Use of Iron- and Manganese-Oxidizing Bacteria for the Combined Removal of Iron, Manganese and Arsenic from Contaminated Groundwater

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The problem of groundwater contamination with arsenic has been under extensive discussion, especially in recent years, because of its adverse effects on human health and its widespread presence in groundwater throughout the world. Large drinking water plants in developed countries normally find alternative and arsenic-free water resources, or they apply conventional arsenic removal methods, such as coagulation/filtration, activated alumina and ion exchange. Smaller towns, communities and individual users in rural areas often rely on local water resources and the respective removal methods developed mainly for larger water treatment plants are not easily applicable, because of high operational and capital costs, or they are simply too complicated and their use is sometimes limited by the specific water composition. Consequently, small drinking water systems face the difficult challenge in providing a safe and sufficient supply of drinking water at a reasonable cost. Alternative treatment methods have been developed for application in these cases. In the present paper, the simultaneous removal of arsenic during biological iron and manganese oxidation is reviewed. The method relies on the use of indigenous non-pathogenic iron- and manganese-oxidizing bacteria. Dissolved iron and manganese species often coexist with arsenic in groundwater. Therefore, the application of this method could provide consumers with water of high quality, which is practically free of iron, manganese and arsenic, complying with the respective legislative limits. In this paper the biological oxidation of iron and manganese has been reviewed and recent findings regarding the removal of arsenic have been summarized. Arsenic(III or V) can be removed efficiently from a wide range of initial concentrations with practically limited operational cost, apart from the capital costs for the installation of treatment units. As a result, the use of chemical reagents for the oxidation of trivalent arsenic can be avoided, because As(III) was efficiently oxidized to As(V) by these bacteria (acting as catalysts) under similar conditions, which are usually applied for the removal of iron and manganese by biological means.

Key words: arsenic, iron, manganese, combined removal, bacterial oxidation, groundwater

Introduction

As the world population increases, one of the most fundamental resources for human survival, i.e., the availability of clean water, is decreasing. Estimates from the World Health Organization (WHO) indicate that around 43% of the world population does not have adequate sanitation and 22% does not have access to drinking water. The rising demands for clean water cannot be met only by the exploitation of surface water supplies. This has led to increased dependence on groundwater resources in many parts around the world, resulting in increased groundwater utilization, although several health issues have been encountered, due to the presence mostly of geogenic inorganic pollutants. The most commonly found inorganic pollutants in groundwater are iron and manganese which must not exceed the respective secondary concentration limits, as imposed by the European Commission and WHO, of 200 and 50 µg/L, respectively (WHO 1996; EC 1998). Apart from these, the presence of arsenic has received increased consideration during recent years due to its worldwide presence in groundwater and the adverse effects on human health (Nordstrom 2002).

The use of biological treatment, either in situ or ex situ, has gained popularity over the last twenty years due to the presence of certain advantages over the conventional physicochemical treatment methods (Bouwer and Crowe 1988). Biological treatment uses microorganisms to reduce, oxidize or eliminate groundwater contaminants, either as the sole treatment technique, or combined with other conventional physicochemical processes, such as sorption, filtration, etc. Its basic principle is that remediation...
tion takes place as the result of oxidation-reduction (usually referred as redox) potential changes (Chapelle 1993). When electron donors and electron acceptors are available to microorganisms, they are able to remove electrons, acting as “circuits” and mediating the redox reactions.

Several metals can be removed from groundwater sources as a result of their reduction, induced by the presence of microorganisms (“bio-reduction”). The most common examples are the cases of chromium, uranium and selenium remediation (Lovley 1995). The reduced forms of these metals are less mobile than the respective oxidized ones and therefore these microorganism-driven reactions can contribute to their overall removal. On the contrary, the remediation of other metals, such as iron and manganese (and indirectly arsenic), is based on their oxidation and the resulting production of insoluble forms, which are subsequently separated mainly by the application of filtration, or even by simple settling (Chapelle 1993).

The usual physicochemical approach to decrease the iron content in groundwater is by the application of aeration, which causes the oxidation of iron and initiates its precipitation. These waters are almost saturated with oxygen, containing about 8 mg/L, before being subjected to filtration. This task is often complemented by the use of a contact tank, settling or flotation, and occasionally by the supplementary addition of chemical reagents. Other conventional methods are the direct chemical oxidation using chlorine dioxide (ClO₂), or potassium permanganate (KMnO₄), and without the application of pre-aeration, but also followed by filtration (Knocke et al. 1991). However, several problems are associated with these physical-chemical processes, when applied for iron and manganese removal. The oxidation stage is characterized by rather slow kinetics, whereas iron can form complexes with silicates or humic substances, decreasing its removal (Theis and Singer 1974). Additionally, the application of chlorination can cause adverse effects, by inhibiting the biological activity (when required), as well as problems related to the flocculation of oxidized forms of iron and manganese.

Although these problems are known today and can possibly be controlled, the conventional methods present certain limitations which cannot be easily overcome. For example, filtration rates are restricted to a maximum of 10 to 15 m/h, the chemical treatment is indispensable when complexing phenomena occur, and the retention capacity of these constituents (Fe and Mn) during an operation cycle, i.e., between two subsequent backwashings of a filter, is low (0.2–1.2 kg Fe/m² and 0.1–0.7 kg Mn/m²) (Mouchet 1992). Alternatively, the biological iron and manganese oxidation has been applied based upon the use of indigenous, non-pathogenic iron- and manganese-oxidizing bacteria (Chekalla et al. 1985; Dimitrakos et al. 1992; Katsoyiannis and Zouboulis 2004b; Strembal et al. 2004). According to several of the aforementioned studies, a shift from abiotic to biotic Fe and Mn removal/precipitation can increase substantially the water treatment plant capacity and reduce the operation costs by up to 80%.

Iron and manganese bacteria are well known to borehole operators as the cause of iron and manganese biofouling, i.e., the build-up of orange- and black-coloured slimes and encrustations on casing, pump and pipe surfaces (Tyrrel and Howsam 1997). Iron-oxidizing bacteria can be divided in two main groups, with respect to the purpose of iron oxidation by bacteria. The first group is the chemosynthetic bacteria, in which the most common iron bacterium, the stalked Gallionella ferruginea belongs (Fig. 1A) (Hallbeck and Pedersen 1990; Katsoyiannis and Zouboulis 2004b). Chemosynthetic bacteria are able to utilize the small amount of...
energy, which is available from the oxidation of ferrous to ferric iron species for the transformation of inorganic carbon, such as bicarbonate, into biomass (Hallbeck and Pedersen 1990). The oxidation of 1 mole of ferrous iron produces 40 kcal of free energy, as compared to the 686 kcal of free energy produced by the oxidation of one mole of glucose (Chappelle 1993). As a relatively small amount of energy is derived from this reaction, large amounts of iron have to be oxidized in order to produce relatively small amounts of biomass.

*Leptothrix ochracea* is the second most common iron and manganese bacterium and the most common eneathel one, occurring all over the world in slowly running ferrous iron-containing water, which is poor in readily degradable organic material (van Veen et al. 1978). Under these conditions the pronounced development and activity of this microorganism can give rise to the accumulation and sedimentation of large masses of ferric hydroxide and manganese dioxide. In contrast, *Gallionella ferruginea*, *Leptothrix ochracea* is a heterotrophic bacterium, thus obtaining energy and carbon by metabolizing organic compounds (van Veen et al. 1978). *Leptothrix ochracea* can immobilize iron and manganese in and around the sheaths, which surround the filaments of cells (Fig. 1B).

The case of biological manganese oxidation by *Leptothrix ochracea* and in general by sheath heterotrophic bacteria is clearer than iron. These bacteria grow at pH values of 6 to 8. Under these conditions manganese cannot be oxidized readily by the presence of dissolved oxygen and, therefore, its oxidation is mainly attributed to the bacterial (catalytic) activity, as well as to autocatalysis by the surfaces of deposited manganese oxides (Diem and Stumm 1984; Stumm and Morgan 1996).

The purpose of this paper is to summarize the present understanding of the nature of iron- and manganese-oxidizing bacteria, as well as to review the applications of these bacteria for the treatment of groundwater. During recent years, apart from the research carried out regarding the biological iron and manganese removal, the removal of arsenic and other geogenic inorganic pollutants such as uranium, strontium and lead, have also been examined by the application of relevant methods, based on the use of the iron- and manganese-oxidizing bacteria (Nelson et al. 1999; Ferris et al. 2000; Katsoyiannis and Zouboulis 2004a). In this review paper we will focus on the application of biological iron and manganese oxidation for the simultaneous removal of inorganic arsenic species from groundwater and will try to summarize the recent findings regarding this important issue of groundwater and drinking water treatment.

**Biological Iron Removal**

Iron-containing groundwater has traditionally been treated by the application of chemical oxidation, pro-

**Biological Manganese Removal**

Biological oxidation of manganese has been reported and applied for the removal of dissolved manganese from groundwater (Mouchet 1992; Gouzinis et al. 1988; Katsoyiannis and Zouboulis 2004b). The concentrations of dissolved manganese in anaerobic groundwater can reach the order of several hundreds of milligrams per litre, however the usual manganese concentrations fall in the range between 0.1 to 1 mg/L (Stumm and Morgan 1996).
The removal of dissolved manganese (Mn$^{2+}$) from groundwater is generally accomplished by oxidation, followed by precipitation and (sand) filtration for the removal of the oxidized insoluble products (Knocke et al. 1991). The abiotic oxidation of dissolved manganese by oxygen can be described by the following general equation (Kessick and Morgan 1975):

$$-\frac{d[Mn(II)]}{dt} = k_0[Mn(II)] + k_1[Mn(II)][MnO_x]$$  \hspace{1cm} (1)

This expression implies that the homogenous manganese oxidation can be accompanied by an autocatalytic action, in the presence of existing manganese solid phases (Stumm and Morgan 1996). The abiotic homogeneous manganese oxidation by the presence of oxygen is a slow process at pH values below 9 (Stumm and Morgan 1996); thus, in the usual pH values encountered in most surface or ground water intended for drinking consumption (i.e., between 6–8), it will not be oxidized. Therefore, manganese is very difficult to remove by simply applying aeration and the subsequent precipitation (Diem and Stumm 1984).

It is for these reasons that chemical oxidation is generally required in order to achieve the precipitation and the effective removal of manganese within reasonable time periods and for the pH values often met in natural waters. It has been well established that KMnO$_4$ is an effective oxidant of dissolved manganese over a broad range of pH values, whereas other oxidants that can also be applied for the oxidation of manganese are chlorine and ozone (Knocke et al. 1991). To avoid the use of chemicals, biological oxidation of manganese has been considered a viable alternative for the efficient treatment of groundwater, which is generally carried out by the presence of microorganisms, which mediate the biotic oxidation of Fe(II), apart from the stalked bacteria of the Gallionella genus (Mouchet 1992).

These bacteria require more stringent conditions to oxidize manganese than those required to oxidize iron. In particular, a completely aerobic environment is required; the dissolved oxygen concentration should be higher than 5 mg/L and redox potential over 300 mV (often between 300–400 mV), depending on the pH value. In any case, the required redox potential is lower than the value corresponding to the introduction of a chemical oxidant agent, which is stronger than oxygen. Under these conditions, manganese removal is very efficient, with residual manganese concentrations below 20 µg/L (Fig. 3). As in the case of iron, the kinetics of biological manganese oxidation are quite fast, rendering the method quite favorable for application. In Table 1, the calculated $k$ value for the biological manganese oxidation is compared with respective values obtained from the literature and it can be noticed that it was significantly higher in all cases.

When ammonia coexists in the groundwater to be treated, the biological removal of manganese can take place only after the previous complete nitrification, due to the necessary evolution of redox potential. Gouzinis et al. (1998) have reported that low ammonia concentrations (<2 mg/L) did not affect the removal of manganese and could take place simultaneously in the same filter, although for higher ammonia concentrations the removal of manganese can take place only after nitrification is completed.

### Arsenic Occurrence and Distribution in Groundwater—Regulation and General Principles of Arsenic Removal Processes

Iron and manganese, in several cases, are associated with elevated arsenic concentrations of geogenic origin in groundwater (Smedley and Kinniburgh 2002). Arsenic is

![Fig. 2. Biological removal of iron; results obtained from a pilot plant operating for almost one year by spiking ferric sulfate as the source of Fe(II). Although the operation was shut down for one month, the efficient restart was achieved after only few days (2–3) of restarting operation (Zouboulis and Katsoyiannis 2005; reprinted with permission).](image)

![Fig. 3. Biological Mn(II) removal from groundwater (Katsoyiannis and Zouboulis 2004b; reprinted with permission).](image)
a toxic metalloid element, causing adverse effects on human health. Several studies have been performed to assess arsenic toxicity and its adverse effects on human health (Pontius et al. 1994; Desesso et al. 1998; Hughes 2002), demonstrating that arsenic is a human carcinogen.

The distribution of inorganic arsenic species [As(III), As(V)] in natural waters is mainly dependent on redox potential and pH conditions. Under oxidizing conditions, such as those prevailing in surface waters, the predominant species is pentavalent arsenic, which is mainly present with the oxy-anionic forms (H$_2$AsO$_4^-$, HAsO$_4^{2-}$) with pK$_a$ = 2.19 and pK$_b$ = 6.94, respectively. On the other hand, under mildly reducing conditions, such as those existing in several groundwaters, As(III) is the thermodynamically stable form, which at pH values of most natural waters is mostly present as the nonionic form of arsenious acid (H$_3$AsO$_3$, pK$_a$ = 9.22).

The sorption of As(V) onto mineral surfaces of soils or sediments is a dominant mechanism for the immobilization and removal of arsenic from aquatic sources (Katsoyiannis and Zouboulis 2002; Zouboulis and Katsoyiannis 2002b). As the respective pH value plays a significant role in the speciation of arsenic in waters and for a given redox potential value, it also comprises the key controlling parameter (factor) in arsenic removal processes, when sorption is used for its removal. In Fig. 4 the effect of pH on arsenic(V) removal by sorption onto iron hydroxides is shown. From 50 µg/L initial As(V) concentration, the removal is more efficient when the pH value was 5 and at higher values it was decreased.

Generally, As(III) is sorbed to a smaller extent than As(V) to a variety of sorbents, thus arsenic(III) is considered more mobile; therefore, the immobilization of arsenic is enhanced by the preliminary oxidation of As(III) to As(V) (Jekel 1994). The higher mobility of As(III) is illustrated clearly by the difference in the respective breakthrough curves, demonstrating the removal efficiencies of both As(III) and As(V) species by their sorption onto hydrous ferric oxides, coated on the surface of the filter medium (Fig. 5). Thus, in drinking water treatment processes, As(III) must be preliminarily oxidized to As(V), in order to produce water with lower arsenic concentrations than the limit of 10 µg/L imposed by WHO, EU and the U.S.A. (WHO 1996; ECD 1998; U.S. EPA 2002).

Despite the limits, elevated arsenic concentrations exist in the groundwater of several areas around the world. In Southeast Asia (Bangladesh, Vietnam, West Bengal, Nepal, Cambodia) over 50 million people depend on the supply of groundwater that contains arsenic concentrations higher than the locally applicable concentration limits of 50 µg/L. It is estimated that over 500 million people might consume water with arsenic over the WHO, U.S.A. and EU limits of 10 µg/L. In the U.S.A. more than 13 million people, mostly in western states, are exposed to arsenic concentrations in drinking water higher than 10 µg/L. In Europe, many regions are also affected by elevated arsenic concentrations (Hungary, Romania, Greece, Spain, Finland, Germany) (Nordstrom 2002; Smedley and Kinniburgh 2002). Therefore, the necessity is emerging for employing new and innovative treatment methods for dealing with this increasing problem.

### Arsenic Removal during Biological Iron Oxidation

Several researchers have reviewed the conventional treatment methods for removing arsenic from contaminated waters (Jekel 1994; Kartinen and Martin 1995; Bissen...
and Frimmel 2003). However, biological oxidation of iron and manganese as a treatment method for arsenic removal is a relatively new method and can be considered as alternative.

During preliminary studies the biological iron and manganese oxidation has been applied to remove As(III) and As(V) from groundwater, without the use of chemical oxidizing agents, apart from oxygen and bacteria as previously described (Katsoyiannis et al. 2002). Arsenic can be removed by direct adsorption or co-precipitation on the preformed biogenic iron or manganese oxides, whereas the oxidation of As(III) was induced by the iron-oxidizing bacteria, leading to improved overall removal efficiency of arsenic content.

The main parameter affecting the efficiency of arsenic(III) removal during the biological iron oxidation (and its subsequent removal) is the respective redox potential (Katsoyiannis et al. 2002). Under specifically applied conditions (i.e., redox potential 270–280 mV, pH 7.2, dissolved oxygen 2.7 mg/L), which are optimized for the removal of dissolved iron content (leading to higher than 95% removals), the trivalent arsenic was found to be removed by about 80%, which was further decreased down to 65% when the initial arsenic concentration was over 150 µg/L (Katsoyiannis et al. 2002). By increasing the dissolved oxygen up to 3.7 mg/L, the removal of trivalent arsenic was enhanced. This caused an additional increase of redox potential to values over 320 mV, which affected positively the As(III) removal (Fig. 6). When the redox potential was increased to values over 320 mV the removal of trivalent arsenic was increased up to 95%. It is also worth mentioning that at these redox values the residual arsenic was always below 5 µg/L, starting from initial arsenic concentrations around 35 to 40 µg/L. When the same experiments were carried out after disinfecting the filtration columns, it was found that the removal of arsenic was drastically decreased, implying that bacteria contribute significantly to the oxidation of As(III) (Fig. 7).

These results indicated that during the biological removal of iron, the oxidation of As(III) took place to the respective pentavalent form, which was considered the cause of the enhanced overall arsenic removal. It was previously described that the oxidation of trivalent arsenic by air or oxygen could take days, weeks or even months, depending on the specific experimental conditions (Kim and Nriagu 2000). However, by the application of biological oxidation the residence time is usually in the range of few minutes (around 7 min) and the dissolved oxygen content far below saturation. Thus, under these conditions oxygen cannot be the sole (or even the major) oxidative agent for arsenic and iron in this treatment system. Bacteria do play an important role in the sufficient remediation of trivalent arsenic.

Long-term experiments, regarding the removal of arsenic(III) during the biological oxidation of iron, over an operational period of 10 months are presented in Fig. 8. During this period the groundwater was continuously spiked with arsenic(III). The removal of trivalent arsenic was efficient during the whole operation period. Even when the filters were shut down and the operation was cut off for one month due to a technical problem, the efficient restart of treatment process and the effective removal of arsenic was accomplished within 4 days. Nevertheless, as expected, the removal of As(V) was very efficient with the application of a specific treatment method (Fig. 9). From a wide range of initial arsenic(V) concentrations (50–200 µg/L) the residual arsenic concentration was always below the legislated maximum concentration limit (MCL) of 10 µg/L. For the removal
of As(V), the presence of bacteria and the existence of aeration are probably not essential parameters, and it has been reported that during the physicochemical oxidation of iron, arsenate removal was around 80% for low initial arsenic concentrations (20–50 µg/L). This was decreased to around 60% when the initial arsenic concentrations were increased up to 188 µg/L, and for influent Fe(II) content 2 mg/L (Edwards 1994).

Fig. 7. As(III) concentration related with the presence of bacteria (living or dead microorganisms); experimental conditions: pH 7.2, [Fe]₀ 2.8 mg/L, DO 3.7 mg/L, linear velocity 8.2 m/h, residence time 7.3 min (Katsoyiannis and Zouboulis 2004a; reprinted with permission).

Fig. 8. Long-term As(III) co-removal experiments during the biological oxidation of iron; experimental conditions: [Fe]₀ 1–1.5 mg/L, pH 6.6, redox potential 320–340 mV, linear velocity 10 m/h (Zouboulis and Katsoyiannis 2003; reprinted with permission).
With the application of biological iron oxidation although the conditions are quite the same, i.e., (Fe)\textsubscript{o} = 2.8 mg/L, the removal efficiency was not affected by the different initial arsenic concentrations. The final concentration of arsenic was always below the MCL of 10 µg/L, corresponding to the percentage of arsenic removal over 95%. This implies that microorganisms are also involved in the removal of As(V). It is assumed that bacteria can act as catalysts by pre-concentrating As(V) on their surface, which is also encrusted with iron oxides, leading to fast reaction (surface precipitation and/or surface complexation) between the dissolved arsenic species and the deposited biogenic iron oxides, and resulting in the production of respective insoluble products. Furthermore, iron oxides produced by bacterial oxidation are considered denser and have greater specific surface areas; therefore, they are expected to adsorb greater amounts of arsenic.

It should also be noted that most physicochemical sorptive treatment methods present the drawback of adsorbate exhaustion (breakthrough). In order to continue the operation, the consumed adsorbing materials need either regeneration or replacement. In this process, the adsorbents were continuously produced by the biological oxidation of dissolved iron, which was also present in groundwater. Therefore, the need for regeneration was excluded and there was no requirement for monitoring the respective breakthrough point. Once set in effective operation, the only consideration would be to perform the backwashing action periodically, in order to avoid filter clogging and to remove the excess sludge.

Arsenic Removal during the Biological Oxidation of Mn(II)

The removal of arsenic(III or V) can be also accomplished when only manganese is present in the groundwater at significant concentrations, during the biological oxidation of manganese (Fig. 10). Around 80% removal of arsenic can be achieved for both inorganic species, when the initial concentrations are in the range of 30 to 45 µg/L. The results are less efficient than those obtained during the biological oxidation of iron from groundwater (Katsoyiannis and Zouboulis 2004a). During iron oxidation the percentage removal of arsenic accounts for more than 90% and the legislative maximum concentration limit (10 µg/L) can be achieved fairly easily, even starting from rather high initial arsenic concentrations (230 µg/L).

The difference in the removal efficiency can be attributed to the fact that iron oxides are efficient adsorbents regarding the removal of arsenic, presenting a strong tendency to create surface complexes with arsenic ions; whereas the use of manganese oxides is not equally efficient. Manganese oxides usually present point of zero charges (PZCs) between 2 and 4.5 (Stumm and Morgan 1996). Therefore, at the pH values of most natural waters (6–8), the net surface charge of manganese oxides...
is negative. As a result, the sorption of arsenic onto manganese oxides can be attributed to chemical interactions through specific adsorption, because the respective coulombic interactions do not favour the sorption.

This technology appears to suit well, regarding the treatment of manganese-containing waters which are slightly contaminated with arsenic and can be applied without the additional use of chemical reagents for the oxidation of Mn(II) or As(III). This renders the method quite economic, while the fact that these filtration systems can also be used for efficient long-term operational periods without replacing the filter medium, further consolidates this statement.

As with the previous case of arsenic removal using iron oxides, the oxidation of arsenic was catalyzed by the presence of bacteria. The mechanism of arsenic(III) removal by biogenic manganese oxides is illustrated in Fig. 11. During this process the depletion of As(III) concentration is faster than the depletion of total arsenic concentration, indicating that the oxidation product of As(III), i.e., As(V), is released in the water stream. The subsequent depletion of total arsenic content is attributed to the sorption of As(V) onto the biogenic (i.e., biologically produced) manganese oxides, which are deposited onto the filter medium, comprising the major solid phase of these filters.

Arsenic(III) oxidation using biological manganese oxidation is faster compared to the respective values obtained for the arsenic oxidation in relevant studies, but applying other oxidants (Table 2). It can be observed that the oxidation of As(III) in the specific treatment system is much faster than the other physicochemical methods usually applied. The faster rates of As(III) oxidation support the conclusion that the oxidation of As(III) was probably catalyzed by the bacteria, i.e., by the same microorganisms, which also mediate the oxidation of Mn(II). Furthermore, the oxidation of As(III) (presenting a half-life $t_{1/2} = 3$ min) was found to proceed almost in parallel with the bacterial manganese oxidation for this specific treatment unit, because the kinetic analysis of Mn(II) oxidation yielded a relevant half-life value ($t_{1/2} = 3.98$ min). A possible oxidation mechanism would be the reaction of As(III) with dissolved oxygen, mediated by the heterotrophic manganese-oxidizing bacteria, most probably by *Leptothrix ochracea*, according to the following reactions (Katsyotiannis et al. 2004):

**Catalyzed oxidation**

$$\text{H}_3\text{AsO}_3 + \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_3\text{AsO}_4 + \text{H}_2\text{O} \quad (2)$$

**Sorption**

$$2(\equiv\text{Mn-OH}) + \text{H}_3\text{AsO}_4 \rightarrow (\equiv\text{MnO})_2\text{AsO}_2 + 2\text{H}_2\text{O} \quad (3)$$

**Effect of Phosphate on Removal of As(III) during the Biological Oxidation of Iron and Manganese from Groundwater**

Among the anions which may be present in aquatic sources and can therefore inhibit the sorption of arsenic, is phosphate. The effect of phosphate on the removal of arsenic by sorption onto iron oxides has been documented previously. Meng et al. (2001) have reported that in order to achieve the efficient removal of arsenic by coagulation, when phosphate is present, a ratio Fe:As of 40:1 is needed, whereas in the absence of phosphate the respective ratio can be only 12:1. Assuming a bidentate bond on the surface of uncharged solids, the competition between arsenic and phosphate at pH 5 can be written as follows (Hongshao and Stanforth 2001):

$$\text{(FeO)}_3\text{PO}_4\text{H} + \text{H}_3\text{AsO}_4 \leftrightarrow \text{(FeO)}_2\text{AsO}_2\text{H} + \text{H}_2\text{PO}_4^- \quad (4)$$

The effect of phosphate on the removal of arsenic by its sorption onto the biogenic manganese oxides is also strong. It was clearly demonstrated that the presence of phosphate inhibits arsenic(III) removal, which from 80% removal efficiency (in the absence of phosphate) drops down to around 30% (Fig. 12). Phosphate competes with arsenic for the available sorption sites on the surface of manganese oxides. The sorption of phosphate onto manganese oxides is a very efficient and fast procedure. The manganese oxides present a high affinity for creating surface complexes with phosphates, with the respective value of logK equal to 29 (Yao and Millero 1996). The presence of phosphate, however, has not shown any particular effect on the oxidation of As(III) (Fig. 13), although it inhibited the overall arsenic removal. As illustrated in Fig. 13, although the effluent concentration of total arsenic was around 20 µg/L, the respective concentration of As(III) accounted only for 1 to 2 µg/L.
Combined Biological Treatment of Groundwater Containing Elevated Concentrations of Iron, Manganese and Arsenic

Groundwater contaminated with elevated concentrations of both iron and manganese is commonly found. In several cases, arsenic may also be present in significant concentrations which have to be removed before the water will be supplied to the consumers. In these cases, the use of biological oxidation would allow the simultaneous removal of iron, manganese and arsenic. The treatment method is based on a design similar to that previously described for the simultaneous biological removal of iron and manganese, namely a two-stage filtration configuration, including a step of initial aeration. The dissolved iron will be removed during the first filtration stage and the dissolved manganese during the second filtration step, by mechanisms already described in the previous sections.

Arsenic either in the trivalent or pentavalent form would be mostly removed during the first filtration step by bacterially catalyzed oxidation and by adsorption onto the surface of freshly precipitated biogenic iron oxides. In cases where the initial arsenic concentration is quite high, or the applied filtration rates are also high (decreasing the respective contact time and the overall removal of arsenic), then additional arsenic removal can take place during the secondary filtration step by its adsorption onto the biogenic manganese oxides. Figure 14 summarizes the sequence of reactions taking place in a treatment system designed for the biological removal of iron, manganese and arsenic.

Conclusions

The problem of arsenic contamination of groundwater has been under extensive discussion, especially in recent years, because of its adverse effects on human health and its worldwide presence in groundwater.

In the present paper, an alternative technology for the removal of both trivalent and pentavalent arsenic

![Image 12](katsoyiannis_and_zouboulis.png)

**Fig. 12.** Effect of phosphates on the removal of As(III) during the biological oxidation of manganese from groundwater (Katsoyiannis et al. 2004; reprinted with permission).

![Image 13](katsoyiannis_and_zouboulis.png)

**Fig. 13.** Effect of phosphates on the oxidation of As(III) during the biological oxidation of Mn(II) in groundwater treatment (Katsoyiannis et al. 2004; reprinted with permission).

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**TABLE 2.** As(III) depletion rates reported in the literature as compared with those obtained in the present study regarding the oxidation of As(III) by manganese oxides

<table>
<thead>
<tr>
<th>As(III) oxidation</th>
<th>Kinetic constant, $k$ (min$^{-1}$)</th>
<th>Half-life, $t_{1/2}$ (min)</th>
<th>Literature cited</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III) oxidation during the biological Mn(II) oxidation</td>
<td>0.23</td>
<td>3</td>
<td>Katsoyiannis et al. (2004)</td>
</tr>
<tr>
<td>Microbial oxidation</td>
<td>0.038</td>
<td>18</td>
<td>Wilkie and Hering (1998)</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td></td>
<td>Langner et al. (2001)</td>
</tr>
<tr>
<td></td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abiotic oxidation by MnO$_2$</td>
<td>0.067 (pH 4)</td>
<td>10.2</td>
<td>Scott and Morgan (1995)</td>
</tr>
<tr>
<td></td>
<td>0.035 (pH 7)</td>
<td>19.8</td>
<td>Oscarson et al. (1983)</td>
</tr>
<tr>
<td></td>
<td>0.0096 (pH 7.5)</td>
<td>72</td>
<td>Moore et al. (1990)</td>
</tr>
<tr>
<td>Oxidation by dissolved oxygen (abiotic)</td>
<td>$2.2 \times 10^{-4}$</td>
<td>3168</td>
<td>Kim and Nriagu (2000)</td>
</tr>
<tr>
<td>Oxidation by dissolved air (abiotic)</td>
<td>$9.7 \times 10^{-5}$</td>
<td>7056</td>
<td>Kim and Nriagu (2000)</td>
</tr>
<tr>
<td>Oxidation by ozone</td>
<td>0.15</td>
<td>4.5</td>
<td>Kim and Nriagu (2000)</td>
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</tbody>
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species is reviewed and conclusions can be drawn. The method for arsenic removal is based on the already established biological iron and manganese oxidation from groundwater. Biological iron and manganese oxidation is caused by several microorganisms which are indigenous in most groundwater, such as Gallionella ferruginosa and Leptothrix ochracea. The main product of biological oxidation of iron and manganese is usually a mixture of poorly ordered iron and manganese oxides often containing significant amounts of organic matter. The intermixing of iron or manganese oxides, organic material and bacterial presence, produces complex, multiple sorbing solids, which exhibit unique metal retention properties. Arsenic(V) can be removed by direct adsorption or co-precipitation on the preformed biogenic iron oxides, whereas As(III) oxidation by bacteria can take place, leading to improved overall removal efficiency.

The use of iron- and manganese-oxidizing bacteria was found to catalyze trivalent arsenic oxidation and the total arsenic content was removed by sorption on biogenic iron and manganese oxides. Arsenic removal was more efficient by sorption on iron oxides than on manganese oxides. The method was examined under long-term operation. Approximately 70,000 bed volumes of groundwater containing arsenic (60–80 µg/L) were treated in an operation which lasted around 10 months. Residual arsenic concentration did not exceed the limit of 10 µg/L. The rates of oxidation of iron, manganese and arsenic are faster than those reported for physicochemical oxidation, indicating the catalytic role of bacteria.

The application of the specific treatment technology offers several advantages over conventional physicochemical treatment methods. Efficient removal of inorganic arsenic can be achieved without the use of any chemicals for oxidation or sorption processes. This renders the technique environmentally friendly and more economical. The operation does not require monitoring of a breakthrough point, like in other column adsorption processes, as the sorbents (biogenic iron and manganese oxides) are produced continuously by the biological oxidation. This contributes to the combined removal of three major groundwater contaminants: iron, manganese and arsenic.

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References


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