$
$$= Total\ As(\mu g)Removed$$

Using these data, approximately 80% of the arsenic was found to be eluted from the columns within 8.5-h (4/5 BV). Comparing the total amount of arsenic eluted from the media by the regeneration process to the amount of arsenic on the exhausted media found the percent removed to vary from 26% with the GFH media to 89% with the E33-G media (Table 4).

A sample of the effluent water from each column effluent container (composite sample) was collected twice after the column tests were completed (at 4 and 77 days). An unfiltered and filtered (0.45 μm) sample of each composite sample was analyzed for arsenic and iron to determine their concentrations and form. The results of these analyses found that the arsenic was almost entirely in the soluble form with only two samples (92% and 95%) having less that 99% in the soluble form. As expected, the iron analyses found that the iron was predominately in the particulate form with one exception, ARM200 (LVS), at day 4.

Arsenic test results from filtered composite samples were also used to determine the amount of arsenic removed from spent media during the column experiments and the removal efficiencies (Table 5). Arsenic removal efficiencies ranged from 59.3% for the GFH media to 99.9% for the KemIron media and

were generally greater than the values calculated using the 13 grab sample results. (Tables 4 and 5). However, the results for GFH, E33-G, and ARM200 (VV) of were reasonably consistent with the results from the caustic batch test.

After the column experiments were completed, a media sample from each column was analyzed to determine the amount of arsenic on the regenerated media. The arsenic analyses of the media products before and after regeneration provided a third method of estimating the arsenic removal efficiencies of the regeneration process on the six media products (Table 6). The arsenic removal efficiencies determined by the media analyses found removal ranged from a low of 30% for the GFH media to a high of 95% for the E33-G media.

A comparison of the results of the three methods to determine the arsenic removal efficiencies is shown in Fig. 4. Fig. 4 also includes the results of the batch test studies on three of the exhausted media samples. In all cases, the calculated regeneration removal results (% removals) are based upon the amount of arsenic on the exhausted media determined by the media analysis procedure. The results show variations in arsenic removals between the methods applied with only one exception; the E33-G media removal results. The lowest removal estimates appear to be with those calculated by using the grab sample data except for the E33-G media results.

The tests results shown in Fig. 4 indicate that regeneration with a 4% caustic solution can remove around 80% of the arsenic on most iron-based media products. The only exception found was the GFH media that had an arsenic removal of

Table 5 – Arsenic removed during column regeneration tests based on composite sample.

Column no. and media type	Total caustic solution passed through column (L)	Volume of samples removed during sampling (L)	Total caustic solution volume in container (L)	Arsenic conc of caustic solution (μg/L)	Total arsenic mass of caustic solution (μg)	Total arsenic mass of samples (μg)	Total arsenic mass removed during Regen (g)	Total arsenic mass on spent media (μg)	Arsenic recovery efficiency (%)
C1-GFH	9.95	0.78	9.17	73,969	678,080	32,714	710,794	1,198,880	59.3
C2-KemIron	9.38	0.78	8.60	40,221	345,764	31,621	377,386	377,600	99.9
C3-E33-G	10.64	0.78	9.87	190,088	1,876,783	394,207	2,270,990	2,516,870	90.2
C4-E33-P	9.61	0.78	8.83	35,355	312,060	42,177	354,237	570,741	62.1
C5-ARM200(VV)	11.15	0.78	10.37	82,105	851,795	48,269	900,064	1,045,548	86.1
C6-ARM200 (LVS)	10.25	0.78	9.47	67,381	638,399	67,470	705,869	855,569	82.5

Table 6 – Arsenic removed during the column regeneration tests based on media analyses.

Column no, and media type	Exhausted media arsenic loading (µg/g)	Regenerated media arsenic loading (µg/g)	Percent removed from media (%)
C1-GFH	2540	1775	30.1
C2-KemIron	590	159	73.1
C3-E33-G	8590	450	94.8
C4-E33-P	1767	146	91.7
C5-ARM200(VV)	2268	419	81.5
C6-ARM200 (LVS)	2123	802	62.2

around 50% or less depending on the method used to determined removal. This GFH media came from water system whose ground water had an extremely high level of silica (around 80 mg/L) that resulted in the media having a very low arsenic removal capacity. Whether the silica had some impact on the regeneration process requires further investigation.

3.3.2. Phosphorous and silica removal

The 13 grab samples from all six column test were analyzed for phosphate (P) and from three columns (GFH, KemIron and E33-P) for silica (as SiO_2) The results of the phosphorous and silica analyses indicate that both were stripped to varying degrees from the exhausted media by the regeneration process (Figs. 5 and 6). Their maximum concentrations in the effluent water varied between the media products with the peaks occurring during the caustic feed step. Phosphate recovery efficiencies ranged from 40 to 88% that was somewhat consistent with those for arsenic (Table 7). Silica removal was highly variable with removal efficiencies ranging from immeasurable to 74% (Table 7). The media analyses data also indicate that the 4% caustic solution is effective in stripping some phosphate and silica as well as arsenic from the media.
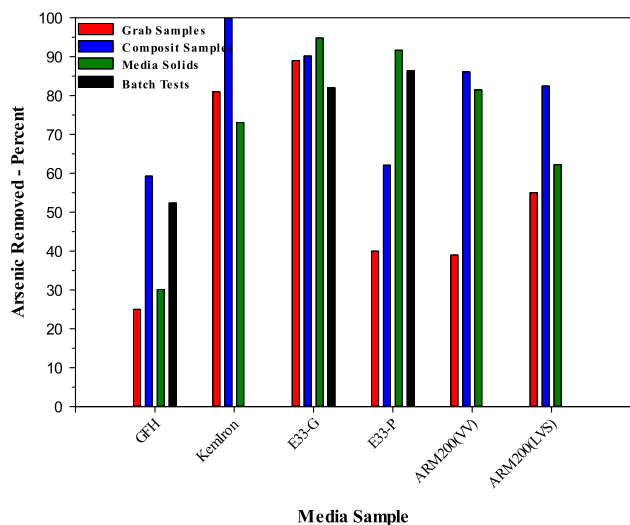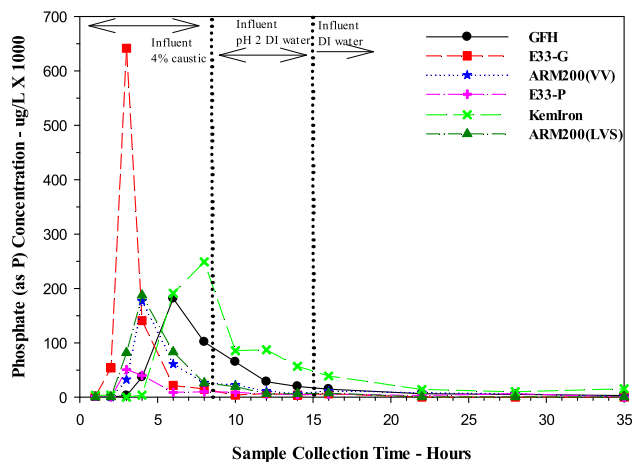

Fig. 5 – Effluent phosphate (as P) concentrations from six column regeneration tests.

3.4. Media dissolution

3.4.1. Caustic exposure

Both the iron results of the regenerant solutions and media dry weight measurements were used to determine media dissolution/loss during the caustic batch tests. The analytical results indicate insignificant media dissolution; all soluble iron results were below the method detection limit of 25 µg/L (Table 3). Likewise, dry weight measurements after the caustic batch test indicated a minimal media loss ranging from immeasurable to 2.5%.

3.4.2. Acid exposure

The acid batch test to determine the effect of low pH on media dissolution found no iron dissolution occurred at the target pH 3.5 and 5.0 except for ARM200 (VV) media (Table 8). Below pH 2, significant media dissolution was observed with iron concentrations ranging from 3056 to 36,777 mg/L in the low pH water. These results indicate that some caution must be taken when using an acid to neutralize the media after the caustic
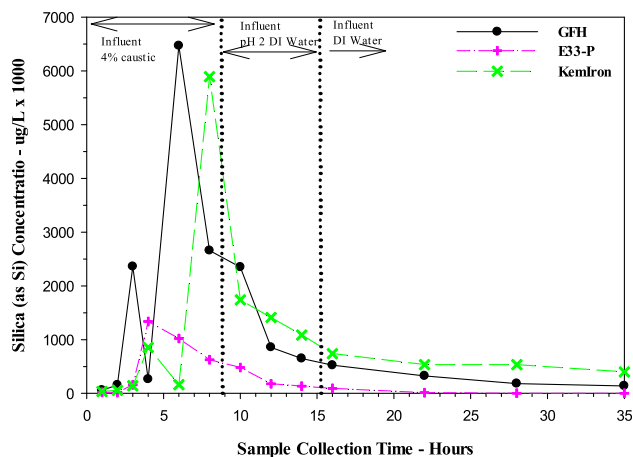

Fig. 4 – Arsenic removed by regeneration of six exhausted media products; column and batch tests results.

Fig. 6 – Effluent silica (SiO₂) concentrations from three column regeneration tests.

Table 7 – Silica and phosphate removal during media regeneration column tests.

Column no. and media type	Before/After Regen	SI		P	
		μg/g	% Recovered	μg/g	% Recovered
C1-GFH	Before	953	–	1912	62
	Afer	968		728	
C2-KemIron	Before	1511	38	1225	40
	After	933		734	
C3-E33-G	Before	188	–	1426	88
	After	204		168	
C4-E33-P	Before	618	53	530	74
	After	289		140	
C5-ARM200(VV)	Before	385	–	1024	70
	After	417		309	
C6-ARM200 (LVS)	Before	1290	74	918	43
	After	330		524	

regeneration step to prevent any media disintegration/dissolution. For the full scale system regeneration process, a media neutralization step is required. This neutralization step is designed to lower the system effluent pH to the system operating pH that is normally in the 6–8 range well above pH 2. Continuous monitoring of the system effluent during the entire regeneration process is therefore recommended as a control mechanism.

3.5. Pilot scale evaluation tests of regenerated media

The six regenerated pilot test columns were operated for 35 weeks with feed water and column effluent water samples collected biweekly. The As(V) feed water to the columns varied from detection limit to 35 ug/L as shown in Fig. 7. The arsenic concentrations, therefore, were not representative of the arsenic in the source waters at the ADP sites from which the exhausted media products were obtained. Furthermore, the many of the other water quality parameters, such as phosphate and silica, were not the same concentrations. Thus, the column test results were not expected to produce

the same results as the full scale systems, but only to give some indication on the ability of the regenerated media to remove arsenic.

Fig. 7 shows the arsenic breakthrough curves for the six column tests. As shown in Fig. 7, all of the regenerated media were able to reduce the arsenic levels to less than 2 ug/L for 10,000 BV after which time the arsenic levels started to increase some faster than others. The E33-P media was the first to breakthrough at 10 μg/L after approximately 36,000 BV which was slightly less than 38,500 BV for virgin E33-P observed previously during the LVS pilot study. E33-G media was close to breakthrough at 9.8 μg/L after approximately 40,000 BV. This compared well to the 40,500 BV for virgin E33-G observed previously at the demonstration site.

As shown in Fig. 7, the feed water arsenic decreased from around 25 ug/L to around 10 ug/L resulting in the arsenic in the effluent of all of the columns to decrease. Because of the changes in arsenic feed concentrations and some operational issues, definite conclusion for actual run lengths of the regenerated media of GFH, KemIron, and the ARM200 (LVS) media cannot be drawn. However, the column arsenic data do

Table 8 – Media dissolution in acidic solutions.

Media sample	Initial (or target) pH	Final pH	Solution volume (mL)		Iron conc. in solution (mg/L)	Iron mass dissolved (mg)
			Initial	Final		
GFH	1.8	1.9	200	200	36,777	7355
	3.5	4.6	200	480	<25	–
	5.0	6.0	200	405	<25	–
KemIron	1.8	1.9	200	200	27,437	5487
	3.5	4.2	200	450	<25	–
	5.0	6.2	200	420	55	23
E33 G	1.8	1.9	200	200	22,664	4533
	3.5	4.6	200	400	<25	–
	5.0	6.6	200	400	<25	–
E33 P	1.8	1.9	200	650	3056	1987
	3.5	4.6	200	480	<25	–
	5.0	6.6	200	370	<25	–
ARM200 (VV)	1.8	1.9	200	780	15,439	12,043
	3.5	4.2	200	440	62	27
	5.0	6.7	200	490	336	165
ARM200 (LVS)	1.8	1.9	200	510	7026	3583
	3.5	4.5	200	390	<25	–
	5.0	6.6	200	450	<25	–
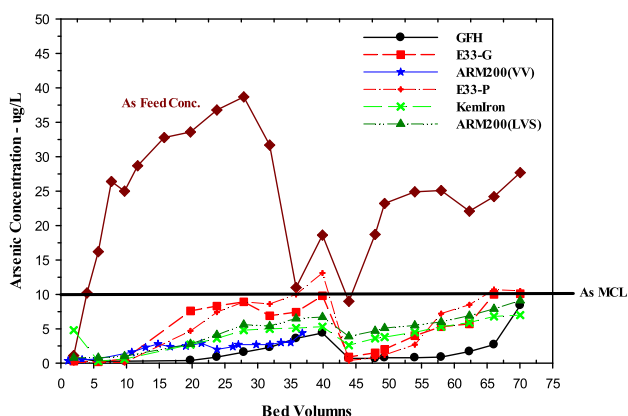
Fig. 7 — **Arsenic removal breakthrough curves of regenerated media.**

indicate that all of the regenerated media products provided some arsenic removal capability, thereby suggesting that a regenerate media can return most, but likely not all, of the arsenic removal capacity. Although the information is not presented in this paper, the authors have conducted a regeneration study of a full scale arsenic removal system with E33-G media that resulted in over 80% of the arsenic being stripped from the media with a 4% caustic solution and the regenerated system's arsenic removal capacity was higher than the virgin media removal capacity (Sorg, 2013).

4. Conclusions

Adsorptive media technology is frequently used by small drinking water systems to remove arsenic and the current practice is to use the media, primarily iron-based products, on a throw-away basis. Media replacement accounts for around 80% of the total operational cost which can be significant for many small systems. The objective of this research was to determine the feasibility of regenerating the iron media products rather than discarding them, thereby, providing an option to reduce the operating cost. Laboratory and pilot tests on the regeneration of several exhausted media products obtained from full scale and pilot scale drinking water systems removing arsenic have lead to the following general conclusions:

- A 4% caustic (NaOH) solution can strip as high as 80% or more of the arsenic from some iron-based exhausted media. Of the four different exhausted media types tested, the regeneration studies found higher arsenic recoveries with E33 and ARM200 than with GFH and KemIron.
- Media dissolution due to the use of caustic solutions during regeneration is insignificant for all media products. Media dissolution under the acidic condition during media neutralization can be problematic only if the pH is below 2.
- Regeneration of an iron-based media to remove arsenic can restore some of its arsenic removal capability providing the possibility of media reuse and lower O/M costs.

Notice

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