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Electrochemical arsenite oxidation for drinking water treatment: Mechanisms, by-product formation and energy consumption

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ABSTRACT

The mechanisms and by-product formation of electrochemical oxidation (EO) for As(III) oxidation in drinking water treatment using groundwater was investigated. Experiments were carried out using a flowthrough system, with an RuO_2/IrO_2 MMO Ti anode electrode, fed with synthetic and natural groundwater containing As(III) concentrations in a range of around 75 and 2 μg/L, respectively. Oxidation was dependent on charge dosage (CD) [C/L] and current density [A/m^2], with the latter showing plateau behaviour for increasing intensity. As(III) concentrations of <0.3 μg/L were obtained, indicating oxidation of 99.9 % of influent As(III). Achieving this required a higher charge dosage for the natural groundwater (>40 C/L) compared to the oxidation in the synthetic water matrix (20 C/L), indicating reaction with natural organic matter or other compounds. As(III) oxidation in groundwater required an energy consumption of 0.09 and 0.21 kWh/m^3, for current densities of 20 and 60 A/m^2, respectively. At EO settings relevant for As(III) oxidation, in the 30–100 C/L CD range, the formation of anodic by-products, as trihalomethanes (THMs) (0.11–0.75 μg/L) and bromate (<0.2 μg/L) was investigated. Interestingly, concentrations of the formed by-products did not exceed strictest regulatory standards of 1 μg/L, applicable to Dutch tap water. This study showed the promising perspective of EO as electrochemical advanced oxidation process (eAOP) in drinking water treatment as alternative for the conventional use of strong oxidizing chemicals.

1. Introduction

Electrochemical water treatment technologies have been gaining considerable interest in recent years, providing a promising alternative to conventional chemical-driven processes. Electrochemical oxidation (EO), being one of the electrochemical technologies of interest, has shown potential to replace the use of (strong) oxidizing chemicals such as $KMnO_4$, HOCl, H_2O_2/UV and O_3, for removal of organics and micropollutants, and for disinfection purposes (Bergmann and Koparal, 2005; Najafinejad et al., 2023; Radjenovic et al., 2011; Rajab et al., 2015). While a range of EO techniques exists, anodic oxidation (AO) is arguably considered most popular and applicable from a practical perspective (Moreira et al., 2017). In AO, contaminants are oxidized following two main pathways; (1) direct surface oxidation by electron transfer, and (2) indirect oxidation by generated oxidizing agents. With the latter being split up in; (2.1) indirect oxidation by OH radicals attached to and/or in close vicinity of the electrode's surface, and (2.2) indirect oxidation by generated oxidizing agents from ions available in the bulk solution (e.g. chlorine from chloride) (Panizza and Cerisola, 2009) (Fig. 1). Innovation in AO mostly focusses on the selection and improvement of electrode materials, with boron doped diamond (BDD) and mixed metal oxide (MMO) based electrodes being favoured due to their stability and broad availability (Moreira et al., 2017; Najafinejad et al., 2023). Interestingly, the use of RuO_2/IrO_2-coated Titanium (Ti) MMO electrodes is gaining preference over BDD electrodes due to relatively low production costs and process scalability. However, the active behaviour and the low chlorine evolution overpotential of the MMO electrodes has a significant downside related to the potential formation of unwanted chlorinated by-products (Radjenovic et al., 2011).

While AO has extensively been studied for the removal of (in)organic trace contaminants and disinfection purposes (e-disinfection), limited attention is given to groundwater-based drinking water treatment. Due to its carcinogenic nature, the presence of arsenic, and especially its

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reduced species arsenite (As(III)), is considered as one of the biggest threats to drinking water production from groundwater (Kapaj et al., 2006; Sodhi et al., 2019). Over 94 million people worldwide are exposed to arsenic contaminated groundwaters with concentrations in produced drinking water exceeding regulations (Podgorski and Berg, 2020), regarding a 10 μg/L total arsenic guideline (Directive (EU) 2020/2184; WHO, 2022). Additionally, Dutch drinking water companies are now aiming for even lower targets (<1 μg/L) due to potential negative health effects below 10 μg/L (Saint-Jacques et al., 2018; Van der Wens et al., 2016). Studies have shown that oxidation of the neutrally charged As(III) to the negatively charged arsenate (As(V)) is key for effective removal of total arsenic, ranging from subsequent removal by membrane technologies to adsorption to (groundwater native) iron (Bissen and Frimmel, 2003; Dixit and Hering, 2003). Hence, while stand-alone As(III) oxidation technologies do not remove arsenic, they do play a crucial role in the removal process of total arsenic for the production of safe drinking water. Despite some studies showing the potential of As(III) oxidation by AO (Lacasa et al., 2012; Sorlini et al., 2023; Wang et al., 2010), insights in relevant mechanisms and relevant settings from a water engineering perspective, such as charge dosage (electrical charge) and current density, are lacking. Additionally, it is yet unknown to what extent the treatment by AO induces undesired side effects. When applying advanced oxidation processes (AOPs) in drinking water treatment it is crucial to be aware of potential by-products (e.g., trihalomethanes, bromate), as they may be as harmful to human health as the target contaminant (WHO, 2022; Yeom et al., 2021). The formation of anodic by-products when oxidizing arsenic could potentially replace one unwanted carcinogenic contaminant with another, or even introduce a range of carcinogenic contaminants. To align with existing literature on AOP in the drinking water context, it is proposed to use the term ‘electrochemical advanced oxidation process’ (eAOP) for anodic oxidation. Besides mitigation of AOP by-products, the reliability of produced non-chlorinated drinking water, in terms of microbial stability, should be considered. Aforementioned perspectives urge research to investigate potential formation of by-products, besides eAOP’s relevant mechanisms in As(III)-relevant conditions.

In this paper, mechanisms of As(III) oxidation by eAOP, related to the behaviour of operational parameters as charge dosage and current density, were investigated. Experiments were performed in synthetic water and natural groundwater, containing environmentally relevant As(III) concentrations ranging from relatively high (±75 μg/L) to low (±2 μg/L). For eAOP in natural groundwater the formation of unwanted (potentially) harmful by-products, as chlorinated and brominated organics and bromate, were tracked. Additionally, its effect on microbial stability of the water, expressed as assimilable organic carbon (AOC) (Van der Kooij, 1992), was investigated. These insights contributed to improved understanding of ongoing processes and gave a relevant perspective on the applicability of eAOP in (non-chlorinated) drinking water treatment.

2. Materials and methods

2.1. Water quality and chemicals

Two types of water were used in the experiments; (1) synthetic water, and (2) natural groundwater. The chemical composition of the groundwater used in the experiments, obtained from a Managed Aquifer Recharge and Recovery (MARR) site, can be found in Appendix A (Table A.1). Note that the groundwater, being collected shortly before the experiments and stored at 7 °C, naturally contained 1.75 ± 0.31 μg/L As(III). The synthetic water was prepared by adding lab-grade sodium chloride (NaCl) and sodium bicarbonate ($NaHCO_3$) (J.T. Baker) to demineralised water to mimic general groundwater characteristics (regarding conductivity and pH) (Table A.2). When needed, the synthetic water and groundwater were spiked with lab-grade sodium (meta) arsenite ($NaAsO_2$) (Sigma-Aldrich) to the desired As(III) concentration of approximately 75 μg/L As(III) just prior the experiment. Spiking with the environmentally-relevant concentration of 75 μg/L As(III) allowed for observable oxidation trends while ensuring feasible operational eAOP settings.

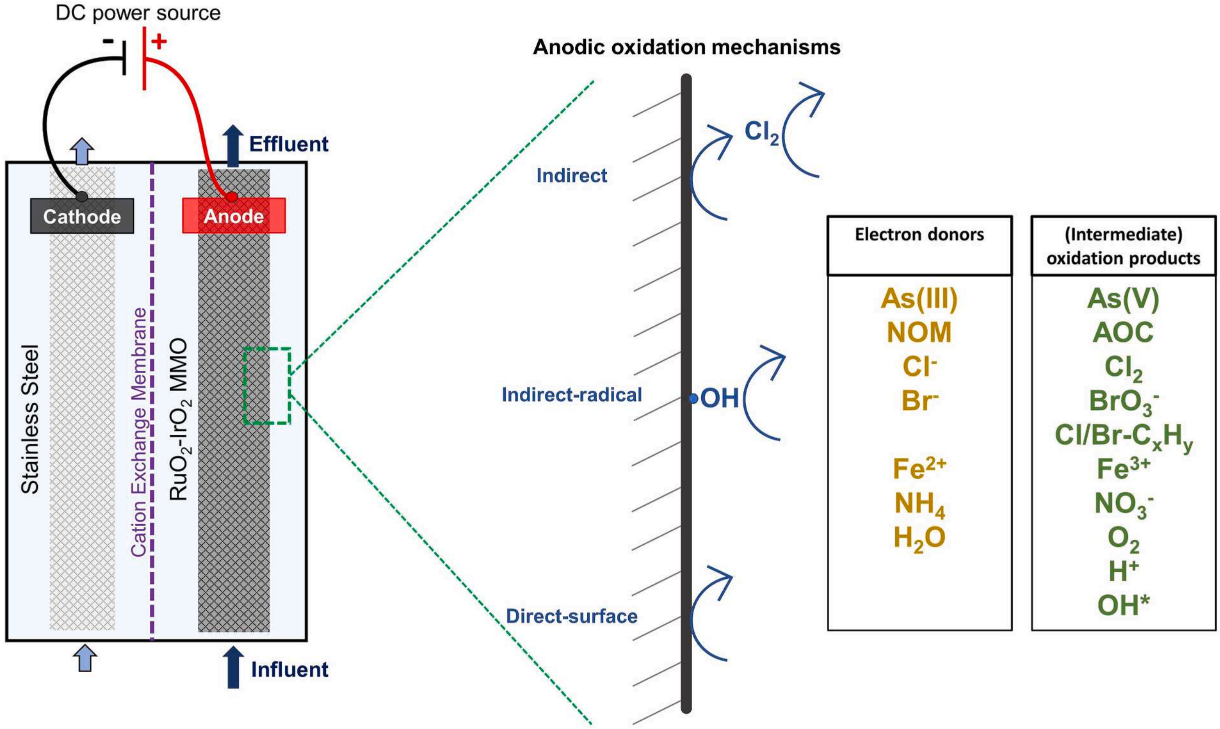

Fig. 1. eAOP system overview and ongoing anodic oxidation mechanisms, including investigated electron donors and (intermediate) oxidation products. MMO: Mixed Metal Oxide.

2.2. eAOP reactor

The eAOP reactor consisted of an anodic and a cathodic chamber (200 mL each), separated by a cation exchange membrane (CEM, Membranes International Inc.) (Fig. 1). Mesh shaped RuO_2/IrO_2-coated titanium (Magneto, Schiedam, 100 cm^2) and stainless steel (Type 316, 100 cm^2) electrodes were used as anode and cathode respectively. The electrodes were fully immersed when the chamber was filled with water. The current (I) [A: C/s], supplied to the electrolysis cell by a DC power source (TENMA 72–10,500), set the current density [A/m^2: $C/s/m^2$], representing the intensity of the electrons [C] that per time interval [s] passed the electrode's projected surface [m^2]. The reactor was operated in continuous-flow mode (up-flow), with individual pumps feeding water to the bottom of the anodic and cathodic chamber at selected flowrates (Q) [L/h]. Flowrates were set based on the targeted charge dosage (CD) [C/L], being the amount of electric charge (electrons) [C] added to a certain volume of water [L].

$$\textbf{\textit{Charge Dosage}}\ (\boldsymbol{CD})\ [\boldsymbol{C}/\boldsymbol{L}] = \frac{\boldsymbol{I}}{\boldsymbol{Q}} \tag{1}$$

with I: current [A:C/s] and Q: flowrate [L/s]

The coulombic efficiency [%] quantified the extent to which the electric charge (the charge dosage) contributed to the (theoretical) targeted oxidation, using an electron balance based on Faraday's law (Eq. (2)), dividing the theoretical charge dosage over the applied charge dosage.

$$\textbf{\textit{Theoretical charge}} \left[\frac{\boldsymbol{C}}{\boldsymbol{L}}\right] = \frac{\boldsymbol{c} * \boldsymbol{NA} * \boldsymbol{e} * \boldsymbol{n}}{\boldsymbol{MW}} \tag{2}$$

with c: concentration [g/L], Na: Avogadro constant [1/mol] = 6.02214 * 10^{23}, e: elementary charge [C] = 1.6022 * 10^{-19}, n: number of electrons transferred during oxidation [-], MW: molecular weight [g/mol].

2.3. eAOP experiments

While the cathodic chamber was fed with synthetic water (cathodic feed water), the anodic feed differed based on the type of experiment (Table 1). Chlorine formation experiments (A) were executed by feeding synthetic water to the anodic chamber, measuring effluent free chlorine (Cl_2) concentrations. Experiments were performed for a range of charge dosage and current density values, with the latter being dependent on the min/max range in flowrate. A similar style of experiment was performed tracking As(III) oxidation in synthetic water spiked with As(III) (B), as charge dosage and current density increased until near-complete oxidation was achieved. Based on these results, experiments with fixed current density and variable charge dosage were performed on the As (III) oxidation in a natural groundwater matrix with spiked As(III) (C). While all experiments with spiked As(III) were performed in the lab, the As(III) oxidation experiment with natural groundwater (D) was performed directly at the source (on-site). Lastly, the formation of AOC was measured at a charge dosage relevant for As(III) oxidation, and formation of potential by-products (halogenated compounds and bromate) was investigated for a larger charge dosage range (E). The range of CD values changed for each system due to the different nature of each experiment, requiring different CDs to achieve the targeted formation of oxidation products (A), near-complete oxidation (B-D), and observable differences in formed by-products (E).

Table 1
Experimental overview of eAOP experiments, with the feed of the anodic chamber consisting of different water characteristics. Specified ranges for charge dosage [C/L] and current density [A/m^2] were given.

Experiment	Water matrix	Charge dosage [C/L]	Current density [A/m^2]
A	Synthetic	10–80	4–40
B	Synthetic + As(III)	10–30	1.5–15
C	Groundwater + As (III)	20–40	>15
D	Groundwater (on-site)	20–40	>15
E	Groundwater (on-site)	30–500	20–60

2.4. Sampling and analytical methods

Samples of reactor effluent were taken after operation of 4 times the hydraulic retention time (HRT) for the according setting. pH and dissolved oxygen (O_2) were measured using WTW electrodes (SenTix 940 and FDO925, respectively). Total free chlorine was measured using a photometric DPD free chlorine test (Spectroquant®, Sigma-Aldrich). As and Fe measurements consisted of unfiltered (direct) and filtered samples. For speciation of As(III)/As(V) an additional resin-filtered sample was taken according the Clifford method (Gude et al., 2018), passing the sample through an anion-exchange resin (Ion exchanger Amberlite IRA-402, Sigma-Aldrich). Fe and As samples were acidified to 1 v/v% HNO_3 (69 %, Rotipuran Ultra) and analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Analytikal Jena model PlasmaQuant MS). Ammonium (NH_4^+) and nitrate (NO_3^-) samples (filtered) were collected and cooled (at 7 °C), and subsequently analysed using Ion Chromatography (IC, Metrohm 881 and 883). Bromide, bromate, chlorinated and brominated products (volatile organic compounds), AOC and dissolved organic carbon (DOC) were analysed by Het Waterlaboratorium (Haarlem, the Netherlands). Bromide and bromate were analysed according the NEN-EN-ISO 10304–1 and NEN-EN-ISO 11206 standard, respectively. For bromide, samples were analysed using Ion Chromatography (IC) with an ICS-1100. For bromate, samples were analysed using high-pressure IC followed by an UV/vis-detector using a Dionex Integrion HPIC. Chlorinated and brominated products, considered as volatile organic compounds, were analysed using a headspace technique, followed by a gas chromatograph mass spectrometer (GC–MS) (Agilent, 8890 GC). Samples (43 ml) were directly acidified using 0.5 ml H_2SO_4 (2 M). AOC analysis was performed equivalent to NEN-EN-ISO 6271, as described in the study of van der Kooij et al. (1982). DOC was analysed according NEN-EN-ISO 1484, using infrared spectroscopy.

3. Results

3.1. Free chlorine formation

Continuous-flow eAOP experiments using synthetic water, i.e. demineralised water with NaCl and $NaHCO_3$, were performed, tracking the formation of free chlorine. At 10 C/L, free chlorine concentrations showed a limited increase of 0.02 mg/L when increasing the current densities from 4 to 12 A/m^2 (Fig. 2). For the CDs of 20 and 40 C/L, chlorine concentrations increased with increasing current densities from 4 A/m^2 onwards until a certain limit was reached. From this limit, chlorine concentrations stabilised, showing plateau behaviour. This plateau behaviour occurred at current densities over 16 and 21 A/m^2 for a CD of 20 and 40 C/L, respectively. CDs of 10, 20, 40 and 80 (the latter not shown in graph) C/L corresponded to observed free chlorine plateau values of 0.02 to 0.29, 0.92, 2.04 mg/L, respectively.

3.2. As(III) oxidation by eAOP in a synthetic water matrix

Synthetic water experiments using a continuous-flow eAOP system showed above 99 % oxidation of 75 ± 6 μg/L As(III) at a charge dosage of 30 C/L and current densities >7.5 A/m^2 (Fig. 3). These settings for As (III) oxidation below detection limits corresponded to HRTs below 1 min. At a CD of 10 C/L, a maximum of 37.8 ± 5.4 %, i.e. 28.0 ± 3.3 μg/L, As(III) was oxidized at current densities >12 A/m^2. Increasing current

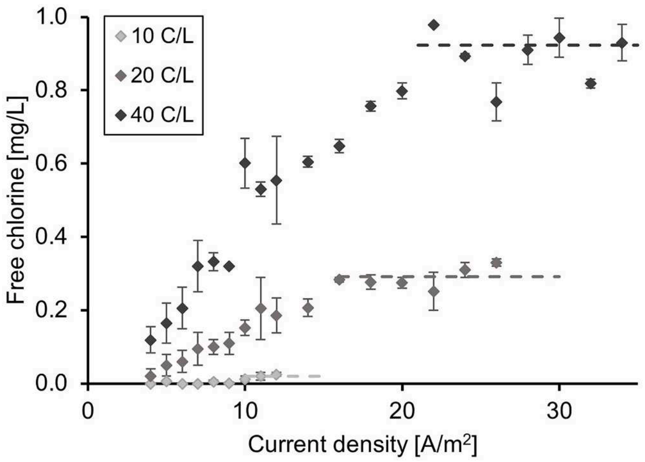

Fig. 2. Free chlorine formation for increasing current density [A/m^2], constant charge dosage (CD) [C/L], and variable flow rate (Q) [L/s] during continuous-flow eAOP in a synthetic water matrix (according Eq. (1)). The plateau behaviour at different CDs has been indicated with dashed lines.

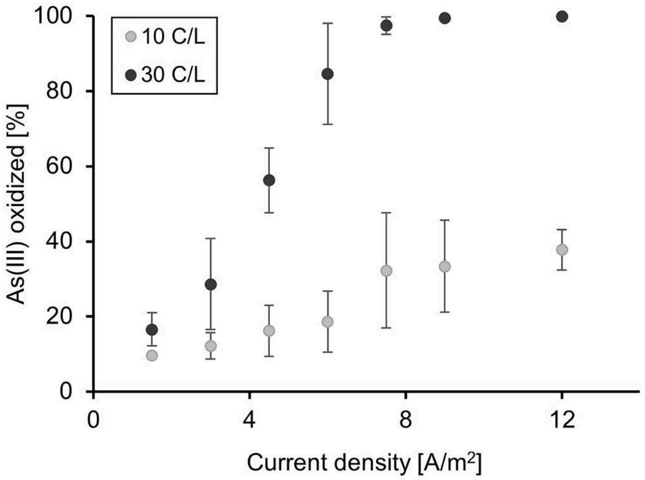

Fig. 3. As(III) oxidation for increasing current density [A/m^2] and constant Charge Dosage [C/L] in a synthetic water matrix spiked with 75 ± 6 µg/L As (III), obtained from a continuous-flow eAOP system.

densities from 2 to 7.5 A/m^2 at 30 C/L showed improved As(III) oxidation efficiency, from 16.6 ± 4.4 to 99.9 ± 0.4 %, corresponding to oxidation of 11.3 ± 3.0 and 74.1 ± 0.29 µg/L As(III), respectively. At a CD of 10 C/L, a similar effect of current density was observed as increasing current densities from 2 to 7.5 A/m^2 improved As(III) oxidation from 9.6 ± 0.1 % to 32.3 ± 15.3 %, i.e. 6.9 ± 1.0 and 24.0 ± 10.6 µg/L As(III) oxidized, respectively. eAOP showed to reduce the pH of the water from 8.13 ± 0.12 in the influent to 7.30 ± 0.05 in reactor effluent at a CD of 30 C/L.

3.3. *As(III) oxidation by eAOP in a groundwater matrix*

Natural groundwater obtained from a MARR site, spiked with 75 ± 4 µg/L As(III), contained 69.4 ± 0.6, 34.0 ± 6.2 and 10.3 ± 0.3 µg/L As (III) in eAOP effluents for CDs of 20, 30, and 40 C/L respectively (Fig. 4). These effluents correspond to approximately 14, 55 and 86 % As(III) oxidation . The groundwater naturally contained 5.02 ± 0.49 µg/L of total arsenic, of which 1.75 ± 0.31 µg/L was As(III) (Table A.1). These low As(III) concentrations are considered environmentally relevant for drinking water companies in the Netherlands, mostly treating groundwaters with As concentrations in this range. This naturally present As (III) was successfully oxidized to As(V) by eAOP, as oxidation up to 91 % was achieved at a CD of 40 C/L (Fig. 4). The naturally present As(III) was oxidized by eAOP to <0.3 µg/L at charge dosages >30 C/L. Total arsenic concentrations in the effluent proved to be constant 4.94 ± 0.60, 4.89 ± 0.61, and 4.95 ± 0.56 µg/L for the different CDs. Current densities were set above relevant plateau values for the range of CDs, at >15 A/m^2 for CDs ≥20, and >25 A/m^2 for CDs ≥30 C/L, in aforementioned groundwater experiments. At a CD of 20 C/L, pH decreased from 8.72 ± 0.06 in the influent to 8.16 ± 0.03 in the effluent of the reactor.

3.4. *eAOP by-product formation*

3.4.1. *Chlorinated and brominated organic oxidation products*

eAOP can lead to chlorination and/or bromination of naturally present organic matter (Forés et al., 2023; Radjenovic et al., 2011). Due to the carcinogenicity of the resulting by-products, these are strictly regulated in drinking water treatment practice (Directive (EU), 2020). WHO and EU guidelines for chlorinated drinking water include a broad range of potential by-products, while in the Dutch drinking water directive (Wettenbank, 2022) even stricter targets are used for non-chlorinated tap water (Table 2). Influent water, i.e., groundwater water, showed the absence of THMs (trichloromethane, dibromochlorimethane, dichlorobromomethane, and tribromomethane) and other halogenated compounds, with concentrations below detection limits. eAOP at CDs of 30, 100 and 500 C/L showed formation of 0.11 ±

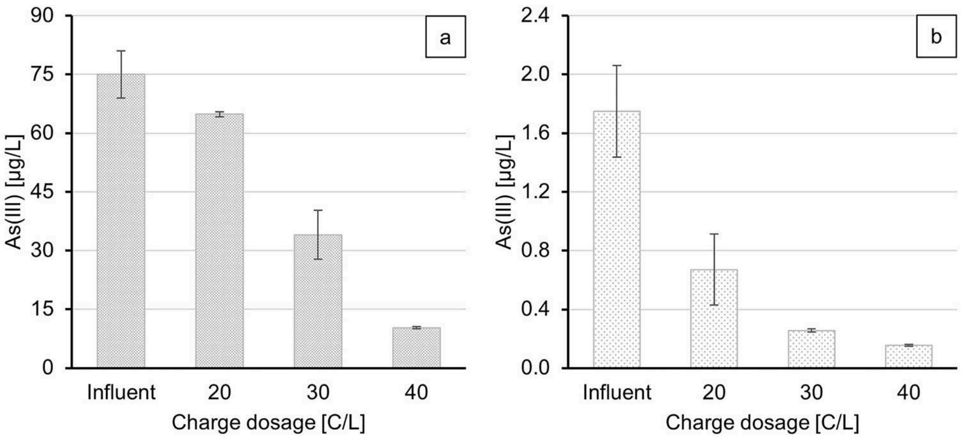

Fig. 4. Effluent As(III) concentrations for a continuous-flow eAOP reactor for a range of charge dosages in groundwater spiked with 75 µg/L As(III) (a) and groundwater naturally containing 1.75 µg/L As(III) (b).

Table 2
Concentrations of chlorinated and brominated (halogenated) organic compounds in groundwater during continuous-flow eAOP experiments, at variable charge dosage [C/L]. When present, Dutch, EU, and WHO standards were reported.

Components [μg/L]	Influent	30 C/L	100 C/L	500 C/L	Regulatory limit
Trichloromethane (chloroform)	<0.02	0.03 ± 0.01	0.10 ± 0.01	1.25 ± 0.05	300[c]
Tribromomethane (bromoform)	<0.02	<0.02	0.22 ± 0.02	2.55 ± 0.35	100[c]
Dibromochloromethane	<0.02	0.04 ± 0.01	0.23 ± 0.02	1.95 ± 0.15	100[c]
Bromodichloromethane	<0.02	0.04 ± 0.00	0.21 ± 0.01	2.35 ± 0.15	15[a*], 60[c]
Sum Trihalomethanes (THMs)	<0.02	0.11 ± 0.01	0.75 ± 0.05	8.00 ± 1.00	1[a], 25[a*], 100[b]
Tetrachloroethene	<0.02	<0.02	<0.02	<0.02	
Trichloroethene	<0.02	<0.02	<0.02	<0.02	
Sum Tetra-Trichloroethene	<0.02	<0.02	<0.02	<0.02	10[a, b], 100[c]
1,2-Dichloroethane	<0.02	<0.02	<0.02	<0.02	3[a, b]
Total halogenated aliphatic hydrocarbons (HAlH)	<0.02	0.11 ± 0.01	0.75 ± 0.04	8.10 ± 0.70	1[a]

[a] *: Dutch regulations, no chlorination.*
[a*] *: Dutch regulations, with chlorination.*
[b] *: EU regulations.*
[c] *: WHO (provisional) guideline.*

0.01, 0.75 ± 0.05 and 8.00 ± 1.00 μg/L total (sum) THMs respectively (Table 2). At a CD of 30 C/L, the sum of THMs consisted of trichloromethane (0.03 ± 0.01 μg/L), dibromochlorimethane (0.04 ± 0.01 μg/L) and dichlorobromomethane (0.04 ± 0.00 μg/L). With tribromomethane concentrations being below detection limits (<0.02 μg/L) at 30 C/L, the component was excluded from the THM summation. The total sum of halogenated aliphatic hydrocarbons (HAlH) was 0.11 ± 0.01, 0.75 ± 0.04, and 8.10 ± 0.70 μg/L for CDs of 30, 100 and 500 C/L respectively. Concentrations of 1,2-dichloroethane and the sum of tetra-trichloroethene proved to be below detection limits for the explored range of CDs.

3.4.2. *Bromate*

The presence of bromate in drinking water, generally known as by-product of ozonation, is restricted due to its cancer potency (WHO, 2022). For this reason the EU set a 10 μg/L standard (Directive (EU), 2020), while Dutch regulations force an even stricter 1 μg/L limit in case ozonation is used for oxidation, and 5 μg/L in case ozonation is used for disinfection. Bromate is formed by oxidation of naturally present bromide (Von Gunten and Hoigne, 1994; Von Gunten and Oliveras, 1998). The bromate concentration in the groundwater was below detection limit (<0.1 μg/L) and the bromide concentration was 160 ± 2 μg/L. At CDs of 30 and 100 C/L, bromate could not be detected in effluent waters of the eAOP reactor (Table 3). At a CD of 500 C/L, 0.6 ± 0.0 μg/L of bromate was formed. While the influent bromide concentration was constant, increasing CDs from 30 to 100 and 500 C/L reduced bromide concentrations in effluents from 150 ± 12 to 120 ± 2 and 20 ± 4 μg/L, respectively.

3.4.3. *Organic carbon breakdown*

AOC control is a key strategy to ensure biological stability, i.e. limit microbial regrowth during distribution of non-chlorinated tap water (Van der Kooij, 1992). While being of considerable importance, no EU regulations on AOC concentrations exist. However, the Dutch drinking water directive describes a 10 μg/L standard (Wettenbank, 2022). In eAOP groundwater experiments at a CD of 30 C/L, total AOC concentrations of 20 ± 3.3 μg/L in reactor influent and 15.2 ± 2.0 μg/L in reactor effluent were observed (Fig. 5). One-Way Anova analysis showed significant differences (i.e. $p < 0.05$) between in- and effluent total AOC concentrations, with a p-value of 0.009. DOC concentrations were found to be 3.17 ± 0.01 mg/L and 3.11 ± 0.04 mg/L for reactor in- and effluent, respectively. Statistical analysis showed that the DOC results could not be considered significantly different, with a p-value of 0.052 (>0.05).

Table 3
Concentrations of bromide and bromate in groundwater during continuous-flow eAOP experiments at variable charge dosage [C/L].

Component [μg/L]	Influent	30 C/L	100 C/L	500 C/L	Regulatory limit
Bromide (Br^-)	160 ± 2	150 ± 12	120 ± 2	20 ± 4	
Bromate (BrO_3^-)	<0.1	<0.1	<0.1	0.6 ± 0.0	1[a], 5[a*], 10[b, c]

[a] *: Dutch regulations, no ozonation.*
[a*] *: Dutch regulations, with ozonation.*
[b] *: EU regulations.*
[c] *: WHO (provisional) guideline.*

4. Discussion

4.1. *As(III) oxidation by eAOP*

Naturally present As(III) in groundwater, at concentrations as low as 1.75 ± 0.31 μg/L, was oxidized to As(III) <0.3 μg/L by eAOP, requiring a CD >30 C/L. At a CD of 30 C/L, 1.49 ± 0.01 μg/L As(III) was oxidized, corresponding to 85.3 % oxidation. Oxidation of As(III) by eAOP at 30 C/L in natural and spiked groundwaters, containing 1.75 and 75 μg/L As (III), resulted in coulombic efficiencies of 0.013 % and 0.352 %, respectively. Oxidation of relatively low As(III) concentrations thus resulted in lower coulombic efficiencies, by a factor of 28. These findings align with observations in chemical oxidants ($KMnO_4$ and Cl_2) dosing studies, as efficiencies showed significant decreases at lower As(III) concentrations for constant oxidant dosages (Bora and Dutta, 2021; Sorlini and Gialdini, 2010).

The results in a natural groundwater matrix showed a loss in efficacy compared to synthetic water at similar CDs (Fig. 6). While at 20 C/L near-complete oxidation (>98 %; 73.9 ± 0.0 μg/L) of As(III) was

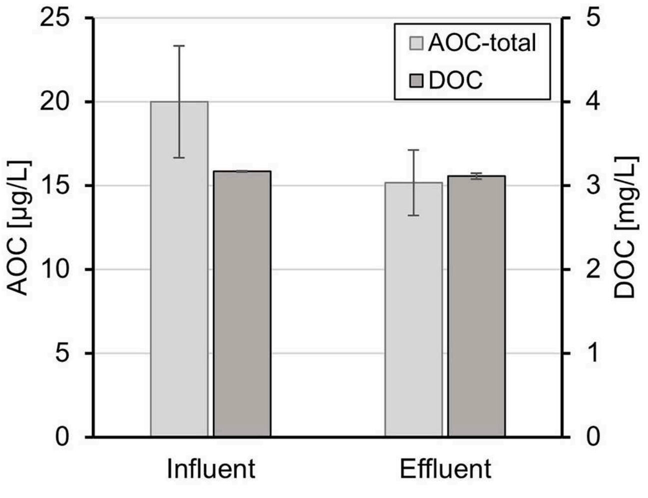

Fig. 5. Concentrations of total assimilable organic carbon (AOC) and dissolved organic carbon (DOC) in continuous-flow eAOP reactor in- and effluent, at a CD of 30 C/L using groundwater.

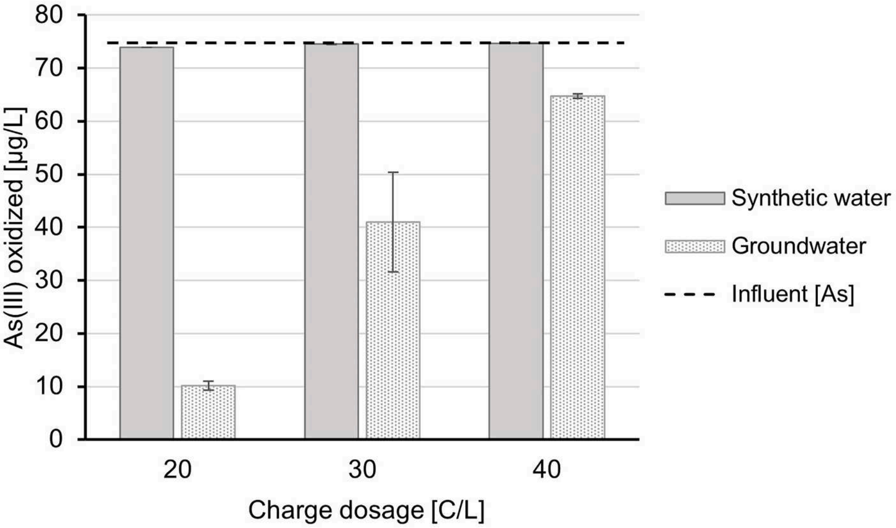

Fig. 6. As(III) oxidation by eAOP for different water matrices spiked with As(III). Similar charge dosage [C/L] and current density [A/m^2] were applied to the continuous-flow system.

achieved in the synthetic water, only 19 % (10.1 ± 0.6 µg/L) of the influent As(III) was oxidized in the groundwater. Coulombic efficiencies for As(III) oxidation decreased from 0.95 to 0.13 % when operating in a groundwater matrix. As(III) oxidation losses in natural groundwater were overcome at 40 C/L, oxidizing 64.7 ± 0.3 µg/L As(III) with a coulombic efficiency of 0.42 %. Similar behaviour of efficiency losses were observed in studies using hypochlorite (ClO^-), requiring oxidant-to-As(III) molar ratios of 1 and 70 to achieve full As(III) oxidation in synthetic and natural groundwater, respectively (Sorlini and Gialdini, 2010). Present oxidizable contaminants as Fe^{2+} and NH_4 did not show oxidation by eAOP when operated at 30 C/L. DOC concentrations did show a slight decrease in concentration from 3.17 ± 0.01 to 3.11 ± 0.04 mg/L, suggesting potential oxidation of organics.

A similar phenomenon was observed in the free chlorine plateau values of the synthetic water matrix experiments. CDs of 10 to 20, 40 and 80 C/L corresponded to observed free chlorine plateau values of 0.02 to 0.29, 0.92 and 2.04 mg/L. When doubling the CD, the electron output driving eAOP doubles. However, doubling CDs from 10 to 20, 20 to 40, and from 40 to 80 C/L did not double chlorine formation, as an increase in the plateau chlorine concentration of a factor 14.6, 3.2, and 2.2 was observed, respectively. Based on these outcomes it was hypothesised that a small fraction of oxidizable components must also have been present in the synthetic water matrix, causing an initial loss of the produced free chlorine. Mass balance estimations (Table B.1), assuming a doubling of chlorine and a fixed initial loss, found a consistent chlorine loss value of 0.27 ± 0.04 mg/L Cl_2. With this consistent initial loss it was found that doubling of CD indeed caused doubling of formed oxidation products. The coulombic efficiencies for chlorine production were observed in the range of 7.6 % and 8.1 %. Electron losses, causing the low coulombic efficiencies, were contributed to oxygen (O_2) production. Dissolved O_2 concentrations were found to increase by eAOP in natural groundwater from 1.85 ± 0.03 to 4.14 ± 0.57 mg/L at a CD of 30 C/L, indicating a coulombic efficiency of 92.1 ± 22.9 %.

Free chlorine, formed by oxidation of present chloride (Cl^-) in the water matrix, is considered to be a relevant indicator for ongoing (indirect) oxidation processes. Chlorine is known for its effective As(III) oxidation and its extremely fast oxidation kinetics, with complete oxidation generally taking several seconds (Annaduzzaman et al., 2022; Dodd et al., 2006). Observed similarities in formation of oxidation products Cl_2 and As(V) suggests a contribution of indirect oxidation. Free chlorine formation showed similar CD and current density plateau behaviour as As(III) oxidation. In line with literature, higher CDs were found to result in increasing concentrations of oxidation products (Arts et al., 2021; Moreira et al., 2017; Moreno-Andrés et al., 2018), resulting in higher observed free chlorine formation and As(III) oxidation. Additionally, for increasing current densities at a constant CD, higher free chlorine formation and As(III) oxidation was observed, until a certain plateau was reached. Similar observations were made in other studies, where it was suggested that this behaviour is related to mass-transfer limitations affecting the formation of oxidizing products at lower current densities (at constant CD), and has an upper limit (Bergmann and Koparal, 2005; Polcaro et al., 2009). With maximum As(III) oxidation and/or chlorine formation at the plateau values (at a constant CD), highest coulombic efficiency could be targeted by operating the system in these ranges.

4.2. Production of harmful by-products during eAOP in groundwater

Halogenated organic oxidation products and bromate were the assessed by-products of eAOP treating groundwater. The presence, i.e. formation, of these by-products has been restricted by EU and Dutch regulations. The strictest regulations prescribe a 1 µg/L limit for the sum of halogenated aliphatic hydrocarbons (HAlH) (when no chlorination techniques are applied) and bromate, a 3 µg/L limit for 1,2-dichloroethane and a 10 µg/L limit for the sum tetra-trichloroethene (Directive (EU), 2020; Wettenbank, 2022). eAOP settings relevant for As(III) oxidation (30 C/L) showed HAlH concentrations (0.11 ± 0.01 µg/L) to be below the EU and Dutch drinking water regulations, suggesting no implications when applied in drinking water treatment plants (DWTPs) based on this study. At 100 C/L, eAOP effluent HAlH concentrations (0.75 ± 0.04 µg/L) still met the standards. However, when applying a CD of 500 C/L HalH concentrations (8.10 ± 0.70 µg/L) were found to exceed the standard. When classified as a chlorination-disinfection technology, Dutch and EU regulations allowed the sum of THMs up to 25 and 100 µg/L, respectively (Directive (EU), 2020; Wettenbank, 2022). This would imply that the eAOP system could still meet drinking water standards at CDs of 500 C/L. 1,2-dichloroethane and the sum tetra-trichloroethylene were not detected during eAOP experiments, indicating these compounds would not form during eAOP in groundwater.

While free chlorine has the benefit of oxidizing As(III), remaining free chlorine might be undesirable, particularly for its effect on smell and taste (observable from 0.3 mg/L). Or, at rather extremely high concentrations (>5 mg/L), free chlorine could even have potential negative health effects (WHO, 2022). However, considering that eAOP is a pre-treatment method for As(III) oxidation prior to an As(V) removal technology (e.g., adsorption, coagulation-filtration, and reverse osmosis), remaining free chlorine is likely removed in these subsequent treatment steps. Also, residual free chlorine in the produced drinking water could even be considered as desired side-effect for post-disinfection during distribution. Either way, it was demonstrated in this study that for As(III) oxidation with eAOP, the operational settings required (e.g., low CD) do not lead to extensive free chlorine production.

With a maximum bromate concentration of 0.6 μg/L at a CD of 500 C/L, the treated water by eAOP was meeting Dutch drinking water regulations (<1 μg/L) and the European Drinking Water Directive (<10 μg/L). However, due to a non-closing bromide mass balance (molar based) a concern on the formation of other bromide-related oxidation products, as brominated compounds, was raised (Table C.1). Effluent bromide concentrations showed a linearly decreasing trend for increasing CD, indicating a correlation to oxidation processes, while the analysed formed products showed a minimal increase.

AOC values proved not to increase by eAOP when the charge dosage was set to 30 C/L. As in Dutch drinking water practice post-chlorination is not applied (similarly to treatment facilities in Belgium, Germany, Switzerland and Denmark), microbial regrowth is prevented by lowering the availability of nutrients (degradable carbons, phosphate, and nitrogen containing compounds). Stable AOC concentrations are believed to be desirable for microbial stability of the water, reducing regrowth potential in the distribution system (Van der Kooij, 1992). Described observations were however contradicting literature on chemical-based advanced oxidation using H_2O_2/UV and/or O_3, as AOC values generally increased (Huang et al., 2005; Ramseier et al., 2011; Timmers et al., 2022). The breakdown of organics (total organic carbon) by electrochemical oxidation has been described in literature (Saha et al., 2021). A reason for the non-observed organic breakdown at a CD of 30 C/L could be found in the anode material itself, with the MMO-Ru/Ir electrode being characterized by its active behaviour. Active electrodes are known for their relatively low O_2-overpotentials compared to passive electrodes, resulting in relatively lower reactivity towards complete oxidation of organics (Panizza and Cerisola, 2009). Subsequent partial degradation of organics could result in the formation of refractory species that would still be identified as DOC and not as AOC. However, insights in effects on AOC are unclear, urging the need for further research on the effect of eAOP on AOC concentrations.

4.3. Perspective on eAOP application for drinking water treatment

Besides oxidizing As(III) to As(V), other benefits of the anodic process of eAOP were identified. The acidifying behaviour of the anodic processes has the capability to lower a relatively high groundwater pH (8–9) towards a more neutral pH (7) through the production of H^+. Studies have shown that this pH correction enhances As(V) sorption to Fe flocks and so the As removal efficiency, lowering required Fe dosages post oxidation (Dixit and Hering, 2003; Gude et al., 2018). Additionally, the anodic acidification behaviour reduces the Saturation Index (SI), lowering the needs for hardness removal (calcium and magnesium). Lastly, besides the produced oxidation products contributing to As(III) oxidation, like free chlorine and radicals, these could provide a desirable barrier for pathogens. Interestingly, eAOP application could potentially be considered as a disinfection technology due to the high expected formed chlorine concentrations (>2 mg/L) at CDs >80 C/L (Moreira et al., 2017; Najafinejad et al., 2023). Typical chlorine doses to treated waters range from 0.2 to 2 mg/L of free chlorine (Brandt et al., 2016), which puts the observed concentrations within the correct range. Several studies have already focussed on quantifying disinfection capacities of eAOP, mostly referred to as electro-chlorination, showing log-removal values ranging from 1 to 6-log (Martínez-Huitle and Brillas, 2008; Valero et al., 2017). However, most studies assessed significantly higher CDs (>60 C/L) than needed for As oxidation and outcomes showed high dependence on the used water matrix (ranging from surface to waste water). To better describe this added benefit, future research should therefore quantify the disinfection capacities of eAOP when applied for As(III) oxidation in groundwater.

Experiments showed that oxidation to below detection limits (to <0.3 μg/L) of naturally occurring As(III) concentrations (± 2 μg/L) in a groundwater matrix was achieved by the eAOP system at a CD of approximately 25 C/L. At this CD, current densities between 20 and 60 A/m^2 showed similar As(III) oxidation performance. Therefore, the current density was considered the main variable affecting the energy consumption, as assumable constant ohmic resistances and increasing current intensities would require higher operating voltages for system operation (Fig. 7). The linearity of the I/V relationship shows that losses are purely ohmic driven, i.e. showing constant Ohmic resistance under constant physical conditions. This behaviour is to be expected given the low conductivity of the drinking water. Elevated operating voltages would increase energy consumption, and thus operational costs (OPEX), of the system. Current densities of 20, 40, and 60 A/m^2 corresponded to energy consumptions of 0.09, 0.15, and 0.21 kWh/m^3, respectively. For energy prices of 0.30 Euro/kWh this would imply operational costs of 0.03, 0.05, and 0.06 Euro/m^3 for increasing current density. A higher current density would on the other hand correspond to a reduced electrode surface area and so reduce investment costs (CAPEX) of the reactor (Cañizares et al., 2009). Based on aforementioned reasoning a trade-off between OPEX and CAPEX should be made. A Net Present Value (NPV) and/or Equivalent Annual Costs (EAC) optimization method would be suitable to find an economic optimum for the current density, considering inflation corrections and interest rates over the service lifespan of components.

5. Conclusions

This study showed the oxidation of As(III) by eAOP in synthetic water and groundwater containing influent As(III) concentrations ranging from 75 to 2 μg/L. As(III) oxidation showed to be dependent on charge dosage and current density, with the latter being related to the observed plateau behaviour in formation of chlorine. In both water matrices As(III) was oxidized to <0.3 μg/L, indicating over 99.9 % oxidation of influent As(III). Oxidation of As(III) to these low concentrations will promote subsequent removal of As(V) in post treatment (e.g., coagulation, adsorption or RO) and allow for drinking water treatment systems to reduce As concentrations below the proposed 1 μg/L Dutch target. However, oxidation of As(III) by eAOP showed lower efficacy in groundwater compared to synthetic water, with coulombic efficiencies decreasing from 0.95 % to 0.13 %. At settings relevant for As

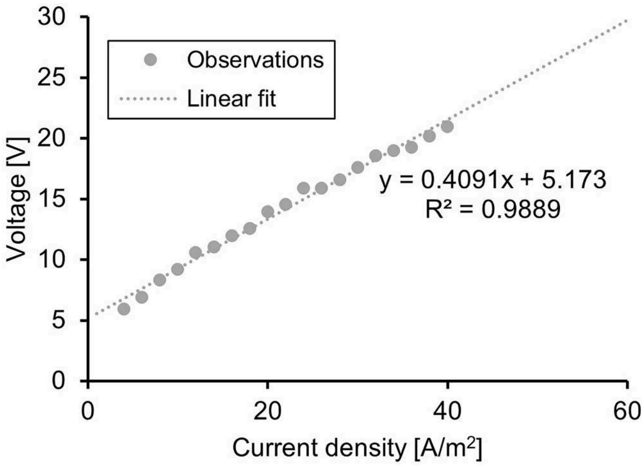

Fig. 7. Observed relation between current density [A/m^2] and voltage [V] in a continuous-flow eAOP system fed with natural groundwater, having an electrical conductivity of ± 550 μS/cm.

oxidation (30–100 C/L range), the presence of formed anodic by-products like THMs (0.11–0.75 μg/L), representing halogenated and brominated organics, and bromate (<0.2 μg/L) proved to be lower than strictest regulatory standards (1 μg/L) applicable to Dutch non-chlorinated and non-ozonated tap water. Additionally, the microbial stability of the water, in terms of AOC, was not affected. To exclude the potential formation of harmful bromide-related oxidation products, as bromine (Br_2) and other bromate-related intermediate species (BrO_2^-, HOB, OBr^-), a more detailed analysis on these components should be performed in future work. Even at low drinking water conductivity (around 550 μS/cm), the energy consumption of the eAOP system was low at 0.09, 0.15, and 0.21 kWh/m^3, for current densities of 20, 40, and 60 A/m^2, respectively. Based on an energy price of 0.30 Euro/kWh, operational costs of the eAOP system for As oxidation would range between 0.03 and 0.06 Euro/m^3. In conclusion, eAOP is a promising technology for As(III) oxidation in drinking water treatment, without formation of harmful by-products.

CRediT authorship contribution statement

E. Kraaijeveld: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing, Funding acquisition, Formal analysis. **S. Rijsdijk:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **S. van der Poel:** Conceptualization, Funding acquisition, Investigation, Project administration, Supervision, Writing – review & editing, Validation. **J.P. van der Hoek:** Formal analysis, Methodology, Supervision, Validation, Writing – review & editing, Funding acquisition. **K. Rabaey:** Supervision, Validation, Writing – review & editing, Methodology. **D. van Halem:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix

A. Characteristics of water matrices

Table A.1
Overview of the groundwater matrix used for the eAOP experiments, obtained post-softening and pre-aeration from a Managed Aquifer Recharge and Recovery (MARR) site.

Constituent / parameter	Average value
pH [-]	8.72
Electrical conductivity [μS/cm]	550
DO [mg O_2/L]	2
As(III) [μg/L]	1.75
Fe(II) [mg/L]	0.07
Fe(III) [mg/L]	0.22
Cl^- [mg/L]	50
Br^- [μg/L]	160
HCO_3^- [mg/L]	165
NH_4^+ [mg N/L]	0.15
NO_3^- [mg N/L]	0.30
AOC [μg/L]	20
DOC [mg/L]	3.17

Table A.2
Overview of the synthetic water matrix used for eAOP experiment, using demineralized water.

Constituent / parameter	Average value
pH [-]	8.5
Electrical conductivity [μS/cm]	470
As(III) [μg/L] (when spiked)	75
Cl^- [mg/L]	45
HCO_3^- [mg/L]	180

B. Free chlorine mass balance in synthetic water

Table B.1

Free chlorine mass balance model for estimation of initial losses in the synthetic water matrix. Input data was obtained from measurements at the plateau values for a range of charge dosages (CDs) [C/L].

CD input data [C/L]	CD factor	Balance equation for initial losses (x)	Estimated initial loss (x) [mg/L]
10–20	2	$(0.02 + x) * 2 = 0.29 + x$	0.25
10–40	4	$(0.02 + x) * 4 = 0.92 + x$	0.28
10–80	8	$(0.02 + x) * 8 = 2.04 + x$	0.27
20–40	2	$(0.29 + x) * 2 = 0.92 + x$	0.34
20–80	4	$(0.29 + x) * 4 = 2.04 + x$	0.29
40–80	2	$(0.92 + x) * 2 = 2.04 + x$	0.20
		Avg.	**0.27 ± 0.04**

C. Bromide mass balance for eAOP in groundwater

Table C.1

Mass balance model of analysed components containing bromine, expressed as μmol Br/L. The mass balance was made for a range of charge dosages (CDs) [C/L].

Analysed components [μmol Br/L]	Influent	30 C/L	100 C/L	500 C/L
Bromide (Br^-)	2.036 ± 0.026	1.848 ± 0.151	1.563 ± 0.028	0.307 ± 0.055
Bromate	<	<	<	0.005 ± 0.000
1,2-dibromo-3-chloropropane	<	<	<	<
Bromochloromethane	<	<	<	<
Bromodichloromethane	<	0.0003 ± 0.0000	0.001 ± 0.000	0.014 ± 0.001
Dibromochloromethane	<	0.0003 ± 0.0000	0.002 ± 0.000	0.019 ± 0.001
Tribromomethane (bromoform)	<	<	0.003 ± 0.000	0.030 ± 0.001
Sum bromide and products	2.0357	1.8491	1.5691	0.3750

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