Comparison between experimental results of different technologies for arsenic removal from water intended for human consumption

Maria Cristina Collivignarelli[a], Silvestro Damiani IWA[a,*] and Sabrina Sorlini[b]

[a] DICAr, Department of Civil and Architectural Engineering, University of Pavia, via Ferrata 1, 27100 Pavia, Italy

[b] DICATAM, Department of Civil, Environmental, Architectural Engineering and Mathematics, University of Brescia, via Branze 43, 25123 Brescia, Italy

*Corresponding author. E-mail: silvestro.damiani01@universitadipavia.it

Abstract

Arsenic contamination in drinking water is a major issue in the present world. Techniques such as oxidation, precipitation and adsorption have been widely used for arsenic removal. The goal of this work is to analyze four case studies where the problem of arsenic contamination in groundwater is faced with an approach that includes experimental activities at laboratory scale and/or pilot scale. The first case study investigates the mechanisms for enhancing arsenic removal with naturally occurring Fe by the addition of an oxidizing agent ($KMnO_4$) or a concentrated basic solution of MnO_4^- and AlO_2^-. In the second case study, different experimental tests are carried out at laboratory scale in order to identify the best combination of treatments to be applied at full scale. The third case study shows the results of experimental studies followed by a full-scale upgrading for a drinking water treatment plant (DWTP) with no specific arsenic treatment in the first configuration. Last, the fourth case study investigates the performance of granular ferric oxide (GFO) with arsenic concentrations close to the Italian regulatory limit. A pilot GFO filter was installed in a DWTP. The monitoring results led to the implementation of the GFO filter at full scale.

Key words: arsenic, coagulation-flocculation processes, drinking water treatment plant, granular ferric oxide, oxidation process

INTRODUCTION

Nowadays, with deteriorating environmental quality, human life is exposed to numerous types of threats. There are a number of harmful chemicals around us: ingestion, breathing or any kind of exposure to them can affect the human health tremendously (Sarkar & Paul 2016; Rusu *et al.* 2018). Arsenic (As) is ubiquitous in the environment and highly toxic to all forms of the life. It is a crystalline 'metalloid', a natural element with features intermediate between metals and non-metals; it occurs naturally as an element, and ranks as the 20th most frequently occurring trace element in the earth's crust, 14th in seawater, and 12th in the human body (Singh *et al.* 2015; Zhou & Xi 2018).

Arsenic exists mainly in four oxidation states – arsenate (As(V)), arsenite (As(III)), arsenic (As(0)), and arsine (As(-III)) and its solubility depends on the pH and ionic environment (Chieh Kao *et al.* 2013; Crognale *et al.* 2017; Li *et al.* 2017). In natural waters, arsenic is usually present as two main species, As(V) and As(III). The latter is usually present in water under anoxic conditions (such as in groundwater), while As(V) is detected in surface water. Moreover, As(III) is much more toxic and mobile than As(V). In general, inorganic arsenicals (i.e. arsenate and arsenite) are more toxic than organic ones (Singh *et al.* 2015; Sarkar & Paul 2016; Crognale *et al.* 2017; Li *et al.* 2017; Wang *et al.* 2018).

As concentration in water varies from one water body to another. In freshwater systems (rivers and lakes), the variation in As concentration is in the range of 0.15–0.45 μg/L, depending on the source, availability and geochemistry of the catchments (Singh *et al.* 2015). Geothermal inputs, evaporation and groundwater contamination are the main cause of high As concentrations in rivers (Mandal & Suzuki 2002; Mukherjee *et al.* 2006; Barringer & Reilly 2013). Instead, As concentration in seawater is usually less than 2 μg/L (Singh *et al.* 2015).

However, global attention is mainly focused on the presence of arsenic in groundwater, as the major part of the global population relies on groundwater to meet the purpose of drinking (Sarkar & Paul 2016). As concentration in groundwater is greatly influenced by the mineralogical characteristics of the aquifer and varies over a very large range, from less than 0.5 to 5,000 μg/L (Singh *et al.* 2015). As can find its way into groundwater by reductive dissolution of arsenic-rich iron oxyhydroxides present in dispersed phases in aquifers or by oxidation of arsenic-rich minerals (Sarkar & Paul 2016).

Natural groundwater containing As used for drinking, irrigation, or agriculture purposes causes serious health problems for people. It is estimated that 140 million people worldwide suffer from the consumption of arsenic-laden groundwater of higher than 10 μg/L (Li *et al.* 2017). Around 110 million of those people live in 10 countries in South and South-east Asia: Bangladesh, Cambodia, China, India, Laos, Myanmar, Nepal, Pakistan, Taiwan and Vietnam (Brammer 2008). Therefore, in 1993 the World Health Organization (WHO) reduced the acceptable threshold for As in drinking water from 50 to 10 μg/L, although some countries have adopted different values as national standards, i.e. 7 μg/L for Australia and New Zealand and 50 μg/L for Bangladesh (WHO 2011; Chieh Kao *et al.* 2013). The WHO arsenic guideline of 10 μg/L was introduced in Italy by the Legislative Decree 2001/31 following the adoption of European Directive 98/83/UE.

Numerous studies have been conducted to assess the toxicity of As and its effects on human health in various As-contaminated regions (Kongkea *et al.* 2010; Maity *et al.* 2012). Arsenic enters into human beings through two pathways: first, direct consumption of As-contaminated drinking water and second, for populations not exposed to elevated As in drinking water, foods represent the main sources of As intake for humans (Singh *et al.* 2015). Irrigation with As-enriched groundwater is the main pathway for As to enter the human food chain (Das *et al.* 2004; Chatterjee *et al.* 2010; Samal *et al.* 2011).

The various effects of As poisoning on human health are melanosis, leuco-melanosis, keratosis, hyperkeratosis, dorsum, non-petting edema, gangrene and skin cancer. Melanosis and keratosis are the most common presentations among the affected peoples (Singh *et al.* 2015).

Excessive and long-term (such as 5–10 years) human intake of toxic inorganic As having a concentration above 50 μg/L leads to arsenicosis, which is a common term used for As-related health effects including skin problems, skin cancers, internal cancers (bladder, kidney, lung), diseases of the blood vessels of the legs and feet, and possibly diabetes, high blood pressure and reproductive disorders (WHO 2011).

Arsenic can be removed from water with various techniques based on different chemical, physical-chemical or biological principles. The most *consolidated technologies* (well-known and widely applied around the world) are:

- Chemical oxidation and filtration (Dodd *et al.* 2006);
- Biological oxidation: oxidation of As(III) to As(V) by microorganisms and As(V) removal by iron and manganese oxides (Katsoyiannis & Zouboulis 2006; Sorlini *et al.* 2014);
- Co-precipitation: oxidation of As(III) to As(V) by adding a suitable oxidizing agent, followed by coagulation, sedimentation and filtration (Li *et al.* 2017);
- Electrocoagulation (Moussa *et al.* 2017; Song *et al.* 2017; Thakur & Mondal 2017; Silva *et al.* 2018);
- Adsorption on: activated alumina, activated carbon, iron-based sorbents, zero valent iron and hydrated iron oxide, etc. (Neumann *et al.* 2013; Thakur & Mondal 2017);

- Ion exchange through suitable cation and anion exchange resins (Nidheesh & Singh 2017);
- Membrane technology: reverse osmosis, nanofiltration and electrodialysis (Jain & Singh 2012);
- Photocatalysis (Xu *et al.* 2014).

Some of these processes can achieve good removal efficiencies for both As(III) and As(V), whereas chemical precipitation and ion exchange are particularly effective for the removal of As(V). Many of the arsenic treatment technologies require pH adjustment for optimization of performance and are effective in removing arsenic in the pentavalent state and hence include an oxidation step as pre-treatment to convert As(III) to As(V) (Bissen & Frimmel 2003).

The aim of this work is to analyze four case studies where the problem of arsenic contamination in groundwater is faced with an approach that includes, preliminarily, experimental activities at laboratory scale and/or at pilot scale.

In Case study 1, Sharma *et al.* (2016) investigated, through laboratory-scale tests, the mechanisms and possibilities for enhancing As removal from Bengal Delta groundwater with naturally occurring Fe in a reliable, low cost and sustainable way. In Case study 2, Sorlini & Gialdini (2014) carried out a series of experimental tests, at laboratory scale, for the simultaneous removal of arsenic, iron and manganese, in order to optimize the operating conditions of treatment processes applied at full scale. In Case study 3, Sorlini *et al.* (2015a), thanks to laboratory scale experimental activities and pilot scale testing, identified four different scenarios for upgrading of a drinking water treatment plant (DWTP) without a specific arsenic removal stage in the first configuration. In Case study 4, Collivignarelli *et al.* (2016) showed the results of a 19-month monitoring campaign for a pilot granular ferric oxide (GFO) filter, installed in a DWTP as a polishing stage with the aim of investigating the performance of GFO with arsenic concentrations in raw water close to the Italian regulatory limit.

METHODS

The following paragraph is divided into two sub-paragraphs. In addition to the methodological approach used, preliminary information relating to each case study and the operative conditions of the activities carried out at laboratory scale and/or pilot scale are reported.

General overview

The methodological approach applied to counter the groundwater arsenic pollution is shown in Figure 1.

The Case study 1 experimental activity was developed only at laboratory scale. To simulate the concentration of contaminants in groundwater of the Bengal Delta, stock solutions of arsenic and iron were prepared. The first stage experiments were conducted to study oxidation and removal of As(III) with $KMnO_4$ in the presence of Fe^{2+} and Fe^{3+}. Based on the results from the first stage, a second stage of experiments was conducted to improve oxidation and removal of As(III) with a basic solution of $KMnO_4 + Al_2(SO_4)_3$. Additional information, like the lab-scale equipment and the analytical methods, are reported in Sharma *et al.* (2016).

In Case study 2, the authors carried out their experimental activity with the aim of optimizing the full-scale treatment chain. The main contaminants in raw water are the following: iron (Fe, mean: 0.13 mg/L); manganese (Mn, mean: 128 µg/L); total arsenic (mean: 15 µg-As_{TOT}/L); trivalent arsenic (mean: 14.5 µg-As(III)/L) and ammonium (mean: 0.9 mg-NH_4^+/L). These values are critical for iron, manganese, arsenic and ammonia since they are always higher than the legislation limit for water for human consumption (Italian Legislative Decree 2001/31).

The DWTP operates with a maximum flow rate of 1,600 m³/h (76,000 inhabitants) and is composed of the treatment processes reported in Figure 2.
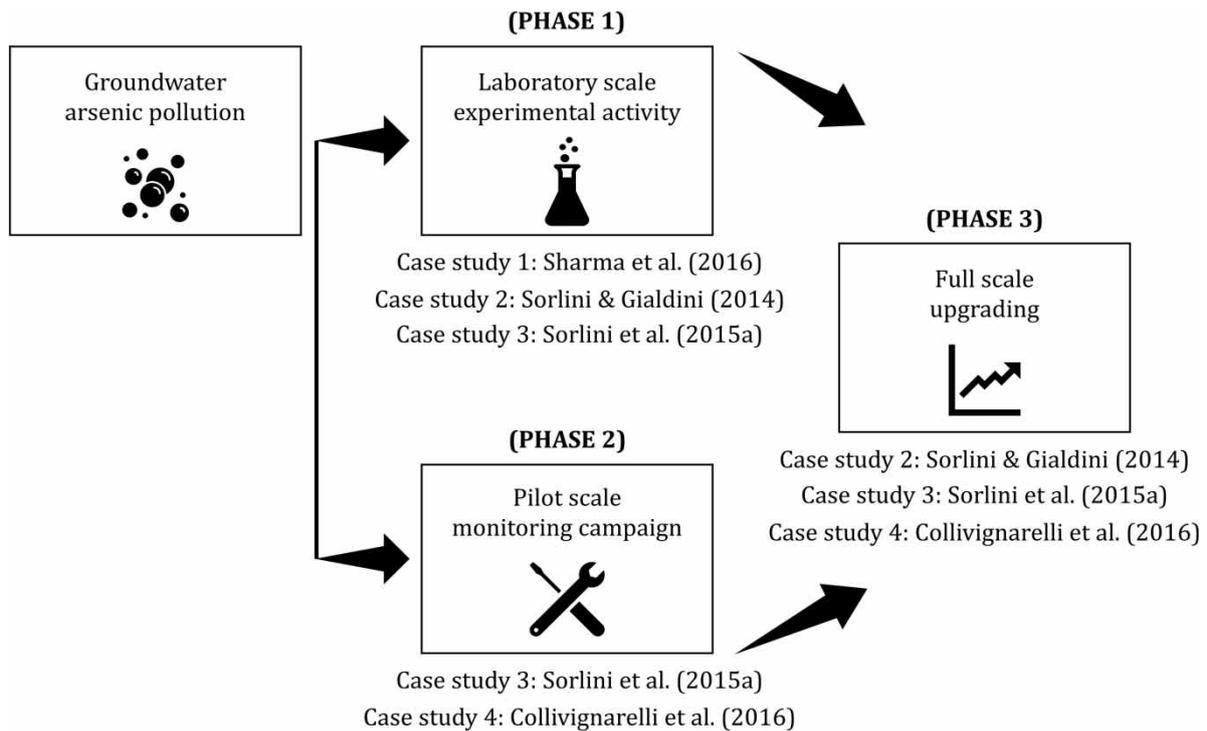
Figure 1 | Scheme of the methodological approach applied in the four case studies.
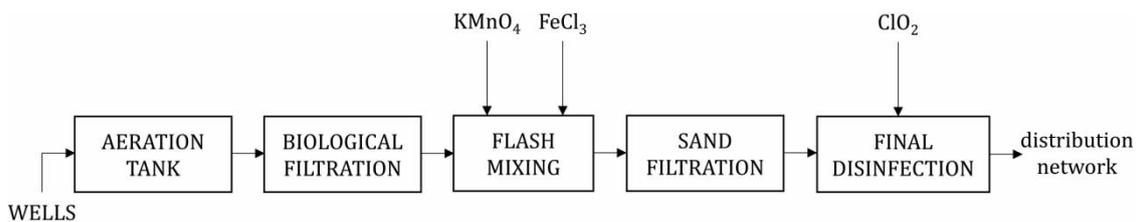

Figure 2 | Case study 2 DWTP block diagram.

Cascade aeration is applied for Fe oxidation; aerated biological filtration (bio-filtration) for Mn, Fe and arsenic oxidation and NH_3 nitrification; flash mixing is used for the dissolution of $KMnO_4$ and $FeCl_3$; sand filtration is necessary for the separation of Fe/Mn and the insoluble arsenic-containing compounds, and final disinfection with chlorine dioxide (ClO_2) is the last treatment before water distribution. The effects of a combination of treatments on the removal of the above-mentioned contaminants have been evaluated at laboratory scale. Water samples were collected from the outlet of the bio-filtration. At the end of each test, the following parameters were determined: As(III), total arsenic, total iron and total manganese. Analytical methods are reported in Sorlini & Gialdini (2014).

The DWTP analyzed in Case study 3 treats a maximum flow of $140\ m^3/h$. The sequence of treatments is reported in Figure 3.
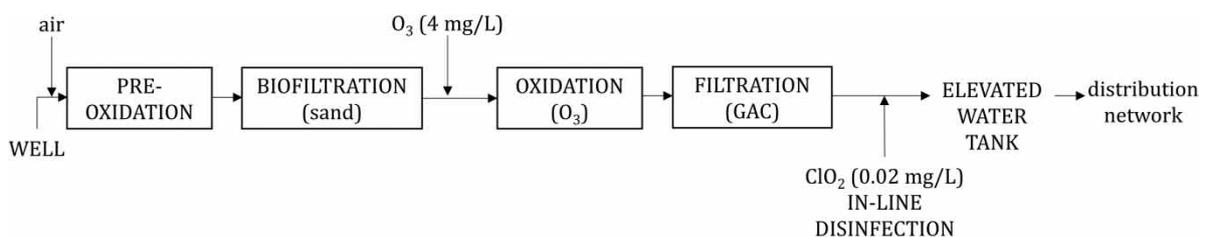

Figure 3 | Case study 3 DWTP block diagram.

The plant is fed with water drawn from a 200-m deep aquifer. The main contaminants are ammonium (mean: 0.79 mg-NH_4^+/L), manganese (mean: 79 µg/L) and total arsenic (mean: 12 µg-As_{TOT}/L). A pre-oxidation with air is used to oxidize iron (Fe) and form the precipitates, which can be removed by sand filtration; the biofiltration removes NH_4^+ through biological nitrification and a second oxidation with ozone (O_3) allows completion of the oxidation of Mn that also partially occurs in the biofiltration. Then, insoluble manganese oxides and organic micropollutants are subsequently removed by granular activated carbon (GAC) filters. Finally, an in-line disinfection with ClO_2 is applied before water distribution. A 6-month intensive monitoring program was carried out, after which the biological activity of the sand and GAC filters was investigated (further details and results are reported in Sorlini et al. (2015a)). Moreover, different experimental tests, at laboratory and pilot scale, were performed to optimize arsenic removal through chemical oxidation and/or media adsorption. Analytical methods are reported in Sorlini et al. (2015a).

In Case study 4, the authors analyzed and commented on the results of installing a pilot GFO filter in a DWTP treating groundwater containing the following main contaminants: ammonium (mean: 0.7 mg-NH_4^+/L), manganese (mean: 94 µg/L) and arsenic (mean: 11 µg-As_{TOT}/L). These concentrations are always higher than the regulatory limit for water intended for human consumption (Italian Legislative Decree 2001/31). Figure 4 reported the schematic diagram of the DWTP.
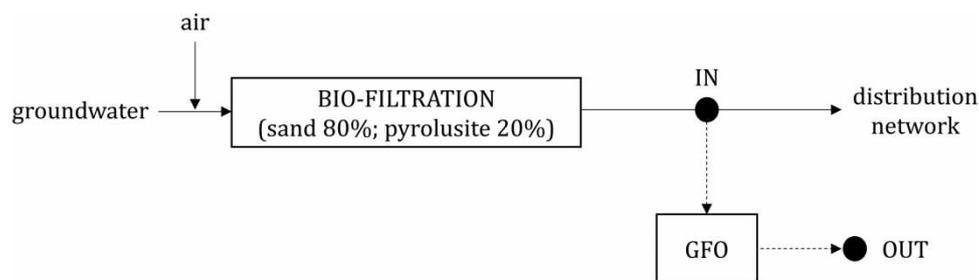

Figure 4 | Case study 4 DWTP block diagram.

In the full-scale plant, contaminants are removed by a pre-aeration stage and two biofilters filled with sand (80%) and pyrolusite (20%). The latter, consisting essentially of manganese dioxide (MnO_2), was introduced for arsenic control. As can be observed from the Figure, the disinfection stage is not in operation in order to minimize the negative effects that can arise from the use of disinfectants such as chlorine dioxide (ClO_2). In fact, if ClO_2 is used for final disinfection, specific removal stages for chlorine disinfection by-products (e.g. activated carbon filtration) could be provided (Sorlini et al. 2015b, 2016). After a monitoring campaign, two main problems have been found: (i) arsenic removal in the biofilters was below 10% because the pyrolusite worked mainly as an oxidizer; (ii) the mass of pyrolusite in the biofilters fell due to backwashing. In agreement with the DWTP utility manager, the suitability of an additional arsenic removal (polishing) stage has been investigated in order to keep arsenic concentration as low as possible.

Water quality monitoring was conducted by taking an average of one sample per week throughout the 19-month test from both the inlet and the outlet of the DWTP. Additional information and analytical methods are reported in Collivignarelli et al. (2016).

Laboratory scale and pilot scale experimental activities

The laboratory-scale experimental activities are reported in Table 1. Pilot-scale experimental activities are described in Table 2.

Table 1 | Experimental tests and related operative conditions investigated on arsenic removal

Case study	Laboratory scale experimental activities on arsenic removal	Operative conditions
Sharma *et al.* (2016)	• Oxidation and removal of As(III) with $KMnO_4$ in the presence of Fe^{2+} and Fe^{3+}	→ Distilled water → 5 mM $NaHCO_3$ as a buffer → Initial As(III) concentration = 1,000 μg/L; Fe concentration = 10 mg/L → pH = 7 by adding dilute NaOH or HCl before the addition of Fe and/or $KmnO_4$ → Fe^{2+}: $KMnO_4$ added at stoichiometric ratio of 0; 0.2; 0.7; 1; 1.3 → Fe^{3+}: $KMnO_4$ added at stoichiometric ratio of 1
	• Oxidation and removal of As(III) with basic solution of $KMnO_4 + Al_2(SO_4)_3$	→ 1:1 mixture of distilled water and tap water (simulation of groundwater conditions in Bengal Delta) → Composition of tap water and Bangladesh water (see Sharma *et al.* 2016) → Initial As(III) concentration = 500 μg/L; Fe concentration ranging from 0 to 10 mg/L using a 2 mg/L concentration-increasing step → pH = 6 ÷ 7.5 (adjusted by adding dilute NaOH or HCl before the addition of Fe and/or oxidant) → Sedimentation time studied: 0; 10; 20 min → As removal by filtration vs prolonged sedimentation time: filtration of samples 2 min after the addition of Fe and oxidant vs 1; 1.5 h of sedimentation time → T ~ 25 °C (room temperature) → Simulation of anaerobic conditions in groundwater: nitrogen gas bubbled through the water for 10 min ($O_2 < 2$ mg/L)
Sorlini & Gialdini (2014)	• Chemical pre-oxidation ($KMnO_4$, ClO_2 or NaClO) + disinfection (ClO_2) • Chemical pre-oxidation ($KMnO_4$, ClO_2 or NaClO) + chemical precipitation ($FeCl_3$ or $Al_2(SO_4)_3$) + filtration + disinfection (ClO_2)	→ Oxidant dosages (batch tests): $KMnO_4$ = 0.73 mg/L; ClO_2 = 1.12 mg/L; NaClO = 0.24 mg/L → coagulant dosages (jar tests): $FeCl_3$ = 9.45 mg/L; $Al_2(SO_4)_3$ = 7.8 mg/L
Sorlini *et al.* (2015a)	• Chemical pre-oxidation (batch tests)	→ Application on raw and pre-oxidized (with air) water → Stirring conditions (130 rpm) → $KMnO_4$ dosages: 0.1; 0.2; 0.5 mg/L; contact time = 5 min → $NaMnO_4$ dosages: 0.5 mg/L; contact time = 5 min
	• Adsorption capacity of pyrolusite (batch tests)	→ Application on raw and pre-oxidized (with air) water → Stirring conditions (130 rpm); contact time = 14.5 min (EBCT)
	• Pyrolusite + chemical dosage of $KMnO_4$ (batch tests)	→ Stirring conditions (130 rpm) → $KMnO_4$ dosages: 0.1; 0.5 mg/L; contact time = 14.5 min (EBCT)

In Case study 1, the first stage experiments were conducted to study oxidation and removal of As(III) with $KMnO_4$ in the presence of Fe^{2+} and Fe^{3+}. Based on the results from the first stage, a second stage of experiments was conducted to improve oxidation and removal of As(III) with a basic solution of $KMnO_4 + Al_2(SO_4)_3$. In Case study 2, the authors carried out a series of experimental tests in order to evaluate the effects of the following treatments on the removal of contaminants: pre-oxidation with $KMnO_4$, ClO_2 or NaClO; chemical precipitation with $FeCl_3$ or $Al_2(SO_4)_3$; sand filtration and final disinfection with ClO_2. In Case study 3, different experimental tests were performed to optimize arsenic removal through chemical oxidation and/or media adsorption. Additionally, pyrolusite was tested in a pilot scale plant. In Case study 4, the authors investigated

Table 2 | Pilot scale experimental tests investigated on arsenic removal

Case study	Pilot scale experimental activity on arsenic removal	Operative conditions
Sorlini *et al.* (2015a)	• Pyrolusite filter	→ Continuous up-flow conditions → Monomedia filter reproduced in a glass column (d = 30 cm; h = 80 cm) fed with water leaving the biofilters → Flow rate = 1 L/h; EBCT = 5 min → Covered filter (to avoid photocatalytic oxidation of As(III))
Collivignarelli *et al.* (2016)	• GFO filter (polishing stage)	→ Continuous down-flow conditions → Bayoxide® E33 filter reproduced in a glass column (d = 3 cm; h = 60 cm) fed with pre-oxidized water from the DWTP → Flow rate = 1 L/h; EBCT = 5 min → No backwashing during testing

the performance of a GFO for arsenic removal. Further information is reported in the individual publications.

RESULTS AND DISCUSSION

Laboratory scale experimental activities

In Sharma *et al.* (2016) the effectiveness of $KMnO_4$ on As(III) oxidation and the effect of the presence of Fe^{2+} on As(III) oxidation are investigated. Results showed that As(III) oxidation was concomitant with the oxidation of Fe^{2+} and was very rapid within the first 10 minutes of the experiment. Furthermore, with a SR = 1, complete oxidation of As(III) occurs within 2 minutes after the addition of $KMnO_4$ in the presence of Fe^{2+}. The influence of the initial oxidation state of added Fe (Fe^{2+} or Fe^{3+} (as sulphate)) on As(III) oxidation and removal of As was also investigated. $KMnO_4$ was added 15 and 40 minutes after the addition of Fe. Results show that better oxidation of As(III) occurred in the presence of Fe^{3+} in comparison to Fe^{2+} and in the case of Fe^{2+} an extra dosage of $KMnO_4$ was required to achieve a final As(III) concentration below 50 μg/L.

It was therefore verified that the addition of $KMnO_4$ will not be sufficient if Fe^{2+} is present, so the removal of As with naturally occurring Fe can be greatly improved by adding adequate amounts of $KMnO_4$ to oxidize both As(III) and Fe^{2+}. Conversely, if Fe^{2+} is present at low concentrations, adding an oxidant ($KMnO_4$) together with an auxiliary coagulant (Al) may be a practical solution, in order to achieve the filtration/sedimentation of flocs with adsorbed As. Then the authors focused on the detection of a solution with both oxidizing capacity and coagulation ability. Laboratory observation shows that a solution of $KMnO_4$ and $Al_2(SO_4)_3$ is stable for years at pH ∼ 11 adjusted with NaOH. Results for the applicability of this solution at varying Fe concentrations at an initial As(III) concentration of 500 μg/L are reported in Table 3.

Table 3 | Case study 1: removal (%) of total arsenic for samples containing different Fe concentrations (initial As(III) concentration: 500 μg/L)

Fe [μg/L]	As(III) final concentration [μg/L]	As(III) removal yield [%]
0	173	65
200	50	90
400	29	94
600	17	97
800	7	99
1,000	2	99

Results reported in Table 3 show that higher Fe concentrations increase As(III) removal and As(III) concentrations below the Maximum Concentration Level (MCL) of 50 µg/L.

Using $KMnO_4$ together with $Al_2(SO_4)_3$ has three advantages: (i) the addition of Al ions increases the filterability of the $Fe(OH)_3$ flocs; (ii) the use of a strongly basic mixture allows the neutralization of the acidity produced due to $Fe(OH)_3$ and $Al(OH)_3$ formation; (iii) by increasing the amount of added Al, this method can be applied in waters with low Fe concentrations.

The results of the experimental activity carried out by Sorlini & Gialdini (2014) at laboratory scale showed that the first combination of treatments (pre-oxidation followed by final disinfection) is not effective in terms of As removal, because As(III) is solely oxidized into As(V). Conversely, the second combination (pre-oxidation followed by chemical precipitation, sand filtration and final disinfection) is the best option for the removal of both arsenic and the above-mentioned contaminants from water. The As_{TOT} removal yields obtained in this combination are shown in Table 4.

Table 4 | Case study 2: total arsenic average removal yields of the second combination of treatments (BF = biological filtration; C1: chemical precipitation with $FeCl_3$; C_2: chemical precipitation with $Al_2(SO_4)_3$; F = filtration; D = disinfection with ClO_2)

Experimental train: Pre-oxidation + Coagulation-Flocculation + Filtration + Disinfection (ClO_2)	
Out BF As_{TOT} concentration = 15 µg/L	
Sampling point	As_{TOT} removal yield [%]
Out BF + $KMnO_4$ + C1 + F + D	80
Out BF + ClO_2 + C1 + F + D	74
Out BF + NaClO + C1 + F + D	60
Out BF + $KMnO_4$ + C_2 + F + D	57
Out BF + ClO_2 + F + D	75
Out BF + NaClO + C_2 + F + D	70

The combined use of $KMnO_4$ and $FeCl_3$ allows the highest As_{TOT} average removal yield to be obtained (80%, considering an average As_{TOT} concentration of 15 µg/L at the outlet of biofiltration). The same performance was highlighted by monitoring the full-scale DWTP operating in the same conditions tested at laboratory scale.

Sorlini et al. (2015a) carried out experimental tests at laboratory scale in order to identify specific treatments able to optimize arsenic removal. Results are reported in Table 5.

Table 5 | Case study 3: results of the oxidation batch tests with different chemical oxidants and dosages on both raw water and water pre-oxidized with air

	As(III) concentration [µg/L]	As(III) removal yield [%]
Raw water	12 (As_{TOT} = 12 µg/L)	–
0.1 mg-$KMnO_4$/L	0.8	93
0.2 mg-$KMnO_4$/L	3	75
0.5 mg-$KMnO_4$/L	2	83
0.5 mg-$NaMnO_4$/L	7	42
Pre-oxidized water (with air)	3.5 (As_{TOT} = 10.8 µg/L)	–
0.1 mg-$KMnO_4$/L	0.4	89
0.2 mg-$KMnO_4$/L	0.3	91
0.5 mg-$KMnO_4$/L	0.5	86
0.5 mg-$NaMnO_4$/L	0.2	94

The results of the oxidation tests with $KMnO_4$ and $NaMnO_4$ on raw water show that a good oxidation efficiency (>80%) can be achieved with $KMnO_4$ after a contact time of 5 minutes and also with sub-stoichiometric dosages (<0.2 mg/L). Moreover, the results of tests carried out with the same dosage of different chemical oxidants (0.5 mg/L) have shown that $NaMnO_4$ led to a lower yield of oxidation than that obtained with $KMnO_4$ (42% with respect to 83%). Furthermore, the dosage of the chemical oxidant in water preventively aerated enables higher yields of oxidation (>85%) with both $KMnO_4$ and $NaMnO_4$, as part of As(III) was oxidized to As(V) during the aeration.

The adsorption of arsenic using pyrolusite was also investigated (data not shown). As reported in Sorlini *et al.* (2015a), good arsenic removal efficiency (>90%) was obtained on both raw and pre-oxidized water (with air). Moreover, no increase in the removal yield with $KMnO_4$ dosages has been observed.

Pilot scale experimental activities

In Case study 3, a monomedia filter composed of pyrolusite was tested by means of a pilot plant fed with pre-oxidized water with an average concentration of 10 μg-As_{TOT}/L (about 70% As(III)). The experimental results (reported in Sorlini *et al.* (2015a)) show that media saturation was reached quickly (before 2,000 bed volumes) even if the oxidation capacity of the filter media was still effective, as shown by the fact that after 6,000 BV the outlet concentration of As(III) was still about 50% of the total As concentration.

Instead, a GFO pilot filter, installed in the DWTP and monitored for 19 months, was evaluated in Case study 4. Figure 5 shows the total arsenic influent and effluent concentration trends.

It can be noted that the GFO performance decreases considerably about a month after the installation of the pilot filter. In fact, as reported in Collivignarelli *et al.* (2016), the arsenic-adsorption capacity of the E33 was substantially exhausted in the first 20,000 BV, when the ratio between the total arsenic concentration in the treated water (C) and the total arsenic concentration in the influent water (C_0) was 0.75. The authors also investigated the prevalent species removed by the E33 (As(III) and As(V)) in four different media response periods (periods that can be assumed to be homogeneous compared to operating conditions): 0–5,000; 5,001–20,000; 20,001–82,000; 82,001–140,000 Bv.
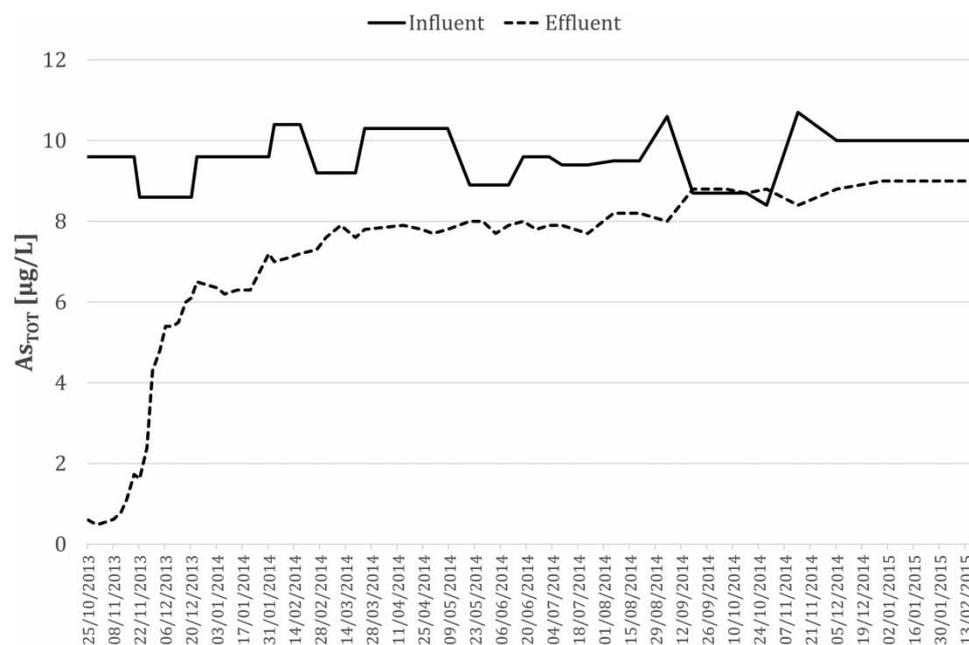

Figure 5 | Case study 4: total arsenic influent and effluent concentration trends on the GFO pilot filter.

For both species, the highest removal efficiencies were obtained in the first period (As(III) and As(V) average removal yields of 96% and 99% respectively), after which removal decreased progressively. At the end of the experimentation, the adsorption capacity of the GFO was estimated as 0.57 µg-As$_{TOT}$/L. Further details are reported in Collivignarelli *et al.* (2016).

Full scale upgrading

The experimental tests carried out at pilot scale allowed a full-scale upgrading to be achieved.

In Case study 2, the results of the laboratory scale tests showed that the best removal of metals from raw water was obtained by pre-oxidation with potassium permanganate, chemical precipitation with ferric chloride, filtration and final disinfection with chlorine dioxide. Therefore, the optimum operating conditions determined at laboratory scale were implemented in the full scale DWTP, as reported in Figure 6.
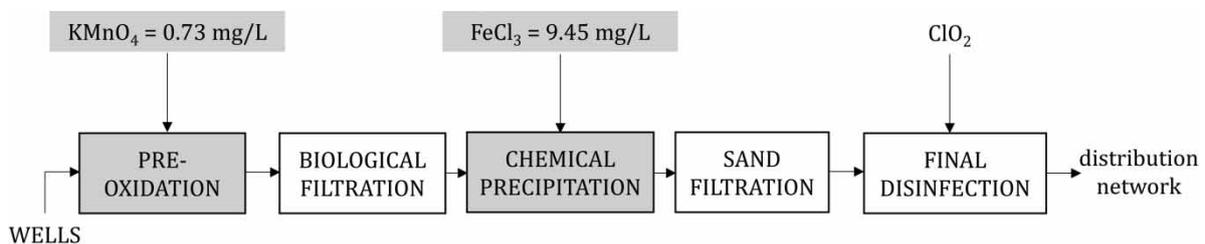

Figure 6 | Case study 2: final configuration of the DWTP (improvements highlighted in grey).

The results of the continuous monitoring of the DWTP showed average arsenic concentration in treated water of 3 µg/L (removal yield of about 80%, considering an average arsenic concentration in raw water of 15 µg/L).

In Case study 3, according to the results obtained in experimental studies, four different scenarios of upgrading were identified and tested at laboratory scale. Among these, the fourth scenario (Figure 7) was chosen as this process was able to optimize the As$_{TOT}$ removal (about 68%, considering an initial As$_{TOT}$ concentration of about 12 µg/L). Further details of the other scenarios are reported in Sorlini *et al.* (2015a).
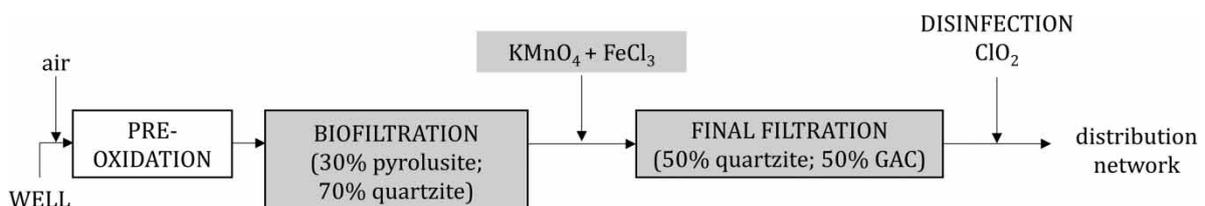
Figure 7 | Case study 3: final configuration of the DWTP (improvements highlighted in grey).

The results of the intensive monitoring of the upgraded DWTP showed that the average arsenic concentration in treated water was equal to 7 µg/L (removal yield of about 40%, considering an average arsenic concentration in raw water of 12 µg/L).

Regarding Case study 4, the results of continuous monitoring at the outlet of the DWTP are reported in Figure 8.

Each As$_{TOT}$ concentration value reported represents the mean value of the quarter considered.

As can be seen from Figure 8, total arsenic effluent concentrations always comply with the MCL of 10 µg/L provided by the Italian Legislative Decree 2001/31.

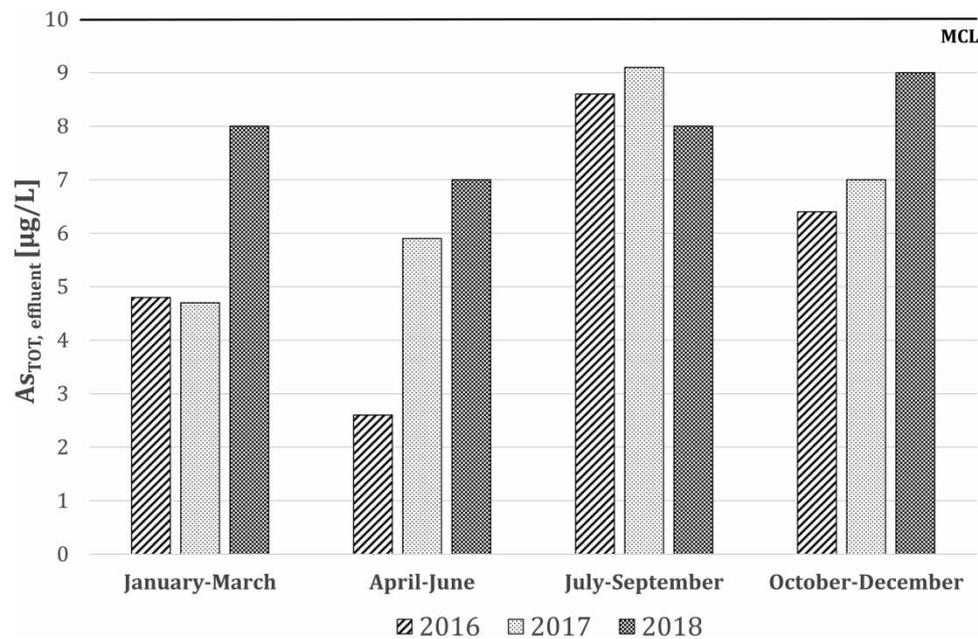**Figure 8** | Case study 4: total arsenic effluent concentration trends of the full-scale DWTP.

CONCLUSIONS

Arsenic contamination in groundwater, used for drinking purposes, has been envisaged as a problem of global concern. The removal of arsenic can be ensured through the application of different processes. Chemical oxidation has been successfully tested, at laboratory scale, by Sharma *et al.* (2016). The authors found that oxidation of As(III) can effectively be obtained by adding $KMnO_4$ immediately after collecting the groundwater. Moreover, the treatment of Fe^{2+} and As(III)-laden groundwater can easily be achieved by the addition of a basic solution of $KMnO_4$ and $Al_2(SO_4)_3$. Starting from an initial arsenic concentration of 500 μg/L, the removal is better if the iron concentration is high: an As removal yield of approximately 100% can be achieved with an Fe concentration of 1,000 μg/L. Future goals concern the applicability of this solution in full-scale DWTPs that already have either a coagulation or filtration unit.

Sorlini & Gialdini (2014) found that, after pre-oxidation followed by final disinfection, As(III) was solely oxidized into As(V) and no removal was obtained. Considering an average total arsenic concentration of 15 μg/L in raw water, pre-oxidation, followed by chemical precipitation, sand filtration and final disinfection represents the best combination of treatments for the removal of this parameter. Moreover, the use of $KMnO_4$ and $FeCl_3$ resulted in being the optimum solution in this experimental train for improving arsenic removal. The monitoring of the full-scale DWTP operating under the same conditions tested at laboratory scale showed an average arsenic removal yield of 80%.

In Sorlini *et al.* (2015a) adsorption, in addition to oxidation, have been tested for arsenic removal by means of laboratory-scale and pilot-scale tests. Regarding the oxidation batch tests on raw water, the highest As(III) removal yield (93%) was achieved with a dosage of 0.1 mg-$KMnO_4$/L. Instead, regarding the oxidation tests on pre-oxidized water (with air), the highest As(III) removal yield (94%) was achieved with a dosage of 0.5 mg-$NaMnO_4$/L. Moreover, the adsorption of arsenic using pyrolusite showed a removal efficiency greater than 90%, as also reported in Katsoyiannis & Zouboulis (2006). The results identified four different scenarios of treatments for the plant upgrading. The fourth scenario resulted in optimization of As removal (about 68%) and, therefore, it was implemented in the full scale DWTP.

895

Among the numerous materials capable of effectively absorbing arsenic, the GFO has been tested by Collivignarelli *et al.* (2016) for the treatment of groundwater with an average total arsenic concentration of 11 μg/L. The results show that the GFO removed some arsenic up to 40,000 Bv (As(III) and As(V) average removal yields of 96% and 99% respectively), with a total adsorption capacity of 0.57 μg-Astot/mgGFO. Beyond this point, the GFO can be considered exhausted technically ($C/C_0 = 0.9$) and GFO replacement must be considered. From the economic point of view, GFO filter installation could be attractive because the operating costs – related to the arsenic concentration in the influent – are comparable to those of other physical-chemical processes. The effectiveness of the GFO filter is also confirmed by the full-scale monitoring: although this treatment is very easy to apply and manage in an existing treatment plant, the costs of purchasing the filter material and disposing of the exhausted material cannot be neglected.

Therefore, both experiments carried out at a pilot scale showed high performance in reducing arsenic, despite the concentrations found in raw water (respectively, 12 μg/L and 11 μg/L) being very close to the Italian regulatory limit.

REFERENCES

Barringer, J. L. & Reilly, P. A. 2013 *Arsenic in Groundwater: A Summary of Sources and the Biogeochemical and Hydrogeologic Factors Affecting Arsenic Occurrence and Mobility.* INTECH Open Access Publisher, pp. 83–116. Available from: https://www.intechopen.com/books/current-perspectives-in-contaminant-hydrology-and-water-resources-sustainability/arsenic-in-groundwater-a-summary-of-sources-and-the-biogeochemical-and-hydrogeologic-factors-affecti.

Bissen, M. & Frimmel, F. H. 2003 Arsenic- a review. Part II: oxidation of arsenic and its removal in water treatment. *Acta Hydrochimica et Hydrobiologica* **31**(2), 97–107.

Brammer, H. 2008 Threat of arsenic to agriculture in India, Bangladesh and Nepal. *Economic and Political Weekly* **43**, 79–84.

Chatterjee, D., Halder, D., Majumder, S., Biswas, A., Nath, B., Bhattacharya, P., Bhowmick, S., Mukherjee-Goswami, A., Saha, D., Hazra, R., Maity, P. B., Chatterjee, D., Mukherjee, A. & Bundschuh, J. 2010 Assessment of arsenic exposure from groundwater and rice in Bengal Delta Region, West Bengal, India. *Water Research* **44**, 5803–5812.

Chieh Kao, A., Chu, Y., Hsu, F. & Liao, V. H. 2013 Removal of arsenic from groundwater by using a native isolated arsenite-oxidizing bacterium. *Journal of Contaminant Hydrology* **155**, 1–8.

Collivignarelli, M. C., Canato, M., Sorlini, S. & Crotti, B. M. 2016 Monitoring of a pilot GFO filter for removal of low-concentration arsenic in water. *Water Practice & Technology* **11**(4), 702–711.

Crognale, S., Amalfitano, S., Casentini, B., Fazi, S., Petruccioli, M. & Rossetti, S. 2017 Arsenic-related microorganisms in groundwater: a review on distribution, metabolic activities and potential use in arsenic removal processes. *Reviews in Environmental Science and Bio/Technology* **16**, 647–665.

Das, H. K., Mitra, A. K., Sengupta, P. K., Hossain, A., Islam, F. & Rabbani, G. H. 2004 Arsenic concentrations in rice, vegetables, and fish in Bangladesh: a preliminary study. *Environment International* **30**, 383–387.

Dodd, M. C., Vu, N. D., Ammann, A., Le, V. C., Kissner, R., Pharm, H. V., Cao, T. H., Berg, M. & Von Gunten, U. 2006 Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: relevance to drinking water treatment. *Environmental Science & Technology* **40**, 3285–3292.

Jain, C. K. & Singh, R. D. 2012 Technological options for the removal of arsenic with special reference to South East Asia. *Journal of Environmental Management* **107**, 1–18.

Katsoyiannis, I. A. & Zouboulis, A. I. 2006 Comparative evaluation of conventional and alternative methods for the removal of arsenic from contaminated groundwaters. *Reviews on Environmental Health* **21**, 25–41.

Kongkea, P., Sthiannopkao, S., Kim, K. W., Wong, M. H., Sao, V., Hashim, J. H., Yasin, M., Salleh, M. & Syed, M. A. 2010 Health risk assessment of inorganic arsenic intake of Cambodia residents through groundwater drinking pathway. *Water Research* **44**, 5777–5788.

Legislative Decree n. 31 2001 Water for Human Consumption Implementation of Directive 98/83/CE Related to Drinking Water Quality. Ordinary Supplement of the Official Gazette no. 52, 2001/03/03.

Li, H., Zhang, X., Wu, M., Zhang, W., Lv, L. & Pan, B. 2017 Highly efficient and environmentally benign As(III) pre-oxidation in water by using a solid redox polymer. *Chemosphere* **175**, 300–306.

Maity, J. P., Nath, B., Kar, S., Chen, C. Y., Banerjee, S., Jean, J. S., Liu, M. Y., Centeno, J. A., Bhattacharya, P., Chang, C. L. & Santra, S. C. 2012 Arsenic induced health crisis in peri-urban Moyna and Ardebok villages, West Bengal, India: an exposure assessment study. *Environmental Geochemistry and Health* **34**, 563–574.

Mandal, B. K. & Suzuki, K. T. 2002 Arsenic round the world: a review. *Talanta* **58**(1), 201–235.

Moussa, D. T., El-Naas, M. H., Nasser, M. & Al-Marri, M. J. 2017 A comprehensive review of electrocoagulation for water treatment: potentials and challenges. *Journal of Environmental Management* **186**, 24–41.

Mukherjee, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Das, B., Nayak, B., Lodh, D., Rahman, M. M. & Chakraborti, D. 2006 Arsenic contamination in groundwater: a global perspective with emphasis on the Asian scenario. *Journal of Health, Population and Nutrition* **24**(2), 142–163.

Neumann, A., Kaegi, R., Voegelin, A., Hussam, A., Munir, A. K. & Hug, S. J. 2013 Arsenic removal with composite iron matrix filters in Bangladesh: a field and laboratory study. *Environmental Science & Technology* **47**, 4544–4554.

Nidheesh, P. V. & Singh, T. S. A. 2017 Arsenic removal by electrocoagulation process: recent trends and removal mechanism. *Chemosphere* **181**, 418–432.

Rusu, T., Cristea, C., Rusu, T., Groze, I.-C. & Stoica, L. 2018 Energy source analysis from the perspective of sustainable development. *Environmental Engineering and Management Journal* **17**(7), 1729–1741.

Samal, A. C., Kar, S., Bhattacharya, P. & Santra, S. C. 2011 Human exposure to arsenic through foodstuffs cultivated using arsenic contaminated groundwater in areas of West Bengal, India. *Journal of Environmental Science and Health Part A Toxic/Hazardous Substances & Environmental Engineerings.* **46**, 1259–1265.

Sarkar, A. & Paul, B. 2016 The global menace of arsenic and its conventional remediation – a critical review. *Chemosphere* **158**, 37–49.

Sharma, A. K., Sorlini, S., Crotti, B. M., Collivignarelli, M. C., Tjell, J. C. & Abbà, A. 2016 Enhancing arsenic removal from groundwater at household level with naturally occurring iron. *Revista Ambiente & Água* **11**(3), 486–498.

Silva, J. F. A., Graça, N. S., Ribeiro, A. M. & Rodrigues, A. E. 2018 Electrocoagulation process for the removal of co-existent fluoride, arsenic and iron from contaminated drinking water. *Separation and Purification Technology* **197**, 237–243.

Singh, R., Singh, S., Parihar, P., Singh, V. P. & Prasad, S. M. 2015 Arsenic contamination, consequences and remediation techniques: a review. *Ecotoxicology and Environmental Safety* **112**, 247–270.

Song, P., Yang, Z., Zeng, G., Yang, X., Xu, H., Wang, L., Xu, R., Xiong, W. & Ahmad, K. 2017 Electrocoagulation treatment of arsenic in wastewaters: a comprehensive review. *Chemical Engineering Journal* **317**, 707–725.

Sorlini, S. & Gialdini, F. 2014 Study on arsenic removal in the drinking water treatment plant of Cremona (Italy). *Journal of Water Supply: Research and Technology-AQUA* **63**(8), 625–629.

Sorlini, S., Gialdini, F. & Collivignarelli, M. C. 2014 Survey on full-scale drinking water treatment plants for arsenic removal in Italy. *Water Practice and Technology* **9**, 42–51.

Sorlini, S., Collivignarelli, M. C., Castagnola, F., Crotti, B. M. & Raboni, M. 2015a Methodological approach for the optimization of drinking water treatment plants' operation: a case study. *Water Science and Technology* **71**(4), 597–604.

Sorlini, S., Biasibetti, M., Collivignarelli, M. C. & Crotti, B. M. 2015b Reducing the chlorine dioxide demand in final disinfection of drinking water treatment plants using activated carbon. *Environmental Technology* **36**(12), 1499–1509.

Sorlini, S., Biasibetti, M., Gialdini, F. & Collivignarelli, M. C. 2016 How can drinking water treatments influence chlorine dioxide consumption and by-product formation in final disinfection? *Water Science and Technology: Water Supply* **16**(2), 333–346.

Thakur, L. S. & Mondal, P. 2017 Simultaneous arsenic and fluoride removal from synthetic and real groundwater by electrocoagulation process: parametric and cost evaluation. *Journal of Environmental Management* **190**, 102–112.

Wang, R., Wei, Y., Wu, Y., Zheng, J. & Zheng, B. 2018 Changes of arsenic speciation during swine manure windrow composting at full scale. *Environmental Engineering and Management Journal* **17**(7), 1563–1573.

WHO 2011 *Guidelines for Drinking-Water Quality*, Vol. 4. World Health Organization, Geneva, Switzerland.

Xu, J., Li, J., Wu, F. & Zhang, Y. 2014 Rapid photooxidation of As(III) through surface complexation with nascent colloidal ferric hydroxide. *Environmental Science & Technology* **48**, 272–278.

Zhou, Q. & Xi, S. 2018 A review on arsenic carcinogenesis: epidemiology, metabolism, genotoxicity and epigenetic changes. *Regulatory Toxicology and Pharmacology* **99**, 78–88.