Arsenic removal – solutions for a world wide health problem using iron based adsorbents

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ABSTRACT: Arsenic contamination of ground water resources used for potable water supply is an emerging problem throughout the world. Beside the use of alternative, uncontaminated water sources, water treatment for arsenic removal is often the only solution to meet the standards. The effective application of arsenic removal processes requires the knowledge of its chemistry in natural water. It is to decide whether arsenic(III) is present and to evaluate the need for an oxidation technique for arsenic(III). Different techniques exist for the removal of arsenic, which include conventional processes like ion exchange and coagulation/filtration and also emerging processes with iron oxide based adsorbents like GEH[®]. The latter are the most promising techniques, as they require quite low investment and are easy to operate, because they avoid dosing of additional chemicals. This article gives a short overview on arsenic removal techniques in potable water treatment and gives examples of the application of iron based adsorbents under different conditions.

1 INTRODUCTION

Arsenic becomes a serious health problem in several countries around the world. This is attributed to new findings about the toxicity of arsenic, especially for long term exposure to low levels in drinking water and food, but also in changes in land use and water sources. From several countries in South America, especially Chile, Argentina and Mexico reported toxic levels of arsenic in the drinking water of some regions. A number of countries have lowered their drinking water standards within the last 13 years (WHO 2001). The lowered standards, mostly to 10 µg/l and the "arsenic calamity" in India and Bangladesh induced world wide activities in research of available treatment methods for arsenic and the development of new technologies.

Several techniques for arsenic removal are used in drinking water treatment: Ion exchange, flocculation and filtration with ferric or ferrous salts, adsorption on activated alumina and on ferric iron based adsorbents (Jekel 1994). These methods are principally applicable in water works. Methods like reverse osmosis are economically restricted for Point-of Use or Point of Entry systems for households. They may have some advantages if several contaminants in the raw water need control and removal.

The flocculation technique with ferric or ferrous iron (Cheng et al.1995) is frequently used in Germany. An acid ferric or ferrous solution is dosed into the raw water and mixed. The ferric iron precipitates and adsorbs arsenic during the flocculation. The arsenic bearing precipitates are removed by filtration, usually in a sand filter. The flocculation technique allows to meet the German drinking water standard for arsenic. The precipitates are removed from the filter bed by backwashing. The residual of this technique is a sludge with a high water content. The advantage of the flocculation is the high efficiency, when the regarding the amount of residuals in dry weight. Great disadvantages are the handling of chemicals, required overdosing, and the maintenance for dosing equipment and backwashing and sludge handling.

The newly developed granular ferric hydroxide GEH[®] is a media which combines the advantages of both techniques. It was especially developed for the removal of arsenic in small water utilities, but is also applicable for the removal of some other elements and water constituents. Ferric hydroxides are controlling the concentration and the mobility of numerous

trace elements, including arsenic, phosphorous and antimony, and if applied in a fixed bed process, provide an ideal media for arsenic removal. The GEH® adsorption process is simple, efficient due to the high adsorption capacity of the media, but without the production of a contaminated sludge and without the necessity to dose any chemicals. The granular ferric hydroxide was developed from 1992 – 1994 at the Technical University of Berlin by Dr. Jekel and the author (DRIEHAUS, JEKEL et al. 1998).

2   AQUATIC CHEMISTRY OF ARSENIC

Arsenic is a semimetal and occurs in natural groundwater mostly as an oxyanion of trivalent (H_3AsO_3) or pentavalent arsenic (H_3AsO_4). They are commonly named arsenite or arsenic(III) and arsenate or arsenic(V).   The occurrence of organic arsenic compounds, especially methylated species is reported from surface water (Anderson & Bruland, 1991), but they rarely occur in groundwater. Elevated arsenic concentrations at a level relevant for human health are mostly caused by inorganic arsenic species in groundwater.

Natural groundwater is commonly in the field between pH 5 – 9 and Eh –0.50 V – 0.50 V. Under this conditions there are two dominating species, arsenic (III) in more reducing environments and arsenic(V) under oxidizing conditions. In strongly reducing environments with hydrogen sulfide present form also a couple of arsenic sulfides, most of them being solids. As this conditions are rare in groundwater bodies used for drinking water supply, these species are excluded from the following description.

The dissociation constants of arsenic(III) are $pK_{S1} = 9.22$; $pK_{S2} = 12.10$; $pK_{S3} = 13.40$ (Ferguson & Gavis, 1972). That means that at pH 9.2 the arsenic(III) is by 50% dissociated. At lower pH, most of arsenic(III) exists as a neutral molecule.

The dissociation constants of arsenic(V) are $pK_{S1} = 2,22$; $pK_{S2} = 6.96$; $pK_{S3} = 11.5$. That means, that a pH 6.96 about 50% of arsenic(V) exists as a monovalent anion and 50% as an divalent anion.

The difference in charge has important effects on the removal characteristics of both arsenic species, because neutral, uncharged molecules can not be removed by a number of treatment techniques (Jekel 1994). Arsenic(III) can be oxidized to arsenic(V) at a relatively low Eh-potential of 0.1 – 0.2 V and, from the energetic point of view, dissolved oxygen is sufficient as an oxidant. Unfortunately, the oxidation of arsenic(III) by oxygen is very slow with conversion rates of a few percent per day. Thus, even oxidizing groundwater with high oxygen concentrations may contain some arsenic(III). Arsenic(III) in its typical stability range is very often associated with dissolved iron and manganese. Arsenic(V) is the stable species in oxidizing water and has a great similarity to ortho-phosphate in terms of dissociation, precipitation, adsorption and ion exchange (Jekel 1994).

Some removal techniques fail completely I removing arsenic(III), that especially activated alumina and ion exchange. New results from existing treatment plants with iron based adsorbents show, that the removal capacity is not much effected bay the oxidation stage of arsenic.

3   ARSENIC REMOVAL USING ACTIVATED ALUMINA AND IRON BASED ABSORBANTS

3.1.1   *Activated alumina*

   The adsorption techniques in the stricter sense rely on a simple filtration process over granular adsorbents like activated alumina or granular iron oxides and ferric hydroxides. Dosing of any chemicals is usually not required. This techniques do not produce a backwash sludge, the residual is the arsenic loaded adsorbent itself. Activated alumina is known since more than 20 years as a good adsorbent for arsenate containing waters, but needs a regeneration, due to the restricted lifetime of the media until exhaustion. It is reported that the optimal pH for arsenic removal with activated alumina is around 6.0. Thus, most of the raw water need a pH-adjustment by adding mineral acids or CO_2. Figure 1 shows the treatment capacities of activated

alumina with a model raw water containing arsenic(III) or, after oxidation, arsenic(V). Obviously is activated alumina not effective in adsorbing arsenic(III).

Activated alumina can be regenerated by rinsing with diluted caustic soda. This causes some problems because it produces a significant loss in capacity and, more important, a liquid waste stream highly enriched with arsenic.
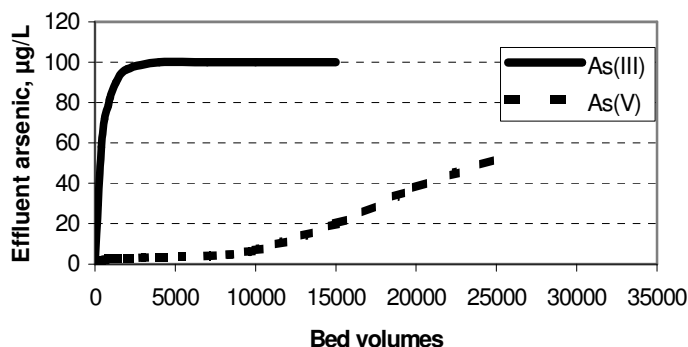

Figure 1: Process life of activated alumina with 100 µg/L arsenic(III) and arsenic(V) at pH 6 (after Frank & Clifford 1986)

Recently, various activated aluminas were pilot tested with ground water from Arizona. They exhibited treatment capacities between 1000 and 4000 bed volumes at raw water pH of 7.5 - 9 (Chang et al. 2004)

3.2   Emerging techniques: Iron oxide based adsorbents

The technique with iron oxide based adsorbents was developed in 1991 – 1994 at the Technical University of Berlin, Department of Water Quality Control, to meet the new treatment goals of the lowered arsenic standard in Germany (Driehaus et al. 1998). The technique provides a simple filtration process over granular adsorbent medias, commonly without any dose of chemicals and without pH adjustment. The media has a 5 - 20 times longer process life of the media compared to activated aluminas and is applied as a through-away media with only one life cycle. This part gives an overview over properties and applications of Granular Ferric Hydroxide (GEH[®]), which is manufactured and distributed by GEH Wasserchemie GmbH & Co. KG (Germany). The adsorbent is distributed in North America by US Filter Inc. under the trade name GFH[™].

Currently more than 60 plants for arsenic removal from drinking water are in operation in Germany, other European countries and in the USA and Japan. There is also a large number of hand pump operated plants in West Bengal, India. Examples are presented in section 5.

The main characteristics of the GEH[®] adsorbent are given in Table 1. The adsorption densities, that are calculated from batch tests at different pH values are given in figure 2. The adsorption density at a residual concentration of 10 µg/L is plotted against pH for both arsenic(III) and arsenic(V). At low pH, the adsorption density of arsenic(V) is much higher than of arsenic (III), but at slightly alkaline pH, adsorption is nearly equal for both oxidation states of arsenic.

Table 1: Specification of granular ferric hydroxide (GEH[®])

Chemical composition:	β-FeOOH, Fe(OH)$_3$: 55 %
Adsorption density	
Arsenic(V)	Up to 55g/kg
Typically for drinking water applications	1 – 10 g/kg

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Physical data:	
Grain size:	0.32-2 mm
Grain density:	1.59 g/cm³
Bulk density:	1.15 g/cm³
Porosity of grains:	72-77 %
Specific surface:	250-300 m²/g

The adsorption density and the lifetime until exhaustion in a treatment plant increases with decreasing pH for arsenic(V). It is nearly at a constant level for arsenic(III). The batch tests were prepared simulating a typical groundwater chemistry with an electrical conductivity of 480 µS/cm.

Natural water has some constituents which interact with the ferric hydroxide surface and lead more or less to a reduction in adsorption density for arsenic. The most important interfering substances are phosphate, dissolved organic matter and at low pH sulphate. Also high silica amounts may interfere with arsenic adsorption, reducing the treatment capacities. For practical evaluations, for the comparison of different media and for economic calculations, the treatment capacity, expressed in bed volumes, rather than the adsorption density is a useful expression.
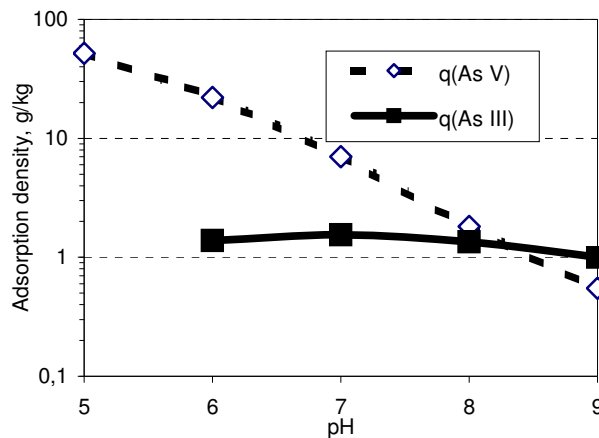

Figure 2: Adsorption densities for arsenic (III) and arsenic (V) in a typical groundwater at different pH values.

1. Example: The OSW Project.

OSW is a small community, located in the eastern part of Hessia, Germany. It has about 6,000 residents. The water supply is based on groundwater resources, withdrawn in the local area. 2 of 5 water wells have a problem with naturally occurring arsenic. The concentrations are 15 to 20 µg/L, present as As(V). The geology is Buntsandstein/Trias, and the aquifers are built up from mostly red coloured sand- and siltstone. The Buntsandstein aquifers often are enriched in arsenic and the groundwater too contains arsenic above the drinking water standard.

The municipal authority was in search for a solution of the arsenic problem which came up in 1996, when the reduced arsenic standard of 10 µg/L had come in force. They contacted the GEH Wasserchemie to get a solution for the arsenic problem, and they favored the GEH®-process, as trained staff for the more complicated flocculation technique was not available.

In 1997 we made a pilot trial with a two column pilot plant. The column diameter was 0.20 m and the column height was 1.30 m. We planned to run the pilot plant for 5-6 months, and the breakthrough at 10 µg/L was expected at 60,000 BV. The media was not exhausted even after seven month. The results of the trial are given in figure 3. The test was conducted at the raw water pH of 7,6 with an EBCT of 3 minutes.
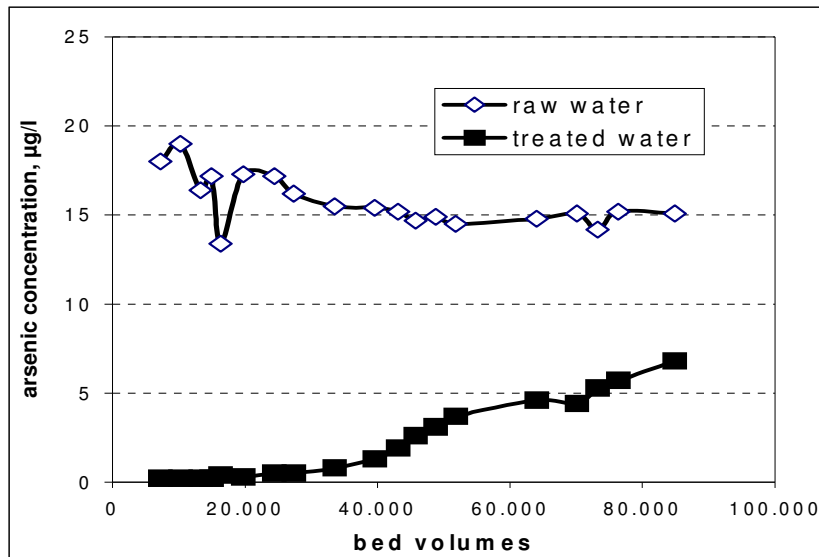
Figure 3: Arsenic concentrations from the pilot trial at Wildeck.

In the first 20,000 bed volumes (BV) arsenic was below the analytical detection limit. After 40,000 BV the arsenic concentrations rose slowly. The test was cancelled after 85,000 BV and the final concentration in the treated water reached 7 µg/L A complete water analysis is presented in table 2.

The plants at the two sites in Wildeck were planned and designed subsequent to the pilot trial. The work included also a calculation of treatment costs based on a lifetime of the GEH®-media of 85,000 BV.

One plant is designed for 180,000 to 200,000 m³/year and a flow rate of 45 m³/h. It is built up with two adsorber vessels in parallel operation, each with a diameter of 1.20 m. Both vessels are equipped with hand-turn valves for operating, backwashing and forward flushing after backwash. The GEH® bed depth is 1.0 m in both vessels, thus giving a bed volume of 2.2 m³. Assuming a treatment capacity of 85,000 BV, the lifetime of the adsorber bed is approx. 11 months. The complete treatment plant fitted into the building of the reservoir, thus avoiding a new construction. A photograph of plant I is shown in figure 5.

The second plant is designed for 100,000 m³/year at a flow rate of 14 m³/h. It is a single step plant with one adsorber vessel with 1.0 m in diameter. The plant is located in the pumping station of the water well. It is equipped with hand-turn valves for operating and backwashing and forward flushing after backwash. Both plants were built in spring 1998 and went into operation in June the same year. The plants have operated without any problems since then and all drinking water standards are met.

3.2.1   *Calculation of treatment capacities*

In order to predict treatment capacities and performance of the applications with GEH®, GEH Wasserchemie developed a mathematical tool to calculate this data from the raw water quality. It was the aim of this tool to use only a small set of quality parameters, which were always and easily available. From the view of practicability, including more parameters does not necessarily lead to more accurate results, because parameters are not always reliable in terms of analytical and sampling errors. For example, there is no detailed knowledge how the content of dissolved organic carbon (DOC) affects arsenic adsorption. On the other hand, we have reliable data about the important competitors in arsenic adsorption. From this competing ions, phosphate is included in the tool, whereas the influence of sulphate and fluoride are far behind and are not included.

Results from the kinetic model and monitoring data from OSW treatment plant is shown in figure 4. The curve of that plant develops a plateau at 4 µg/l after 130,000 BV treated, and shows only a slight increase of treated arsenic with ongoing operation. Surprisingly, the

capacity of this plant is much higher than predicted with the kinetic tool. This behaviour of the media is in a sharp contrast to the model prediction, where the curve gets steeper after the initial breakthrough, until around 50 % removal is achieved.
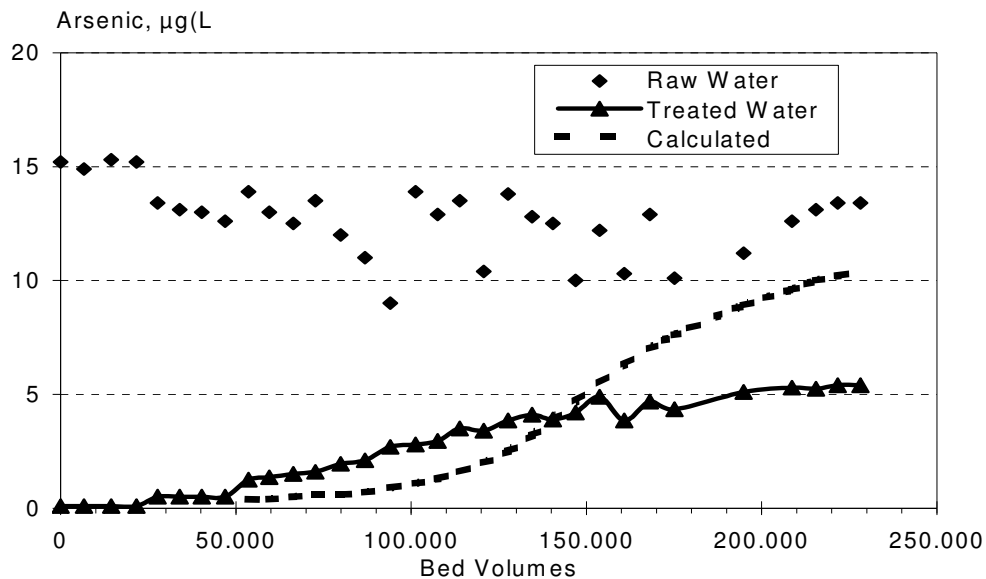

Figure 4: Treatment data from the full scale plant *OSW* at a raw water pH of 7.1 and calculated exhaustion.

This behaviour is not yet clearly understood. The kinetic tool calculates with a fixed amount of adsorption sites, depending from initial pH and the concentration of competing ions. The number of sites does not change with time. The development of a plateau does not meet this assumption, because a further increase is expected with ongoing uptake of arsenic and consumption of adsorption sites. We conclude, that there is another mechanism behind the adsorption in a monomolecular layer on the surface sites. This is thought to be a slow, long term surface modification, where the surface itself develops new adsorption sites with time, while the adsorbed arsenic is incorporated into the structure of the material. Another possibility is adsorption not only in a monomolecular layer, but multi-layer adsorption.
This examples show, that a kinetic model with a small number of input parameters is able to describe the exhaustion in full scale applications, but with a tendency to underestimation.
Treatment costs were calculated including capital and investment costs for the plant and the consumption costs. The consumption costs include also the loading and removal of the adsorbent and the disposal in a landfill. The total costs for arsenic removal in plant I are about 0.10 EUR/m³
At this time, the plant is still in operation in the third exchange cycle. It has treated about more than 1,000,000 m³ of drinking water and the arsenic concentration in treated water never exceeded 6 µg/L. The better treatment capacity of the full size plant can be explained by differences in the EBCT and water chemistry. The EBCT in the pilot plant was 3 minutes, whereas the EBCT of the full size plant is 6.4 minutes as yearly average, but this effect can not be solely responsible for the extended capacity. In fact the pH in the full scale plant is 0.5 lower than in the pilot plant. By this time, we have a lot of experience with the design of treatment plants and we are able to design GEH® treatment plants without performing pilot trials in most cases.

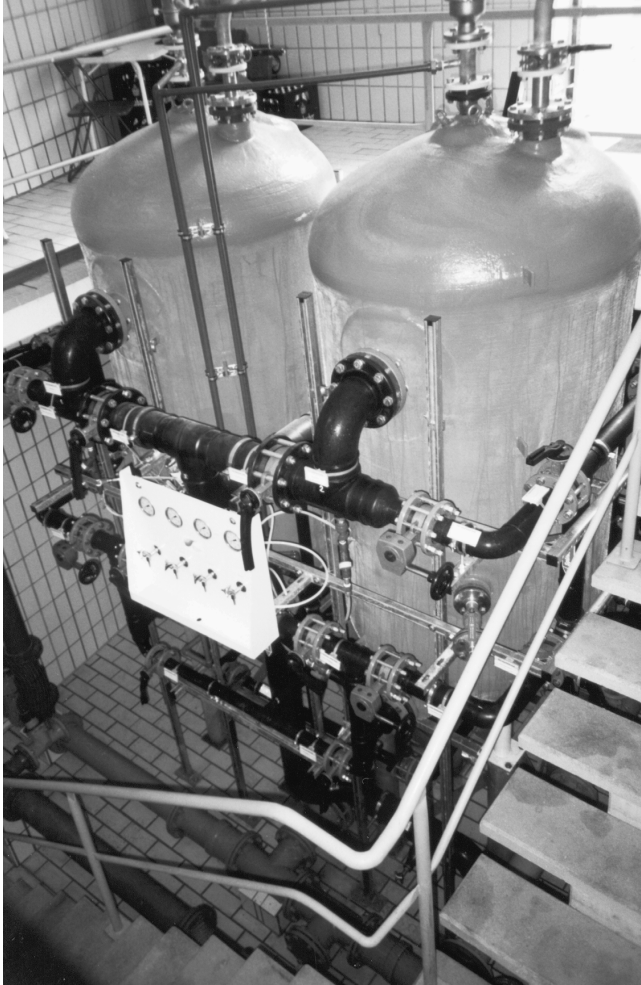Figure 5: Treatment plant for arsenic removal for 45 m³/h with two adsorber vessels in parallel operation, Plant OSW, Germany.

3.3 2. Example: Mineral water treatment

At another site we had the task to treat a mineral water in order to remove arsenic(III). The water contains some ferrous iron, manganese and traces of sulphide. The pH is 5.5 and the concentration of arsenic is 300 µg/L, and the water should be used for medical purpose. In contrast to a drinking water treatment, the ferrous iron and manganese should not be oxidised and removed and the water should not be aerated. In this case the treatment system consists of a sand filter to remove traces of sulphide, followed by two adsorbers with the GEH® media. Arsenic(III) is removed specifically without any effect to other water constituents, especially iron and manganese are not removed. The treatment capacity is about 15,000 BV at a cut off concentration of 8 µg/L. This example illustrates the possibility of the application of GEH® for a special and unusual treatment option. The GEH® is also applied for arsenic removal from mineral water by two mineral water manufacturers.

3.3.1 Arsenic treatment: Examples from other countries

The iron oxide based adsorbents, namely GEH® are widely used in several countries to solve arsenic problems. The probably most important applications are in West Bengal, India, and in Bangladesh with actually a couple of hundreds small treatment plants. This treatment plants are designed for operation behind a hand pump. Thus, no external energy is required. Treatment results for five randomly selected plants are given in figure 6. All plants are located in West Bengal. This plants are mounted beneath the contaminated well and water is pumped on

demand. One of this small plants supplies water for an average of 200 people, which gives an daily throughput of about 1000 – 2000 liters.
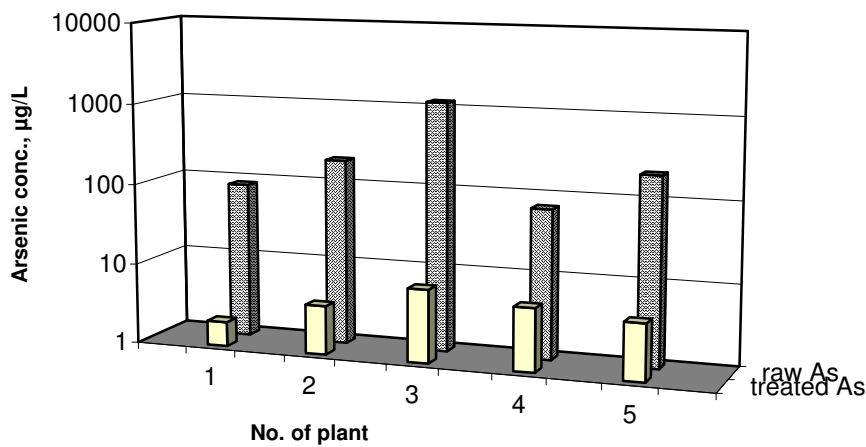

Figure 6: Treatment results of selected arsenic removal plants from West Bengal, India. Plant 1 has treated 14,000 BV for 20 month, plant 2: 19,500 BV for 42 month, plant 3: 39,000 BV for 56 month, plant 4: 34,000 BV for 47 months and plant 5: 32,200 BV for 47 month

All plants operate very well and have, even at highest raw water arsenic, no indication for breakthrough. This may be attributed to the low hydraulic load of the adsorption media AdsorbAs® (equivalent to GEH®) in this plants. The specific load is at 20 – 30 BV per day. This value is ten times less than in a water works treatment plant. Figure 7 gives an image of this treatment plants in West Bengal.

Great attention is also given arsenic treatment techniques in the USA, because the drinking water supply in the USA is hardly affected by the recent issued arsenic standard. Compared to the European conditions, water supply in the USA is characterized by a much higher water consumption per person and by far differing raw water profiles, especially in arid Southwest. The first two arsenic treatment plants with GFH™ (equivalent with GEH®, distributor: US Filter) are in operation since 2002 and 2003. Treatment results will be reported shortly.

Figure 14: AdsorbAs® arsenic removal plant in West Bengal, India. The plant is designed for a supply of up to 500 L/h flow rate.

4 CONCLUSION

The new techniques with iron oxide based adsorbents, which were developed and introduced into the market during the last 8 years could overcome the shorts of the previously mentioned techniques. The actually best medias have bed life cycles of 100,000 to 300,000 BV until exhaustion. Exhausted adsorbents are disposed of and replaced by factory fresh adsorbent. After 7 years of experience with Granular Ferric Hydroxide (GEH®) they have proven their high performance under various conditions.

The operation and maintenance of treatment plants is quite simple and fulfills all expectations of a simple adsorption process. No chemicals need to be dosed to the water and the only task for maintenance is backwashing of the adsorber vessel bed on a monthly frequence. The plants meet all standards for drinking water, the water quality is only influenced with regard to arsenic and phosphate. During the last 3 years of experience with this adsorption process there was no case of downtime or any extraordinary maintenance. All drinking water standards were met in all plants and the breakthrough of arsenic in the treated water is very slow.

During the last years, especially driven by the implementation of a new arsenic standard in the USA, came up a number of new adsorption medias for arsenic removal. Some are still under development or only lab tested, others are commercially available. Also some of the offered adsorbent medias are not really suitable for arsenic removal, others have been proven under pilot plant conditions to have a suitable performance. There is no doubt that iron oxide based adsorbents will play a major role in arsenic removal in the future..

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