Granular ferric hydroxide—a new adsorbent for the removal of arsenic from natural water

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ABSTRACT: Granular ferric hydroxide (GFH) is an adsorbent, developed for arsenic removal from natural water. It can be applied in simple fixed bed reactors, similar to those for activated alumina or activated carbon. GFH has a high adsorption capacity in model systems and in natural waters. The application of GFH in test adsorbers showed a high treatment capacity of 30 000–40 000 bed volumes, until the new German and WHO drinking water standard for arsenic of 10 μg/L was exceeded. The residue of this technique is a solid waste, enriched with arsenic. The typical residual mass is in the range of 5–25 g/m^3 treated water. This new technique for arsenic removal provides a simple and effective method, particularly for small water facilities.

INTRODUCTION

Arsenic is a contaminant in the ground water and drinking water of some regions. It is mostly geogenic and known for its high toxicity and its ability to induce skin cancer after long-term ingestion. The WHO has lowered the drinking water standard to 10 μg/L due to new results on the chronic toxicity of arsenic [1]. New regulations for the maximum contaminant level of arsenic in drinking water have been proposed by the US EPA [2] and the Commission of the European Community, aiming at a standard in the range of 2–20 μg/L. The German drinking water standard had been reduced to 10 μg/L at January 1996. Given this background, some research on evaluating treatment methods for arsenic removal has been carried out [3,4].

The requirements for a removal technique of arsenic from drinking water are: (i) safe operation with respect to the maximum contaminant level, (ii) efficiency, (iii) simple processing for application in small water facilities, and (iv) minimal residual mass of arsenic contaminated waste. All residuals from arsenic removal are enriched with arsenic and may be handled as dangerous waste.

The most common technique is the removal of arsenic by coagulation with ferric salts, followed by filtration. This technique allows residual arsenic concentrations below 10 μg/L and the doses of ferric salts below 10 mg/L [5]. Alum as coagulant is less effective than any ferric salt. A problem with this technique is the safe separation of the ferric hydroxide precipitate, for example by filtration or sedimentation and filtration, and the handling of the contaminated coagulant sludge. The coagulation technique is costly and is not suitable for small water facilities. Another technique, which is simpler but less effective,

is adsorption on activated alumina in fixed bed reactors [6]. The typical capacity of these fixed bed reactors is 3000–10 000 bed volumes with respect to a tolerable effluent arsenic level of 10 μg/L. The residual mass of spent adsorbent is in the range of 50–200 g/m^3 treated water, This is nearly 10-fold more than the amount of coagulant sludge in the coagulation with ferric salts.

A new removal technique, which has recently been developed at the Technical University of Berlin (Germany), Department of Water Quality Control, is adsorption on a granular ferric hydroxide in fixed bed reactors. An activated ferric oxide or ferric hydroxide should demonstrate a larger capacity for arsenic removal than activated alumina, as within the coagulation-filtration ferric salts show better removals compared to alum at equal dosage. Furthermore, a granulated ferric hydroxide should be as easy to apply as is activated alumina in fixed bed reactors. It is the aim of this technique to combine the advantages of the coagulation-filtration technique, efficiency and small residual mass, with the fixed bed adsorption on activated alumina, simple processing.

MATERIALS AND METHODS

Granular ferric hydroxide (GFH) was prepared from a ferric chloride solution by neutralisation and precipitation with sodium hydroxide. The ferric hydroxide precipitate was washed several times with demineralised water, and then centrifuged and granulated by a high pressure process, which led to enhanced de-watering.

Granular ferric hydroxide is a poorly crystallised β-FeOOH, which resembles the mineral Akaganeit, and contains some chloride which is incorporated into the tunnel structure typical for this modification. It has a specific surface of 250–300 m^2/g

and a porosity of 75–80%. The bulk density of GFH saturated with water is 1.32 g/cm^3. The grain size ranges from 0.2 to 2.0 mm. As no drying procedure was included in its preparation, all the pores are completely filled with water, which leads to a high density of available adsorption sites and thus to a high adsorption capacity.

Batch studies

Granular ferric hydroxide was crushed to a grain size < 63 μm, and suspended in demineralised water, giving a stock suspension of $\approx$ 1 g Fe/L. Different amounts of this suspension were added to test flasks, containing an arsenate (v) solution to give a set of suspensions with different GFH:arsenate ratios. In each batch test set, five pH values of between 5 and 9 were obtained by adding hydrochloric acid or sodium hydroxide. The ionic strength in standard setting was set at 10 mmol/L using sodium chloride. The flasks were placed on a shaker and the pH was controlled and adjusted after 48 h. Samples were taken after 96 h, filtered by a 0.2 μm membrane filter and analysed for arsenic by hydride generation atomic absorption.

The adsorption density was calculated from the residual concentrations of arsenic and the known initial concentrations of arsenate and GFH. The data fit the Freundlich isotherm satisfactorily. Freundlich parameters were obtained by linear regression of the logarithm of the data, giving a regression coefficient R^2 better than 0.98 in most of the adsorption tests. With the Freundlich parameters the adsorption density at residual arsenic concentrations of 10 and 40 μg/L or 0.13 and 0.5 μmol/L, respectively, were calculated and plotted against pH. The adsorption density is given in mmol Arsenic /g Fe. This evaluation allows the best comparison of the several experiments with regard to new drinking water standards for arsenic.

Adsorber tests

Adsorber tests were performed in adsorbers which consisted of one or two segments which allowed sampling from each segment. The GFH grain sizes in the adsorber tests were 0.2–0.4 mm and 0.4–2.0 mm.

RESULTS AND DISCUSSION

Arsenate adsorption in model systems

Arsenate adsorption on GFH in model systems was examined in order to obtain values of maximum adsorption density at a given residual concentration and to compare adsorption on GFH with that of freshly prepared ferric hydroxide. In batch tests the adsorption density in competition of other water components, i.e. sulphate and phosphate, was also tested.

Figure 1 shows the arsenate adsorption density on GFH and on freshly prepared ferric hydroxide (4 h old). The adsorption on freshly prepared ferric hydroxide is somewhat greater, but the difference is quite small. Apparently, granulation does not lead to a considerable decrease in adsorption capacity. At a residual arsenate concentration of 0.13 μmol/L and pH 7 adsorption density on GFH is 1 mmol/g Fe. Arsenate adsorption decreases with pH, which is typical for anion adsorption.

The influence of other anions on arsenate adsorption was tested with sulphate and phosphate. The competition of phosphate is of particular interest, as phosphate is known to adsorb quite well on ferric hydroxide [7], and is often present in higher concentrations than arsenate in ground water. In this way, phosphate should substantially reduce arsenate adsorption.

Figure 2 shows the influence of sulphate on arsenate adsorption at initial concentrations of 2 and 10 mmol/L. At a residual arsenate concentration of 0.13 μmol/L adsorption density is only reduced below pH 7, compared to a model system without sulphate. Nonetheless, the competing effect of sulphate is not very strong.

The competition of phosphate on arsenate adsorption was tested by batch tests at various initial molar ratios (IMR) of phosphate to arsenate. The IMR varied between 0 (no phosphate) and 20. Figure 3a shows the results of the test sets. Arsenate adsorption density decreases with the IMR, showing
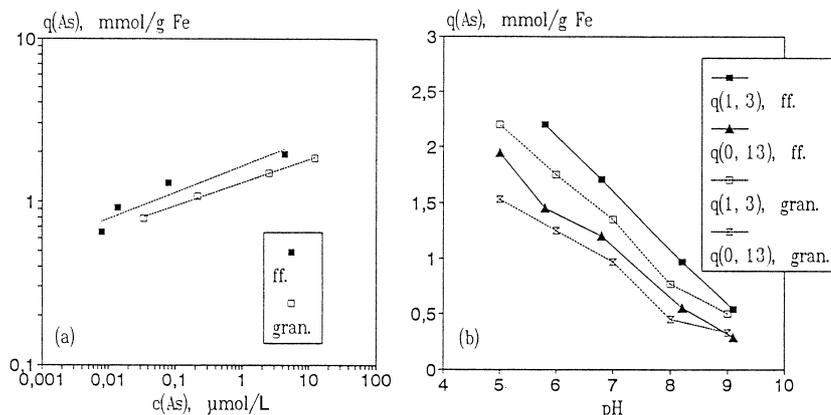

Fig. 1 Arsenate adsorption density q (As) on GFH (gran.) and on freshly prepared ferric hydroxide (ff.) at residual concentrations of 0.13 and 1.3 μmol/L in the pH range 5–9.

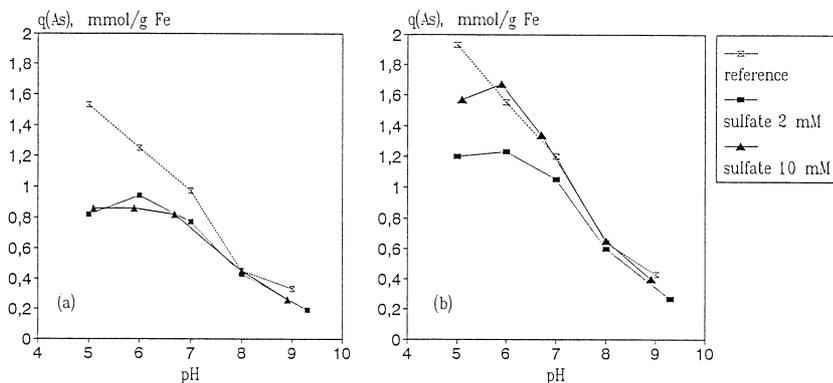**Fig. 2** Arsenate adsorption density q (As) with sulphate as competing anion. Residual arsenate concentrations (a) 0.13 μmol/L and (b) 0.5 μmol/L.
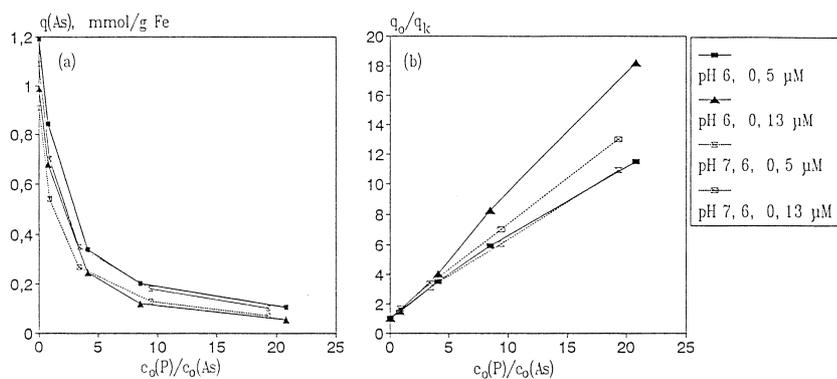

Fig. 3 Competition of phosphate on arsenate adsorption on GFH at various pH and residual concentrations. (a) Arsenate adsorption density *9* (As) at different initial molar ratios (IMR) of phosphate to arsenate. (b) Linearised plot of the ratios of adsorption densities vs. IMR.

a hyperbolic dependence. A linearisation is plotted in Fig. 3b, where the ratios of q_0 to q_k, that are the adsorption densities without and with phosphate added, are used as ordinate parameter. The linearisation is quite good, but the gradients differ in the range of 0.5–0.8. The gradient values are < 1 and imply that the adsorption of phosphate is quite lower than that of arsenate. This corresponds to the results of Ryden *et al.* [8], who found a higher adsorption density of arsenate on hydrous ferric hydroxide gel with equimolar addition of arsenate and phosphate. Phosphate competes strongly with arsenate, and in this way phosphate is the major water constituent, which reduces arsenate removal with GFH.

Arsenate adsorption in natural waters

Arsenate removal was tested with two types of natural water. The results of the batch experiments and an adsorber test with Berlin tap water, as well as pilot studies at three water facilities in Germany, all having some arsenic, are presented here.

As Berlin tap water (BTW) has an arsenic concentration below 2 μg/L, arsenate was added in the experiments. Berlin tap water has a pH of 7.7 and contains some calcium (3 mmol/L), sulphate (1.5 mmol/L), phosphate (6 μmol/L) and 3–4 mg/L dissolved organic carbon. The arsenate concentration in the filter test was 1.3 μmol/L, this results in a molar ratio of phosphate to arsenate of nearly 5.

The results of batch adsorption tests are given in Fig. 4. The tests were carried out with two initial molar ratios of phosphate to arsenate, the first with the natural phosphate content (IMR 0.16), the second with added phosphate, leading to an IMR of 5. The adsorption densities without added phosphate are only about 50% of the model system at a given pH in Fig. 1. With added phosphate (IMR 5), the adsorption density decreases to 0.18 mmol/g Fe at pH 7.7, the natural pH of BTW. Thus, we can conclude that the effective adsorption density in natural water is only 10–20% of that in model systems without competing ions. For BTW, the value of 0.18 mmol/g Fe results in an arsenic content of GFH of 8.5 g/kg.

Fixed bed adsorber tests were performed with natural water, to verify the data from the batch tests and to show the performance of the arsenic removal with GFH. Fixed bed adsorbers with GFH operate like conventional filters with a bed of GFH and a downward water flow. The technique is comparable to that of granular activated carbon.

The first test was performed with Berlin tap water in an adsorber consisting of two in-line columns. The GFH in the adsorbers had a grain size of 0.2–0.4 mm. Berlin tap water was spiked with arsenic to an inflow concentration of 100–180 μg/L. The influent and effluent arsenic concentrations are given in Fig. 5. In the first column, the concentration limit of 10 μg/L was reached after 20 000 bed volumes, and did not increase until 30 000 bed volumes were treated. In the following period,
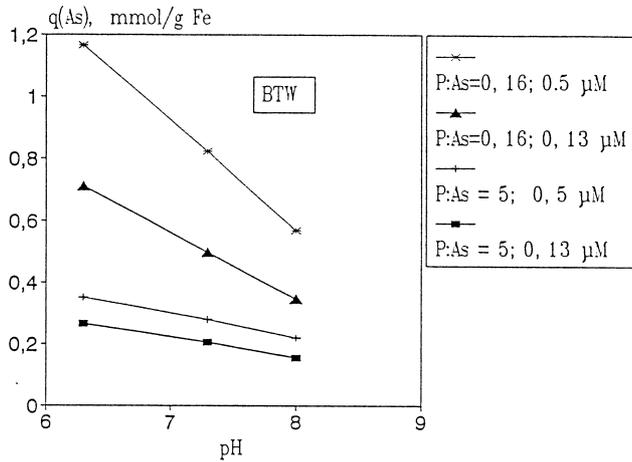
Fig. 4 Arsenate adsorption on GFH in Berlin tap water at two IMR of phosphate to arsenate vs. pH. Adsorption densities vs. pH at residual concentrations of 0.13 and 0.5 μmol/L are given.

the concentration increased, but the average adsorption of arsenate was more than 50%. The effluent concentrations of the second segment reached the concentration limit of 10 μg/L at the end of the test. When referring to both segments, 34 000 bed volumes were treated. The arsenic content in the spent GFH was 13 g/kg in the first segment and 3.7 g/kg in the second, which gives an average content of 8.4 g/kg. This value is equal to that from the batch adsorption test. The specific mass of spent adsorbent was 20.5 g/m^3 dry weight or 38 g/m^3 wet mass. The latter value is the mass for waste disposal.

Pilot studies were carried out with natural ground water from the Buntsandstein formation in the southern part of Lower Saxony, Germany. The first test at water facility SD had raw water with a pH of 7.8 and an arsenic concentration of 21 μg/L. The results of these continuous adsorbance tests are shown in Fig. 6. The arsenic concentration in treated water increased from nearly 1 μg/L to 9 μg/L when 37 000 bed volumes were treated. After a break of 10 days, the effluent arsenic concentration was 5 μg/L at the beginning and reached nearly 10 μg/L
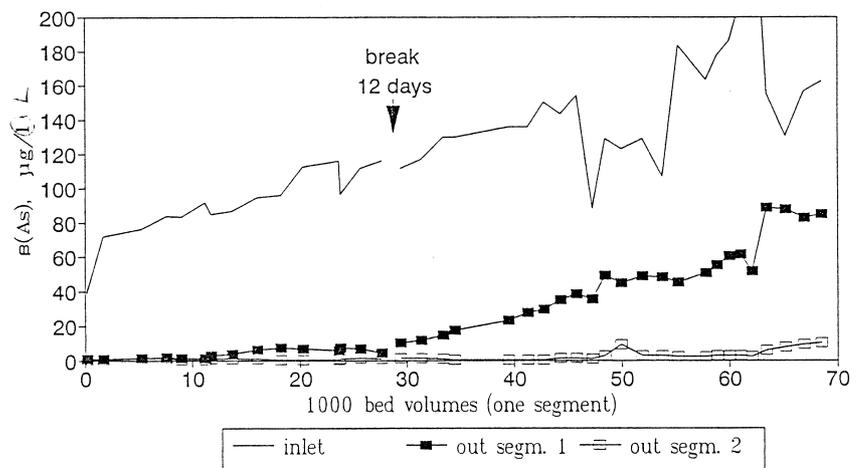

Fig. 5 Arsenic concentrations of a fixed bed adsorber with GFH and raw water BTW, spiked with arsenate. Bed height in each segment was 0.12 m and the filter rate was 6–10 m/h.
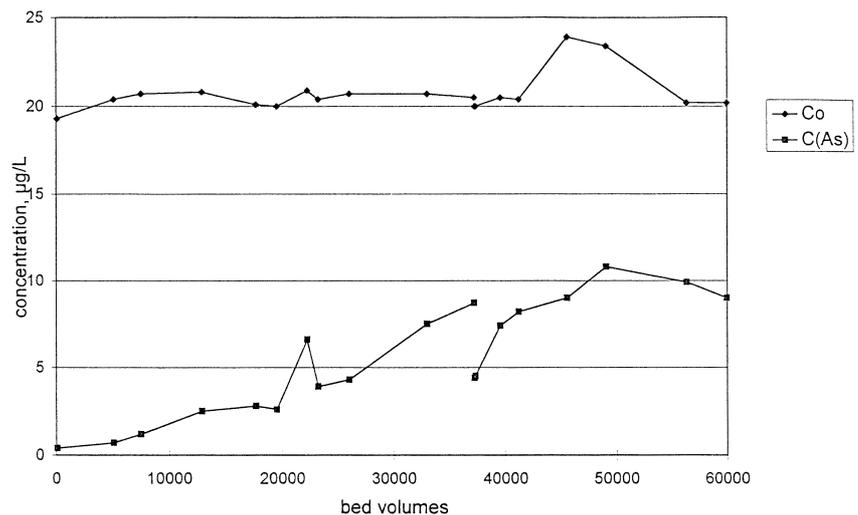

Fig. 6 Arsenic concentration of a fixed bed adsorber with GFH at water facility SD. Filter rate was 7.6 m/h and the bed height 0.16 m.
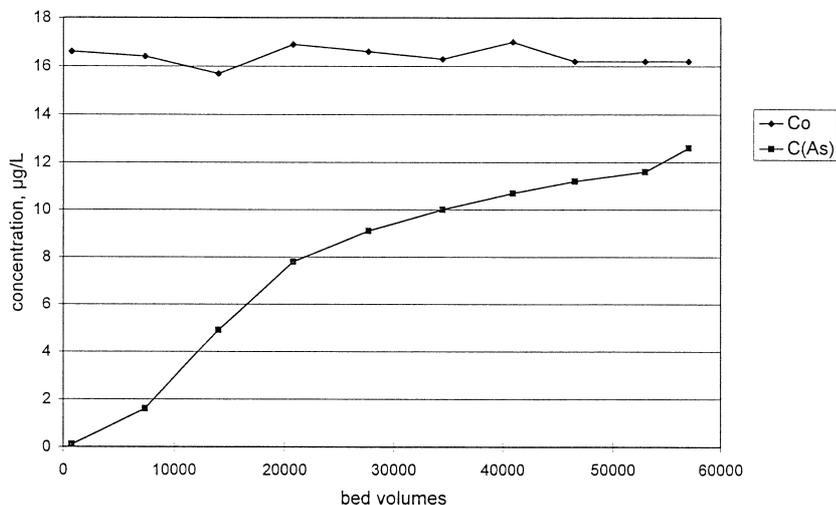
Fig. 7 Arsenic concentrations of a fixed bed adsorber with GFH at water facility HM. Filter rate was 5.7 m/h and the bed height 0.15 m.

after 60 000 bed volumes. The filter rate throughout the test was 7.6 m/h and the bed height was 0.16 m. This resulted in 25 s effective contact time. The arsenic content in spent GFH was 1.4 g/kg and the specific mass of spent GFH was 26 g/m^3 (wet) or 12 g/m^3 dry weight.

Another fixed bed adsorber was tested in the water facility HM. The raw water at this site had a pH of 8.2 and an arsenic content of 16 μg/L. The influent and effluent arsenic concentrations are given in Fig. 7. The arsenic content of the treated water rose to 8 μg/L at 20 000 bed volumes and then to 12 μg/L at 58 000 bed volumes. The maximum contaminant level of 10 μg/L was reached after 34 000 bed volumes. The specific lifetime of the adsorbence GFH is reduced to that which has

been observed at the SD facility, but the decrease is low when we include the higher pH.

A bed height of 0.15 m in this test, in addition to the 0.16 or 0.24 m of the other adsorbance filters, is rather low and does not resemble the bed heights of technical scale equipment. In the test at facility HM the filter rate was 5.7 m/h and the effective contact time was 32 s. Spent GFH had an arsenic content of 0.8 g/kg. The specific mass of the spent GFH was 33 g/m^3 (wet) or 18 g/m^3 dry weight.

A complete analysis of the raw and treated water showed that the water characteristic was not altered apart from the removal of arsenic and phosphate.

A pilot plant test at a third water facility was recently completed. The equipment was made up of two in-line adsorbers. The raw water at facility W had a pH of 7.6 and an arsenic content of 15–18 μg/L. The bed height was 0.30 m in the first adsorber and 0.52 m in the second. The filter rate was adjusted to 15 m/h. The results are presented in Fig. 8. The adsorber test lasted for more than 6 months and gave a specific capacity of more than 80 000 bed volumes at a maximum effluent arsenic concentration of 7 μg/L. This test showed a better performance of the arsenic removal with GFH when the bed height in the adsorber was increased. Nonetheless, the conditions for arsenic removal at facility W were poor compared with the other facilities, because of the higher concentration of phosphate.

Data of water chemistry and the results from the adsorber studies at the four sites are given in Table 1.
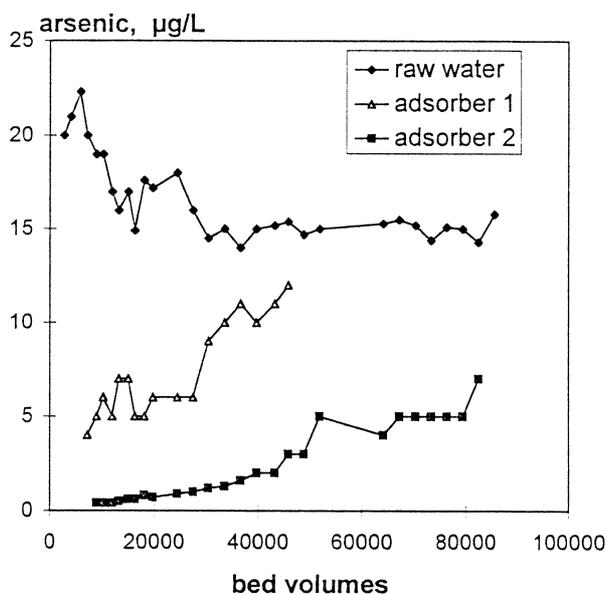
CONCLUSIONS

Granular ferric hydroxide is an effective adsorbent for arsenate removal. The adsorption density in model systems without competing water constituents is in the range of 1 mmol As/g Fe at a residual concentration of 10 μg/L and a pH of 7. It is reduced with increasing pH and phosphate content. The adsorption density in natural water is 10–20% of this value,

Fig. 8 Arsenic concentrations of a pilot plant test with two adsorbers in line at water facility W. Bed height was 0.30 m in the first adsorber and 0.52 m in the second.

Table 1 Data of the adsorbent tests and the pilot plant studies

	unit	BTW	SD	HM	W
Raw water parameters					
pH			7.8	7.8	8.2	7.6
Arsenic concentration	μg/L	100–180	21	16	15–20
Phosphate concentration	μg/L	0.70	0.22	0.15	0.30
IMR (P/As)		5	7	6	16
Conductivity	μS/cm	780	480	200	460
Adsorption capacity for arsenic (batch test)	g/kg	8.5	4.5	3.2	n.d.
Adsorber			.		
Bed height	m	0.24	0.16	0.15	0.82
Filter rate	m/h	6–10	7.6	5.7	15
Specific treatment capacity	BV	34 000	37 000	32 000	85 000
Max. effluent arsenic concentration	μg/L	10	10	10	7
Arsenic content of GFH	g/kg	8.5	1.4	0.8	1.7
Specific mass of spent GFH (dry weight)	g/m^3	20.5	12	18	8.6

n.d.: not determined

depending on the pH and the amount of phosphate. In fixed bed adsorbers, the effluent arsenic concentration of 10 μg/L was not exceeded, and the specific capacity was more than 30 000 bed volumes.

The specific capacity of fixed bed adsorbers with GFH depends on pH, phosphate content and on the raw water concentration of the arsenate. It has been shown that in technical scale adsorbers more than 50 000 bed volumes can be treated, and filter rates of 15 m/h are possible. This corresponds to lifetimes of GFH of at least several months.

The specific residual mass depends on the adsorption density and the raw water concentration. Typical values are in the range of 5–25 g/m treated water. The residue is a solid with an arsenic content of 1–10 g/kg. A treatment for leaching arsenic and the regeneration of GFH seems possible, but it leads to an alkaline solution with arsenate and requires a further treatment to obtain a solid waste. Thus, a direct deposition of spent GFH as dangerous waste should be favoured.

The new adsorption technique with GFH is a simple and safe method for arsenic removal from natural water, particularly for small water facilities. The research on this method continues to benefit from technical scale adsorption reactors and the production of GFH.

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