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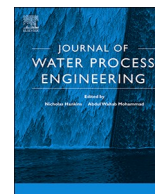
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# Using an adsorption isotherm framework to classify removal efficiency of arsenic in full-scale groundwater treatment plants



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## ABSTRACT

Arsenic is mainly removed from groundwater by adsorption onto, or co-precipitation with iron flocs and -deposits. The efficiency of this process depends on various factors, amongst which the oxidation state of arsenic, adsorption competition or poor iron floc removal.

The aim of this study was to assess the adsorption efficiency of arsenic in full-scale groundwater treatment plants in the Netherlands. Adsorption efficiency is dependent on the concentration of adsorbent (Fe) and adsorbate (As), both of which vary considerably at the various treatment plants. To allow comparing treatment plants at these different Fe and As concentrations, the framework of a linearized isotherm graph was used.

As a reference, jar tests were executed to derive adsorption isotherms of As(III) and As(V) based on co-removal with Fe<sup>2+</sup> precipitation.

All treatment plants have a higher adsorption efficiency than the As(III) reference, and lower adsorption efficiency than the As(V) reference. Treatment plants with an efficiency close to the As(III) reference may suffer from incomplete arsenic oxidation, although other causes cannot be ruled out. Classifying removal efficiency can be used in an initial research phase to identify treatment plants with relatively poor performance as candidates for improvement. Furthermore, treatment plants can be grouped into categories with similar adsorption efficiency, aiding in identification of common factors responsible for As removal.

## 1. Introduction

Arsenic (As) contaminated ground waters can be found worldwide, and are a serious health hazard in, for example, India and Bangladesh [1]. In contrast, arsenic concentrations in Dutch ground waters are often already below the WHO guideline of 10 µg/L, and are reduced further during treatment. It is possible that this guideline could be lowered in the future, and in order to be prepared, drinking water companies investigate if As concentrations in treated water can be reduced to below 1 µg/L.

The main removal mechanism for As during passive groundwater treatment, i.e., aeration-filtration, is by adsorption onto, or co-precipitation with iron (Fe) flocs or deposits. In well-aerated groundwater, Fe flocs are typically formed in the water phase, while with limited aeration and at relatively low pH values, Fe tend to form deposits onto the filter material [2].

In adsorption processes in general, the adsorbent loading ( $q_e$ ) at equilibrium decreases, when a low adsorbate concentration in the water

phase ( $C_e$ ) is reached. In other words, the native groundwater Fe is less effectively used (i.e. has a lower density of adsorbed As) when aiming at lower As concentrations ( $C_e$ ). Besides this inherent aspect of adsorption, the water composition can affect As adsorption as well. Phosphate, silicate or organic matter can compete with As for adsorption sites [3–6], or can prevent effective iron floc formation [7,8].

As is originally present in groundwater as its reduced form, As(III), but when it is oxidized to As(V), its adsorption onto Fe oxides improves considerably [9–11]. Although the oxidation of As by oxygen is slow, it was found that within sand filters, As can be effectively oxidized by bacteria [12,13].

The aim of this study was to assess the adsorption efficiency of As in full-scale passive aeration-filtration groundwater treatment plants in the Netherlands. Adsorption efficiency is dependent on the concentration of adsorbent (Fe) and adsorbate (As), both of which vary considerably at the various treatment plants. To allow comparing treatment plants at these different Fe and As concentrations, the framework of a linearized isotherm graph was used.

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**Table 1**  
Number of Fe and As measurements in groundwater and treated water per site.

Groundwater		Treated water	
# Fe measurements	# As measurements	# Fe measurements	# As measurements
6 - 21	1 - 8	21 - 22	6 - 7

Our modelling approach is to consider each treatment site as an adsorption batch reactor, where a unique  $C_e$  and  $q_e$  are reached in the treated water. In addition, a series of supplementary jar tests with either As(III) or As(V) were carried out as a reference with known oxidation state for As.

## 2. Materials and methods

### 2.1. Database

The database was provided by Vitens water company, and includes data from 75 treatment sites with a wide range in groundwater compositions (collected in 2016). The quantity of Fe or As measurements varied per site, with more intensive and consistent measuring programs for treated waters as compared to groundwaters (Table 1).

Sites were excluded when the average raw groundwater contained either (i) As below 0.2 µg/l or Fe below 0.3 mg/l (35 sites), or (ii) water quality varied widely (amongst others due to mixing of different groundwater wells; 7 sites). After exclusion, 33 sites remained for further elaboration. In the raw groundwater of these sites, Fe concentrations ranged from 0.2 to 8.4 mg/l (average 2.4 mg/l), As from 0.11 to 20.4 µg/l (average 2.7 µg/l), PO<sub>4</sub> from 0.02 to 1.0 mg/l (average 0.3 mg/l), TOC from 0.2 to 8.8 mg/l (average 2.4 mg/l) and pH from 6 to 8 (average 7.2). The water treatment schemes at these sites varied from basic aeration-filtration alone, to inclusion of pellet softening, activated carbon filtration or split stream treatment with reverse osmosis. However, in none of the water treatment schemes a chemical oxidant was applied.

### 2.2. Isotherm approach

The arsenic concentration in the treated water is considered as the equilibrium concentration,  $C_e$ . Equilibrium loading ( $q_e$ ) of the iron flocs is calculated according to Eq. 1. The isotherm graph is linearized by taking the logarithm of  $C_e$  and  $q_e$ .

$$q_e = \frac{\Delta As}{\Delta Fe} = \frac{As_{groundwater} - As_{treated\ water}}{Fe_{groundwater} - Fe_{treated\ water}} \quad (1)$$

### 2.3. Supplementary jar tests

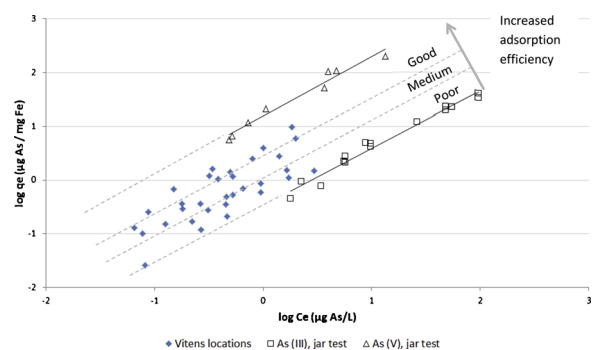
Fe<sup>2+</sup>, As(III) and As(V) were dosed as FeSO<sub>4</sub>·7H<sub>2</sub>O, NaAsO<sub>2</sub>, HAsNa<sub>2</sub>O<sub>4</sub>·7H<sub>2</sub>O. These chemicals were obtained as powder from Sigma-Aldrich/Merck, with a purity of at least 90%.

For the jar test, Delft tap water was used after adjusting the pH to 7, where HCl was used for pH adjustment. The main characteristics of this water are shown in Table 2.

Fe doses were varied between 0.5–2 mg Fe/l, and the dose for As(III) or As(V) varied between 5–50 µg/l. Fe and As were analysed after filtration over 0.45 µm by ICP-MS (PlasmaQuant MS, Analytik Jena) at

**Table 2**  
Composition of Delft tap water.

HCO <sub>3</sub> <sup>-</sup> (mg/l)	Cl <sup>-</sup> (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	NO <sub>3</sub> <sup>-</sup> (mg/l)	Na <sup>+</sup> (mg/l)	Ca <sup>2+</sup> (mg/l)	Mg <sup>2+</sup> (mg/l)	Fe (µg/l)	HPO <sub>4</sub> <sup>2-</sup> (mg/l)	pH (adjusted)
121	70	58	10	45	46	8	< 5	< 0.02	7.0



**Fig. 1.** Adsorption isotherms for As(III) (squares), As(V) (triangles) and individual data points of the full scale treatment site within the isotherm matrix (diamonds). Parallel zones with similar adsorption efficiency are indicated by dashed grey lines.

the start of a jar test, and after a contact time of 60 min. While previous jar tests showed that this was sufficient time for complete flocculation [14], it is relative long as compared to contact times in practice. During the jar test, a mixing rate of 60 RPM was maintained, and the experiments were carried out at room temperature.

## 3. Results and discussion

Both the data points of individual treatment sites, and of the adsorption isotherms obtained by the jar tests are included in Fig. 1. With the adsorption isotherm for As(V), higher equilibrium loadings ( $q_e$ ) are found as compared to As(III), when reaching a similar equilibrium concentrations ( $C_e$ ). This indicates that As(V) adsorbs more efficiently to iron flocs than As(III), which is in-line with previous research [9–11]. Furthermore, it can be observed that the linearized adsorption isotherms for As(III) and As(V) are in parallel. According to Pikaar et al., the slope of a linearized isotherm depends on the heterogeneity of adsorption sites on the adsorbent surface, while the adsorption affinity of the adsorbate affects the vertical position of the isotherm [15]. For the parallel isotherms of As(III) and As(V), this would imply that both have access to the same number of sorption sites, and that As(V) has a higher adsorption affinity with the Fe oxide surface than As(III).

The data points of individual treatment sites are found to be higher than the isotherm of As(III). This could indicate that a base level of As oxidation occurred, possibly due to reaction with an intermediate Fe species that is formed during Fe oxidation [16].

However, none of the treatment sites show As adsorption as efficient as the theoretical isotherm of As(V). One of the reasons could be incomplete As(III) oxidation during treatment. Acceleration of As(III) oxidation early in the treatment chain could solve this problem, and aid in the more effective use of adsorption sites on the precipitated Fe. In addition, adsorption of As might also be hindered by e.g. adsorption competition, premature loss of Fe in a softener, or less effective Fe floc formation. Furthermore, the iron hydroxides present in rapid sand filters are probably more aged than the iron hydroxides flocs formed during the jar tests, which could also contribute to the higher As(V) removal observed in the jar tests, as compared to the treatment locations.

The results in Fig. 1 are insufficient to explain differences in arsenic adsorption efficiency, but it could be useful to classify them. The region between the As(III) and As(V) isotherms can be divided in (arbitrary)

parallel zones, as shown by the dashed grey lines in Fig. 1. Data points within a zone represent treatment sites with similar adsorption efficiency, and a guided attempt can be made to find similarities between treatment sites within the same zone, or differences between treatment sites with low and with high adsorption efficiency.

#### 4. Conclusions

The linearized adsorption isotherms for As(III) and As(V) both had a similar slope, with As(V) showing more effective removal than As(III). These isotherms can be considered to be boundary conditions for As removal in passive aeration-filtration systems, without application of a chemical oxidant. Groundwater treatment was simplified as an adsorption batch reactor, with a unique equilibrium concentration ( $C_e$ ) and loading ( $q_e$ ) for each treatment site. It was found that these data points for each treatment site are between the adsorption isotherm for As(III) and As(V). It is possible to classify the adsorption efficiency at the treatment sites based on its affinity to either the As(III) or As(V) isotherm. Classifying removal efficiency can be used in an initial research phase to identify treatment plants with relative poor performance as candidates for improvement. Furthermore, treatment plants can be grouped into categories with similar adsorption efficiency, aiding in the identification of common factors responsible for As removal, including water quality matrix, applied treatment technologies or operational modes.

#### Declaration of Competing Interest

None.

#### Acknowledgement

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