

## Study on arsenic removal in the drinking water treatment plant of Cremona (Italy)

S. Sorlini and F. Gialdini

### ABSTRACT

This study investigates the simultaneous removal of arsenic, iron and manganese in a full scale drinking water treatment plant (DWTP) located in the city of Cremona (North of Italy), treating a groundwater contaminated by As and other pollutants ( $H_2S$ ,  $NH_3$ , Fe and Mn). Different experimental tests were carried out at laboratory scale in order to optimize the operating conditions of the treatment process applied in the DWTP. The combination of pre-oxidation with  $KMnO_4$  and  $FeCl_3$  showed the best results for arsenic removal (yield of 76%). The monitoring of the full scale DWTP operating in the same conditions tested at laboratory scale showed that the plant efficiently removed arsenic (yield = 80%), ammonia (yield = 98%) and manganese (yield = 95%).

**Key words** | arsenic, chemical oxidation, chemical precipitation, iron, manganese

S. Sorlini (corresponding author)

F. Gialdini

Department of Civil Engineering, Architecture,  
Land, Environment and Mathematics,  
University of Brescia,  
Via Branze 43,  
Brescia,  
Italy  
E-mail: [sabrina.sorlini@unibs.it](mailto:sabrina.sorlini@unibs.it)

### INTRODUCTION

The presence of arsenic in the environment is related to both human activities and natural factors (Mandal & Suzuki 2002; Bissen & Frimmel 2003a). The most widespread forms in natural waters are arsenite (As(III)) and arsenate (As(V)) depending on pH and redox conditions. The inorganic arsenic forms are predominant in groundwater and As(III) is prevalent in deep reducing waters (Bissen & Frimmel 2003a; Choong *et al.* 2007).

Millions of people in the world are exposed to chronic arsenicosis through drinking water consumption with consequent toxic, carcinogenic and non-carcinogenic effects (Pontius *et al.* 1994; Smedley & Kinniburgh 2002; Bissen & Frimmel 2003a; Ng *et al.* 2003; Tchounwou *et al.* 2004; ATSDR 2005; WHO 2011). The WHO guideline value of 10  $\mu g/L$  for the arsenic concentration in drinking water was applied by the European Directive 98/83/EC and was implemented in Italy by Legislative Decree 2001/31 in 2003.

Arsenic can be effectively removed from water through chemical precipitation with iron or aluminium hydroxide salts, ion exchange, reverse osmosis and adsorption on granular ferric hydroxide or activated alumina. In some of these processes, especially chemical precipitation and

ion exchange, good arsenic removal yields are provided only if arsenic is oxidized from As(III) to As(V). Since As(III) is dominant in deep groundwater, its removal with chemical precipitation in drinking water treatment plants (DWTPs) needs a pre-oxidation (Bissen & Frimmel 2003b; Ghurye & Clifford 2004) that can be performed by means of chemical (chlorine, chlorine dioxide, potassium permanganate) or biological processes (Katsoyiannis & Zouboulis 2004). Chemical oxidation with  $KMnO_4$  is very effective since a complete arsenic oxidation can be obtained after 1 minute with the stoichiometric dosage of potassium permanganate (Sorlini & Gialdini 2010). Moreover, pH conditioning greatly improves the arsenic removal using  $KMnO_4$  and  $FeCl_3$  (Bordoloi *et al.* 2013a, b).

This study analyses the case of the full scale DWTP of Cremona (North of Italy) treating groundwater contaminated by As,  $H_2S$ ,  $NH_3$ , Fe and Mn by means of conventional treatment processes (pre-oxidation, chemical precipitation, sand filtration and disinfection). A series of experimental tests was carried out at laboratory scale in order to optimize the operating conditions of treatment processes applied in the full scale plant.

## MATERIALS AND METHODS

### DWTP of Cremona (Italy)

The DWTP operates with a maximum flow rate of 1,600 m<sup>3</sup>/h (76,000 inhabitants). The DWTP is composed of the following treatment processes: wells, one aeration tank, four biological filters, four sand filters, final disinfection. Cascade aeration is applied for CH<sub>4</sub>, H<sub>2</sub>S stripping and Fe oxidation; aerated biological filtration (bio-filtration) for Mn, Fe and As oxidation and NH<sub>3</sub> nitrification; flash mixing is used for the dissolution of KMnO<sub>4</sub> and FeCl<sub>3</sub>; sand filtration is necessary for the separation of Fe/Mn and of the insoluble arsenic containing compounds and final disinfection with chlorine dioxide is the last treatment before water distribution.

### Groundwater quality

The average concentrations of the main chemical parameters in natural groundwater are pH = 8.1, total organic carbon (TOC) = 4.10 mg/L, Fe = 0.13 mg/L, Mn = 128 µg/L, Astot = 15.0 µg/L, As(III) = 14.5 µg/L and NH<sub>4</sub><sup>+</sup> = 0.90 mg/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](#)).

### Laboratory scale experimental tests

The experimental tests were carried out at laboratory scale in order to evaluate the effects of the following treatments on the removal of contaminants: pre-oxidation with KMnO<sub>4</sub>, ClO<sub>2</sub> or NaClO; chemical precipitation with FeCl<sub>3</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>; sand filtration and final disinfection with ClO<sub>2</sub>.

The water samples were collected from the outlet of the bio-filtration.

The experimental tests were carried out as follows:

- chemical pre-oxidation (KMnO<sub>4</sub>, ClO<sub>2</sub> or NaClO) followed by disinfection (ClO<sub>2</sub>);
- chemical pre-oxidation (KMnO<sub>4</sub>, ClO<sub>2</sub> or NaClO), chemical precipitation (FeCl<sub>3</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), filtration and disinfection (ClO<sub>2</sub>).

The oxidant dose for each reagent was determined at laboratory scale by mixing a 500 mL volume of water, sampled from the outlet of the biological filter, with a fixed amount of each oxidant (2.5 mg/L) for a contact time of 4 minutes (contact time applied in the flash mixing of the full scale DWTP). The oxidant dose (oxidant demand) was the amount of reagent consumed after 4 minutes and it was calculated as the difference between the initial dose (2.5 mg/L) and the residual concentration. Thus the determined doses were: 0.73 mg/L for KMnO<sub>4</sub>, 1.12 mg/L for ClO<sub>2</sub> and 0.24 mg/L for NaClO. During the experimental tests on chemical precipitation, the optimum coagulant dosages were determined according to the ASTM jar-test procedure ([ASTM D2035-08](#)) and they resulted in 9.45 mg/L for FeCl<sub>3</sub> and 7.80 mg/L for Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. A 1 mm-membrane filter was employed for water filtration after the coagulant addition.

At the end of each test the following parameters were determined: As(III), total arsenic, total iron and total manganese.

### Analytical methods

The As(III) and the total arsenic were determined by means of stripping chronopotentiometry, with deposition of elementary arsenic onto an electrode followed by stripping with constant current ([Jurica et al. 2000](#); Eca Flow of Bophuthatswana). Manganese and iron (ferrous and total) were determined by the PAN-[1-(2-pyridylazo)-2-naphthol] method ([Goto et al. 1977](#)) and the o-phenanthroline ([Standard Methods for the Examination of Water and Wastewater 1995](#)) method respectively. Ammonia was analysed according to [APAT IRSA \(2003\)](#).

## RESULTS AND DISCUSSION

The data of arsenic concentration regarding the monitoring of the full scale DWTP showed that a good arsenic removal (about 70%) was achieved in the water sampled at the outlet of the sand filtration after the treatments of aeration, bio-filtration, chemical oxidation with KMnO<sub>4</sub>, chemical precipitation with FeCl<sub>3</sub> and sand filtration. The results of the laboratory scale experimental tests show a low arsenic

removal (yield 15%) in the case of chemical pre-oxidation followed by final disinfection of course, since during these processes arsenic is oxidized but not removed (Figure 1). The best arsenic removal (about 75%) during the laboratory scale tests was obtained with pre-oxidation with  $\text{KMnO}_4$  followed by chemical precipitation with  $\text{FeCl}_3$  (C1), filtration and final disinfection with  $\text{ClO}_2$ . This result is fully in agreement with the arsenic concentration observed in the treated water in the full scale DWTP. Otherwise, the use of aluminium sulphate (C2) was better than  $\text{FeCl}_3$  (C1) only in the case of pre-oxidation with  $\text{ClO}_2$  or  $\text{NaClO}$ .

As concerns iron (Figure 2), a removal yield higher than 90% was already observed in the full scale DWTP after aeration and bio-filtration. The results of the experimental tests show that the addition of a chemical precipitation/filtration step increased iron concentration in treated water if  $\text{FeCl}_3$  was used as coagulant.

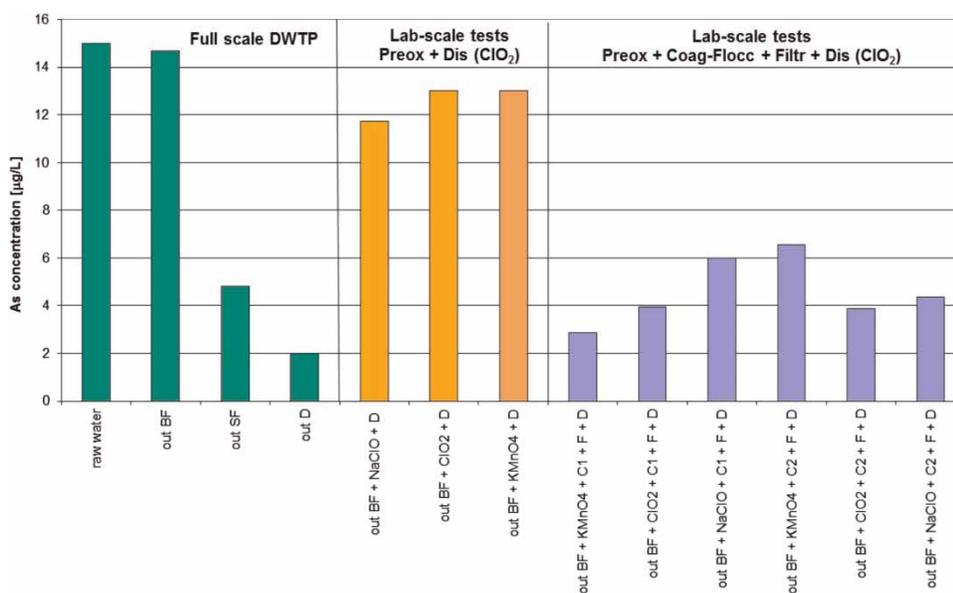
As concerns manganese (Figure 3), a removal yield higher than 90% was observed in the full scale DWTP after aeration and bio-filtration, as observed for iron. When the complete treatment train was tested, the best removal of manganese was obtained in the case of pre-oxidation with  $\text{KMnO}_4$  or  $\text{ClO}_2$  followed by chemical precipitation with Fe or Al salts.

The results of the laboratory scale tests showed that the best removal of metals from raw water was obtained by

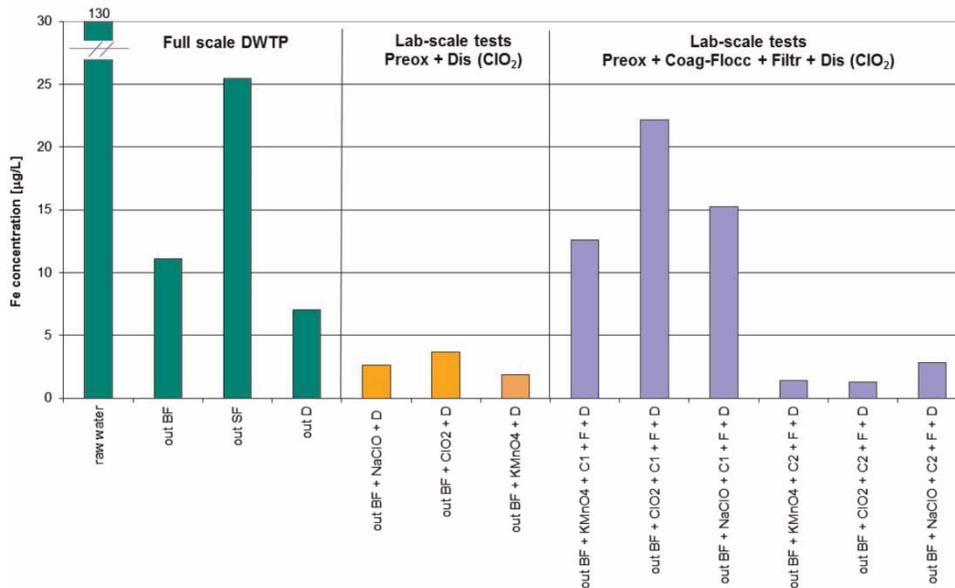
pre-oxidation with potassium permanganate, chemical precipitation with ferric chloride, filtration and final disinfection with chlorine dioxide. Therefore, the optimum operating conditions determined at laboratory scale were implemented in the full scale DWTP (potassium permanganate dosage of 0.73 mg/L and ferric chloride dosage of 9.45 mg/L) and the following final concentrations in treated water were obtained: ammonia lower than 0.05 mg/L (initial concentration 1.50 mg/L), 10  $\mu\text{g/L}$  iron (initial concentration 55  $\mu\text{g/L}$ ), 2  $\mu\text{g/L}$  manganese (initial concentration 41  $\mu\text{g/L}$ ) and 3.0  $\mu\text{g/L}$  arsenic (initial concentration 15.0  $\mu\text{g/L}$ ). Moreover, the biological filtration efficiently removed ammonia (yield = 98%), manganese (yield = 95%) and a removal yield of 27% was obtained for iron.

## CONCLUSIONS

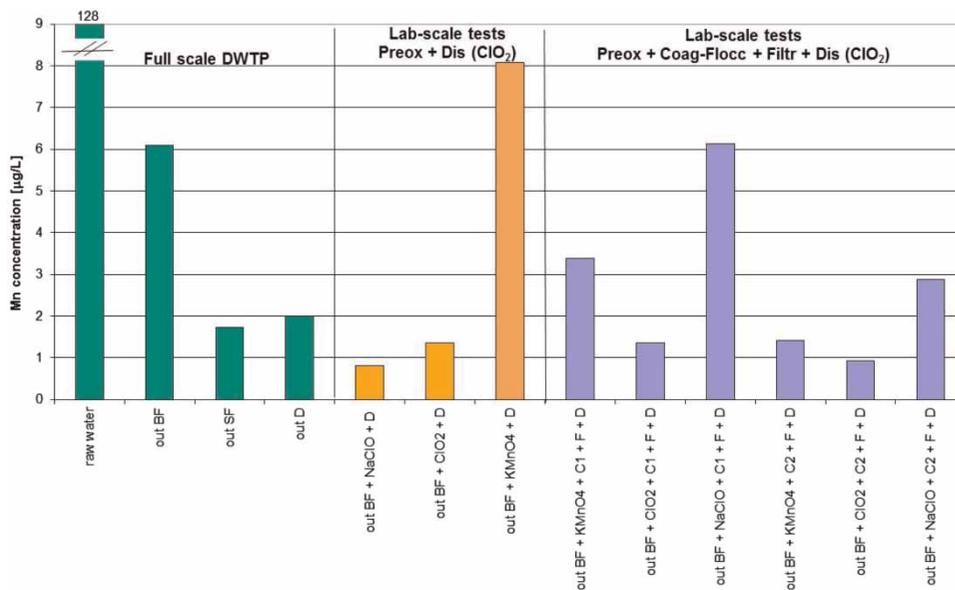
The results of the laboratory scale tests showed that, after pre-oxidation followed by final disinfection, As(III) was solely oxidized into As(V) and no removal was observed. The pre-oxidation, followed by chemical precipitation, sand filtration and final disinfection represents the best option for arsenic removal from water; in this experimental train, the use of  $\text{KMnO}_4$  and  $\text{FeCl}_3$  resulted to be the



**Figure 1** | Arsenic removal in the full scale DWTP and in the laboratory scale experimental tests (BF = biological filtration, SF = sand filtration, C1: chemical precipitation with  $\text{FeCl}_3$ , C2: chemical precipitation with  $\text{Al}_2(\text{SO}_4)_3$ , F: filtration, D: disinfection with  $\text{ClO}_2$ ).



**Figure 2** | Iron removal in the full scale DWTP and in the laboratory scale experimental tests (BF = biological filtration, SF = sand filtration, C1: chemical precipitation with  $\text{FeCl}_3$ , C2: chemical precipitation with  $\text{Al}_2(\text{SO}_4)_3$ , F: filtration, D: disinfection with  $\text{ClO}_2$ ).



**Figure 3** | Manganese removal in the full scale DWTP and in the laboratory scale experimental tests (BF = biological filtration, SF = sand filtration, C1: chemical precipitation with  $\text{FeCl}_3$ , C2: chemical precipitation with  $\text{Al}_2(\text{SO}_4)_3$ , F: filtration, D: disinfection with  $\text{ClO}_2$ ).

optimum solution for improving arsenic and manganese removal. The monitoring of the full scale DWTP operating in the same conditions tested at laboratory scale showed that the plant efficiently removed arsenic (yield = 80%),

ammonia (yield = 98%) and manganese (yield = 95%). Iron, although with a lower efficiency of removal (yield = 27%), has never exceeded the limit in the treated water.

## ACKNOWLEDGEMENTS

The authors thank the staff of Caffaro spa (BS) for the collaboration in the research and AEM Gestioni srl (CR) for providing the groundwater samples. Thanks also to Luca Bussi and Valentina Ventura, who performed the experimental works. Sabrina Sorlini supervised and coordinated the research and the paper elaboration and Francesca Gialdini carried out the experimental activity, the data elaboration and the paper draft.

## REFERENCES

- APAT CNR IRSA 4030 29/ 2003 Metodi analitici per le acque. Manuali e Linee Guida. Rapporti 29/2003, APAT, Rome.
- ASTM D2035-08 2008 *Standard Practice for Coagulation Flocculation Jar Test of Water*. ASTM International, USA.
- ATSDR 2005 *Toxicological Profile for Arsenic*. Agency for Toxic Substances and Disease Registry, Department of Health and Human Services, USA.
- Bissen, M. & Frimmel, F. H. 2003a *Arsenic – a review. Part I: occurrence, toxicity, speciation, mobility*. *Acta Hydroch. Hydrob.* **31** (1), 9–18.
- Bissen, M. & Frimmel, F. H. 2003b *Arsenic – a review. Part II: oxidation of arsenic and its removal in water treatment*. *Acta Hydroch. Hydrob.* **31** (2), 97–100.
- Bordoloi, S., Nath, M. & Dutta, R. K. 2013a *pH-conditioning for simultaneous removal of arsenic and iron ions from groundwater*. *Proc. Safety Environ. Protect.* **91** (5), 405–414.
- Bordoloi, S., Nath, S. K., Gogoi, S. & Dutta, R. K. 2013b *Arsenic and iron removal from groundwater by oxidation-coagulation at optimized pH: laboratory and field studies*. *J. Hazard. Mater.* **260**, 618–626.
- Choong, T. S. Y., Chuah, T. G., Robiah, Y., Koay, F. L. G. & Azni, I. 2007 *Arsenic toxicity, health hazards and removal techniques from water: an overview*. *Desalination* **217**, 139–166.
- Directive 98/83/EC of Council of 3 November 1998 on the quality of water intended for human consumption. *Off. J. Euro. Commun.* **n. L330**, pp. 32–54, 05/12/1998.
- Ghurye, G. & Clifford, D. 2004 *As(III) oxidation using chemical and solid-phase oxidants*. *J. Am. Water Works Assoc.* **96** (1), 84–96.
- Goto, K., Taguchi, S., Fukue, Y., Ohta, K. & Watanabe, H. 1977 *Spectrophotometric determination of manganese with 1-(2-pyridylazo)-2-naphthol and a non-ionic surfactant*. *Talanta* **24**, 752–753.
- Katsoyiannis, I. A. & Zouboulis, A. I. 2004 *Application of biological processes for the removal of arsenic from groundwaters*. *Water Res.* **38** (1), 17–26.
- Jurica, L., Manova, A., Dzurov, J., Beinrohr, E. & Broekaert, J. 2000 *Calibrationless flow-through stripping coulometric determination of arsenic(III) and total arsenic in contaminated water samples after microwave assisted reduction of arsenic(V)*. *Fresen. J. Anal. Chem.* **366**, 260–266.
- Legislative decree n. 31, 2 February 2001 Water for Human Consumption Implementation of Directive 98/83/CE Related to Drinking Water Quality. Ordinary Supplement of the Official Gazette no. 52, 2001/03/05.
- Mandal, B. K. & Suzuki, K. T. 2002 *Arsenic round the world: a review*. *Talanta* **58** (1), 201–235.
- Ng, J. C., Wang, J. & Shraim, A. 2003 *Review: a global health problem caused by arsenic from natural sources*. *Chemosphere* **52** (9), 1353–1359.
- Pontius, F. W., Brown, K. G. & Chen, C. J. 1994 *Health implication of arsenic in drinking water*. *J. Am. Water Works Assoc. Special Arsenic Issue* September, **86** (9), 52–63.
- Smedley, P. L. & Kinniburgh, D. G. 2002 *A review of the source, behaviour and distribution of arsenic in natural waters*. *Appl. Geochem.* **17** (5), 517–568.
- Sorlini, S. & Gialdini, F. 2010 *Conventional oxidation treatments for the removal of arsenic with chlorine dioxide, hypochlorite, potassium permanganate and monochloramine*. *Water Res.* **44**, 5653–5659.
- Standard Methods for the Examination of Water and Wastewater* 1995 19th edn. American Public Health Association/ American Water Works Association/Water Environment Federation, Washington, DC.
- Tchounwou, P. B., Centeno, J. A. & Patlolla, A. K. 2004 *Arsenic toxicity, mutagenesis, and carcinogenesis – a health risk assessment and management approach*. *Mol. Cell Biochem.* **255** (1–2), 47–55.
- WHO 2011 *Guidelines for Drinking-water Quality*, 4th edn. World Health Organization, Geneva, Switzerland.

First received 16 December 2013; accepted in revised form 14 April 2014. Available online 19 May 2014