



Review

Removal processes for arsenic in constructed wetlands

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ABSTRACT

Arsenic pollution in aquatic environments is a worldwide concern due to its toxicity and chronic effects on human health. This concern has generated increasing interest in the use of different treatment technologies to remove arsenic from contaminated water. Constructed wetlands are a cost-effective natural system successfully used for removing various pollutants, and they have shown capability for removing arsenic. This paper reviews current understanding of the removal processes for arsenic, discusses implications for treatment wetlands, and identifies critical knowledge gaps and areas worthy of future research. The reactivity of arsenic means that different arsenic species may be found in wetlands, influenced by vegetation, supporting medium and microorganisms. Despite the fact that sorption, precipitation and coprecipitation are the principal processes responsible for the removal of arsenic, bacteria can mediate these processes and can play a significant role under favourable environmental conditions. The most important factors affecting the speciation of arsenic are pH, alkalinity, temperature, dissolved oxygen, the presence of other chemical species – iron, sulphur, phosphate –, a source of carbon, and the wetland substrate. Studies of the microbial communities and the speciation of arsenic in the solid phase using advanced techniques could provide further insights on the removal of arsenic. Limited data and understanding of the interaction of the different processes involved in the removal of arsenic explain the rudimentary guidelines available for the design of wetlands systems.

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1. Introduction

Arsenic (As) is mostly found in the earth's core and in clay- and sulphide-rich portions of the earth's crust (Henken, 2009b). Being a metalloid in group 15 on the periodic table (along with antimony, bismuth, nitrogen and phosphorus), arsenic is well known for its chronic toxicity, particularly when exposure occurs over prolonged periods. Arsenic exposure via drinking-water is related to lung, kidney, bladder and skin cancer. For example, drinking-water arsenic concentrations in excess of $50 \mu\text{g L}^{-1}$ have been associated with increased risks of cancer in the bladder and lung, whilst drinking-water arsenic levels even below $50 \mu\text{g L}^{-1}$ have been associated with precursors of skin cancer (IPCS, 2001). Therefore, the presence of arsenic in water supply poses a serious risk to human health.

Surface and ground waters in many parts of the world have been found to naturally contain As concentrations that make these waters unsuitable for human use. Significant concentrations of As have been reported in various countries such as Bangladesh, Chile, USA, China, and India. In Bangladesh, for example, about 100 million people currently drink water with As concentrations up to 100 times the World Health Organisation (WHO) drinking water guideline, which is $10 \mu\text{g L}^{-1}$ (Mohan and Pittman Jr., 2007). Two of Northern Chile's main rivers, the Loa River and the Luta River, have As concentrations of around 1400 and $240 \mu\text{g L}^{-1}$ respectively (Romero et al., 2003; Dirección General de Aguas, 2008).

To remove As from potential drinking water sources, a variety of conventional and non-conventional technologies have been studied, and these technologies have been reviewed by several authors (Mohan and Pittman Jr., 2007). However, it is known that conventional engineered treatment technologies are costly and create problems of sludge generation and disposal (Kosolapov et al., 2004; Cohen, 2006; Nelson et al., 2006). In addition, these systems often become sources of As-rich effluents and are typically located in remote isolated areas (such as mining sites), thus precluding the transportation of the effluents to large centralised treatment facilities. As such, to prevent As pollution of watercourses, it is essential to find onsite, decentralised treatment systems that are robust and have low maintenance requirements and operating costs.

Constructed wetlands are low-energy 'green' systems that have been increasingly applied in wastewater treatment since the mid-1980s (Sun and Saeed, 2009). Since the late 1990s, the application of wetland systems has accelerated, primarily due to rising costs of fossil fuel-derived energy sources and worldwide concern about the emission of greenhouse gases and climate change (Lee et al., 2009). Currently, the applications of wetland systems are mostly in the treatment of domestic sewage, especially in rural areas in developed countries in Europe and the USA (Cooper et al., 1996; Scholz and Lee, 2005; Kadlec and Wallace, 2009).

Constructed wetlands have considerable potential to remove metals and metalloids, including arsenic (Ye et al., 2003; Buddhawong et al., 2005). Some studies have been carried out to investigate the removal of metals in wetlands (Kleinmann and Girts, 1987; National Rivers Authority, 1992; Sobolewski, 1999; Sjöblom, 2003), but most have focused on acid mine drainage (AMD) treatment, primarily to remove sulphate, iron (Fe) and manganese (Mn) (Wallace and Knight, 2006). Despite their potential, few experimental studies have been specifically designed to investigate As removal in wetland systems. Kadlec and Wallace (2009) reviewed

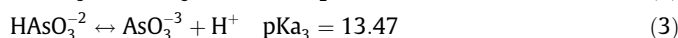
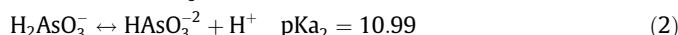
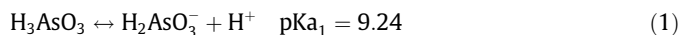
some key aspects of As behaviour in treatment wetlands, but the review was largely based on unpublished data or data found in the North American Treatment database NABD (US EPA, 1998). Other reviews are available in the literature on the removal of metals using constructed wetlands (Dunbabin and Bowmer, 1992; Sheoran and Sheoran, 2006; Yeh, 2008; Marchand et al., 2010), but they provide a general overview of metals and metalloids. Therefore, arsenic removal is only briefly covered, with little information available on the processes responsible for transformation and retention of arsenic, and the factors which control these processes.

This review aims to summarise what is currently known about the physicochemical processes for As removal in constructed wetlands, including major environmental factors that affect these processes. Microorganism-mediated mechanisms, which can also remove As by direct and indirect means, are discussed. Major knowledge gaps that currently impede wetland modelling and design for As removal are identified, together with research directions and tools that could potentially address these gaps.

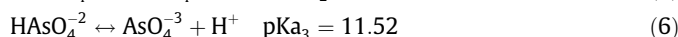
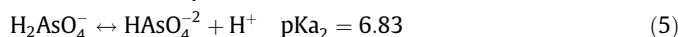
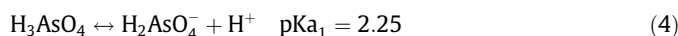
2. Arsenic chemistry

Arsenic is a highly reactive metalloid that can be found in oxidation states -3 , 0 , $+3$ and $+5$. In natural waters, arsenic occurs as arsenite (AsO_3^{-3}) and arsenate (AsO_4^{-3}), referred to as As(III) and As(V). As(III) mostly exists in reducing groundwaters and hydrothermal waters, whilst As(V) is more often present in surface waters and oxidising groundwaters (Henken and Hutchison, 2009). The main factors that control arsenic speciation are the oxidation state and pH.

As(III) commonly hydrates to arsenious acid; therefore its chemistry depends strongly on pH. The predominant As(III) species is arsenious acid, H_3AsO_3 , due to the high value of pK_{a1} (pK_a values reported by Wolthers et al. (2005) under the condition of 25°C and 1 bar pressure). The reactions of the dissociation of arsenious acid and its respective anions are shown below, along with the associated pK_a values (where $\text{pK}_a = -\log(\text{K}_a)$, and $\text{K}_a =$ equilibrium constant of the reaction):



As(V) commonly hydrates to arsenic acid, and its chemistry also depends on pH. The most common species are H_2AsO_4^- and HAsO_4^{-2} , due to the low pK_{a1} value (pK_a values reported by Wolthers et al. (2005)). The reactions of dissociation of arsenic acid and its respective anions are shown below along with the associated pK_a values:



The toxicity of arsenic depends on its speciation; for example, arsenite is significantly more toxic than arsenate (APHA et al., 2005). It is typically more difficult to remove arsenite than arsenate from contaminated water; this is because in natural waters, under normal pH conditions (6)–(9), arsenite is mostly found as an uncharged species (H_3AsO_3), and negatively charged species

(H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-}) are found only at high pH (>9). On the other hand, arsenate is commonly found as negatively charged species (H_2AsO_4^- and HAsO_4^{2-}); which are easier to remove than are uncharged species, because the charges of the As(V) oxyanions allow them to be removed by sorption, anion exchange or precipitation/coprecipitation (Henken and Hutchison, 2009).

Arsenic species in water can have different transformation pathways: (1) methylating or demethylating by interacting with biological organisms, (2) oxidising or reducing biotically or abiotically, (3) sorbing onto solids, (4) precipitating, and (5) coprecipitating. Generally, the chemistry of the water determines the chemistry of arsenic (Henken and Hutchison, 2009). Since the biogeochemical cycles of iron and arsenic are coupled in natural systems (Kneebone et al., 2002), the presence of Fe affects the speciation of As. Iron (oxy)(hydro)oxides are especially important and effective in sorbing and/or coprecipitating arsenic in both natural and artificial system (Henken, 2009a). In natural aquatic systems, arsenic speciation is often controlled by reactive surfaces with which As can associate, such as soils, clays, colloids, minerals, organic matter, and metal oxides and oxyhydroxides. Constructed wetlands can provide most of these surfaces to remove As, which suggests that in theory they should have the potential to remove arsenic, provided that the environmental conditions are conducive.

3. Arsenic removal mechanisms in constructed wetlands

Being considered complex bioreactors due to interactions between microbial communities, plants, soil and sediments, subsurface flow wetlands may remove pollutants via various physical, chemical and biological processes (Kadlec and Wallace, 2009).

The occurrence and rate of these processes depends on the nature of the pollutants and environmental conditions.

Metal removal processes in wetlands have been reviewed by different authors (Kleinmann and Girts, 1987; National Rivers Authority, 1992; Sobolewski, 1999; Sjöblom, 2003; Sheoran and Sheoran, 2006; Yeh, 2008; Garcia et al., 2010). Some authors have focused on microbially-mediated processes (Kosolapov et al., 2004; Faulwetter et al., 2009), whilst most of them have referred more generally to a wide range of removal processes. Because the removal pathways are dependent on each other, the overall removal process is very complex, making the identification of specific removal pathways and functions more difficult (Sheoran and Sheoran, 2006). In addition, the reactivity of As differs from that of metals such as copper (Cu), zinc (Zn), Fe and Mn. Therefore, As removal processes may differ from those of other “common” metals and, As removal may occur under quite different environmental conditions. Metals such as Cu and Zn are cations and precipitate easily at basic pH, whereas arsenic species are either neutral or anions and require more specific environmental conditions (for example, the presence of other species as detailed in Section 3.1). Furthermore, the removal mechanisms for As in constructed wetlands have not been well understood (Singhakant et al., 2009a), due to the complexity of As chemistry and lack of experiments on As removal in constructed wetlands.

However, it can be observed from the studies to date that the main processes responsible for the removal of arsenic in constructed wetlands are precipitation and sorption. Arsenic speciation plays a role in the removal, but environmental factors such as pH and the presence of other chemical species are also important. Microorganisms can enhance the removal of As by mediating redox and precipitation processes. The main arsenic transforma-

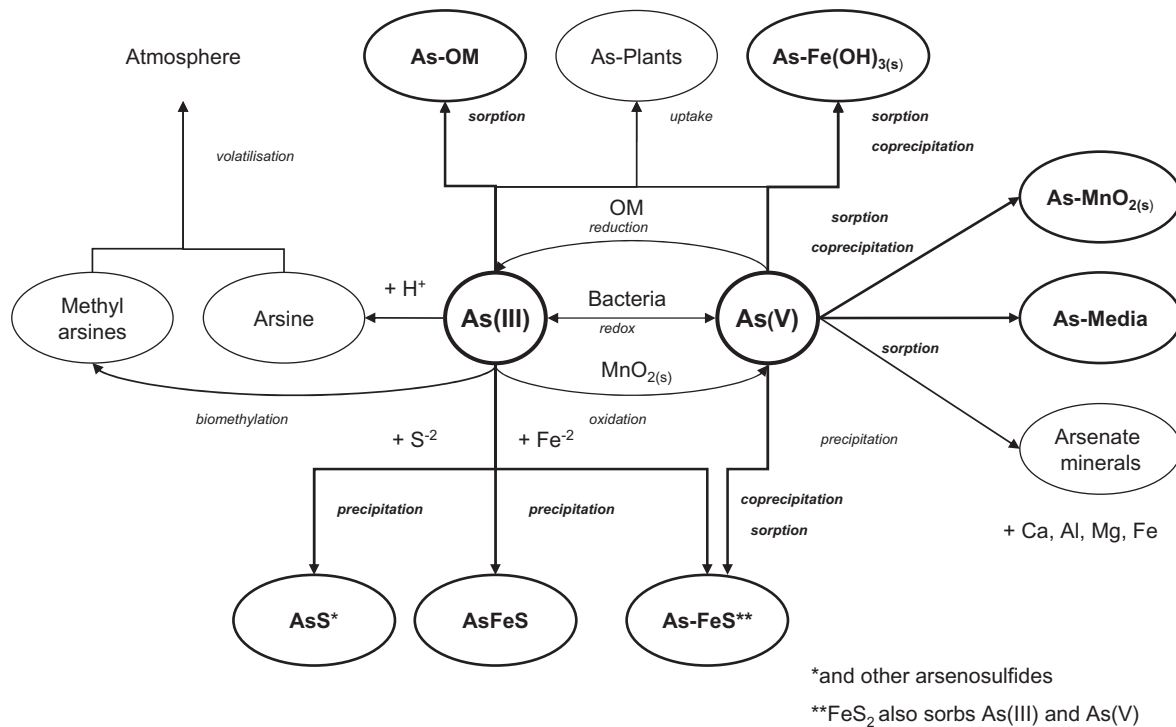


Fig. 1. The routes of arsenic transformations in a constructed wetland. The processes considered to be most important in the overall removal are highlighted in bold. Arsenite and arsenate species are located in the centre, and the black arrows show that the oxidation/reduction process can be mediated by bacteria, oxidation by manganese oxides ($\text{MnO}_{2(s)}$), and reduction by organic matter (OM). The upper section shows that both arsenite and arsenate can be sorbed by OM, uptaken by plants, and sorbed/coprecipitated by iron oxyhydroxides ($\text{Fe}(\text{OH})_{3(s)}$). The section to the right indicates that arsenate can be sorbed/coprecipitated by $\text{MnO}_{2(s)}$, sorbed by the media, and precipitated as minerals in the presence of calcium (Ca), magnesium (Mg), aluminium (Al) and Fe. The section to the left illustrates that arsenite can react with hydrogen (H^+) and form arsine, which can be subsequently removed through volatilisation. Arsenite also can be biomethylated, being the final methyl compounds volatile. The bottom section shows that arsenite can precipitate as sulphide/iron minerals such as realgar (AsS) and arsenopyrite (AsFeS), and can also be sorbed/coprecipitated with iron sulphide (FeS). In addition, pyrite (FeS_2) can not only sorb arsenite, but also arsenate.

tion routes in a constructed wetland, in the presence of other species (such as Fe, S and Ca), are illustrated in Fig. 1, and are discussed in more detail in the following sections. Those processes considered to be most important in the overall removal are highlighted in bold.

3.1. Precipitation

Precipitation refers to dissolved species (such as H_2AsO_4^- and HAsO_4^{2-}) reacting with other dissolved species (such as Fe(III) and Ca) to form solid insoluble reaction products. This process may result from oxidation, reduction, pH changes or the mixing of chemicals into a solution (Henken and Hutchison, 2009). In oxidising environments with high levels of As(V), precipitation of the As(V) with Ca, Mg, Al and Fe(III) may occur (Henken, 2009a). Under reducing environments and in the presence of S and Fe, As can form insoluble sulphide compounds (Buddhawong et al., 2005; Singhakant et al., 2009a), such as orpiment As_2S_3 , in which arsenic is present as As(III), and arsenopyrite AsFeS . Orpiment may precipitate in a low Fe and S rich environment, especially under acidic conditions (Wilkin and Ford, 2006). The formation of As_2S_3 was considered to be abiotic prior to the study of Newman et al. (1997), which reported a bacterium able to precipitate As_2S_3 .

In constructed wetland environments, arsenic is retained mostly in sediments (Ye et al., 2003) or media (Buddhawong et al., 2005; Singhakant et al., 2009a,b), rather than accumulated in plants. Singhakant et al. (2009a) analysed the forms of As in a wetland using Tessier extraction and found that the residual fraction of As was the predominant As form, concluding that As was mainly retained in the pores of the wetland media (sand and gravel). In addition, the oxidisable fraction (binding to organic matter and sulphides) was the second most important fraction. Singhakant et al. (2009b) also found that the major removal mechanisms were trapping within porous media (residual fraction) and trapping with Fe and Mn on the media surface (reducible fraction).

The redox potential (Eh) may indicate the presence of sulphide precipitates. Buddhawong et al. (2005) attributed the removal of As and Zn to processes that exclude precipitation as sulphides: the authors did not measure redox potential levels below 100 mV, so they assumed unfavourable redox conditions for sulphate-reducing bacteria and concluded that sulphides could not precipitate. No further details were provided about the required redox conditions for sulphide precipitation by sulphate-reducing bacteria. Different authors have reported different redox potential values required by sulphate-reducing bacteria to thrive: less than -200 mV (Cabrera et al., 2006; Diels et al., 2006), less than -100 mV (Willow and Cohen, 2003), or between -150 and -200 mV (Tuttle, 1969). Rahman et al. (2008) noted that microbial sulphate reduction was greater under redox potential values between -160 and -190 mV, and this higher sulphate removal contributed to higher removal of As. It should be noted that different redox potentials can be found in different parts of the wetland and they cannot necessarily be represented by the measurements, since plants generate microzones of oxidising or reducing conditions in the substrate (Cohen, 2006). Therefore, measured redox potential values can be used to assess the presence of oxidising or reducing conditions, but they must be evaluated carefully.

Sulphate-reducing bacteria (SRB) can mediate the precipitation of arsenosulphide minerals. These bacteria occur primarily in near-neutral anoxic environments (Sjöblom, 2003), preferring pH conditions between 5 and 8 (Cohen, 2006). Some examples are *Desulfobacter hydrogenophilus* (autotrophic, growth on H_2 and CO_2) and *Desulfovibrio sulfodismutans* (heterotrophic) (Ehrlich, 2002).

Sulphate-reducing bacteria transform sulphate to sulphide according to the following reaction (Cohen, 2006):



where CH_2O represents a simple organic molecule, such as acetate (National Rivers Authority, 1992). The available sulphide reacts with As(III), forming insoluble As–S minerals.

Sulphate reduction requires a reducing environment and an electron donor. Rahman et al. (2008) reported that under oxidising conditions and with a deficiency of electron donors, sulphate reduction was limited and the removal of As was achieved via mechanisms other than precipitation of As(III) sulphides. On the other hand, under more reducing conditions and surplus carbon, sulphate reduction by sulphate-reducing bacteria contributed to an efficient As removal (Rahman et al., 2008). However, their conclusions were drawn based on their measured water quality parameters (Eh, TOC), without monitoring microbial community composition or function directly. Groudev et al. (2008) reported a numerous and diverse population of sulphate-reducing bacteria mainly in sediments of constructed wetlands treating acid mine drainage, where As and other heavy metals were precipitated as sulphides (Groudev et al., 2008); this was one of few studies that monitored sulphate-reducing bacteria communities contributing to As removal in a constructed wetland. Another example is Duncan et al. (2004), who reported appreciable numbers of sulphate-reducing bacteria and iron-reducing bacteria. They suggested that the main As removal pathway was the biogenic precipitation of As sulphides, given that As concentrations were positively correlated with sulphur concentration, and negatively correlated with organic carbon concentration. Recently, Mattes et al. (2010) provided more details of the wetland system described in Duncan et al. (2004), highlighting that not only sulphate-reducing bacteria played a role in As removal, with iron-oxidising bacteria also making a significant contribution. However, the As removal mechanisms are not yet clearly identified (Mattes et al., 2010).

Despite the fact that some studies have reported that arsenosulphide minerals accumulate in wetland sediments when bacterial sulphate reduction was active (Langner et al., 1999; Duncan et al., 2004; Groudev et al., 2008), the importance of As_2S_3 precipitation caused by sulphate-reducing bacteria remains poorly understood (Buddhawong et al., 2005). In acid mine drainage, the initial As removal process in the presence of sulphate-reducing bacteria is not clear (adsorption or coprecipitation with other metals sulphides or ferrihydrite have been proposed). Formation of insoluble arsenic sulphide can occur after initial removal when reducing conditions have been established (Neculita et al., 2007).

Other microorganisms, such as arsenite-oxidising bacteria, arsenate-reducing bacteria and iron-oxidising bacteria, can also mediate the removal of As (directly or indirectly). Many microorganisms can oxidise or reduce arsenic, even if it is present in the mineral form (Reddy and DeLaune, 2008), and these microorganisms coexist in the soil environment (Macur et al., 2004). In constructed wetlands, some researchers have isolated different types of bacteria responsible for arsenite oxidation. Recently, in constructed wetlands treating acid mine drainage in Bulgaria, Groudev et al. (2008) isolated heterotrophic bacteria (related to the genus *Pseudomonas*) able to oxidise As(III) to As(V) at slightly acidic and neutral pH, in addition to acidophilic chemolithotrophs also able to oxidise As(III). In natural and constructed wetlands in Korea, Chang et al. (2010) isolated heterotrophic arsenic-oxidising bacteria, and despite the fact that natural and constructed wetlands presented different environments, the microorganisms presented similar bacterial groups and genes responsible for microbial arsenite oxidation (Chang et al., 2010). Regarding arsenate reduction, Macy et al. (2000) isolated two heterotrophic bacteria able to reduce As(V) and SO_4 , from an As-contaminated reed bed in Bendigo, Australia (Macy et al., 2000).

Iron-oxidising bacteria have an important role in the oxidation of Fe at pH levels below 4.5 (Hedin et al., 1994). Fe(II) oxidation occurs in the absence of bacteria at pH 6 or above (Singer and Stumm, 1970; National Rivers Authority, 1992). Iron oxidation followed by oxyhydroxide precipitation is considered by some researchers to be the most important iron-removal mechanism in wetlands (National Rivers Authority, 1992). Since Fe oxyhydroxides can sorb/coprecipitate As (Fig. 1), iron-oxidising bacteria may cause the removal of both Fe and As. Different microorganisms (autotrophs and heterotrophs) are able to oxidise Fe (Emerson et al., 2010). Nicomrat et al. (2006) characterised the microbial communities in a constructed wetland receiving acid mine drainage and found that the acidophilic chemolithotrophs *Acidithiobacillus ferroxidans* and *Acidithiobacillus thiooxidans* were the dominant microbial species, both able to oxidise Fe and S (Nicomrat et al., 2006). Hallberg and Johnson (2005) enumerated different groups of microbes from constructed wetlands, among them iron-oxidising bacteria, which encouraged ferrous iron precipitation and concomitant arsenic removal (Hallberg and Johnson, 2005). This study was important in that it was able to demonstrate clearly that the presence of iron-oxidising bacteria caused the removal of As.

Despite the fact that several studies have shown that the role of bacteria is crucial in the removal of metals and As in constructed wetlands (e.g., Sobolewski, 1999; Kosolapov et al., 2004; Hallberg and Johnson, 2005; Sheoran and Sheoran, 2006; Groudev et al., 2008), this role has largely been inferred from processes observed in other water treatment systems and/or natural wetlands. Many publications corroborated these assumptions based on measurements in water chemistry, but they lack direct evidence of specific microbial consortia responsible for the removal of As in constructed wetlands (Faulwetter et al., 2009). These indirect studies have used a variety of approaches to the role of microorganisms in the removal. In the previously mentioned example of Rahman et al. (2008), it was assumed that under certain environmental conditions, sulphate-reducing bacteria were active and contributed to the removal. Ye et al. (2003) explained the sequestration of As in the sediments as being due to high rates of microbial activity, but no further details were provided as to how this implication was drawn. Singhakant et al. (2009a) mentioned that anoxic conditions could promote the growth of sulphate-reducing bacteria, and despite the fact that they found that As was mostly retained in bed material, they concluded that this capability could be enhanced by As sulphide precipitation. Buddhawong et al. (2005) discarded the influence of sulphate-reducing bacteria due to the high redox potential values reported (as detailed previously). These facts suggest that even though the presence of bacteria depends on environmental conditions, their actual presence in wetland systems and their role in the removal of As remains poorly understood, suggesting that further, more direct studies are required.

Faulwetter et al. (2009) reviewed more than fifty articles on microbial techniques (investigating microbial density, microbial activity and microbial diversity) in the study of wetlands. However, few studies employing microbial diversity techniques have been published (Faulwetter et al., 2009). The three most commonly applied methods for exploring microbial diversity are fluorescence in situ hybridization (FISH), denaturing gradient gel electrophoresis (DGGE) and ribosome gene cloning (Truu et al., 2009). Studies are more often undertaken on the quantity rather than on the diversity of microbial communities (Jin and Kelley, 2007), but the communities associated with wetland systems remain poorly characterised (Lloyd et al., 2004). Various authors have recommended further studies of microbial density, diversity (Faulwetter et al., 2009) and activity (Kosolapov et al., 2004; Stein et al., 2007); suggesting a general agreement about the need for more detailed studies of the microbial communities, so as to optimise their role

and improve the performance of constructed wetlands. In addition, the available reviews on microbial processes of heavy metal removal in constructed wetlands (Kosolapov et al., 2004; Faulwetter et al., 2009) refer only briefly to the removal of arsenic driven by microorganisms.

3.2. Coprecipitation

Coprecipitation refers to As that adsorbs onto or within the developing or fresh precipitates of other chemical species. Coprecipitation occurs at the same time as or shortly after the host solids precipitate from the solution, such as arsenic coprecipitating with iron (oxy)(hydro)oxides. On the other hand, sorption involves the incorporation of pollutants onto or within pre-existing solids (Section 3.3). Coprecipitation might also involve arsenic-bearing colloids or other fine-grained particles becoming trapped (adsorbed) in the interiors of precipitating compounds (Henken and Hutchison, 2009). In constructed wetlands, Buddhawong et al. (2005) suggested that Fe could act as a coprecipitating agent for As, particularly in the oxic zones, whereas Singhakant et al. (2009a) concluded that organic sulphides produced by biodegradation of roots and microorganisms can co-precipitate As and Fe under reducing conditions, and also can precipitate As directly.

3.3. Sorption

Sorption refers to a treatment process when both adsorption and absorption are involved simultaneously, or when adsorption and absorption cannot be distinguished. Adsorption refers to the removal of ions and other dissolved species from liquids or gases by their accumulation on the surfaces of solid materials, and the adsorbed species are not a major component in the internal chemistry of the solid. Adsorption processes usually involve ion exchange. Absorption is the assimilation of chemical species into the interior of a solid substance (Henken and Hutchison, 2009). Various surfaces are able to sorb arsenic. The adsorption capacity depends on the properties of the surface, the arsenic species and concentration, presence of competing ions, and the pH (Stollenwerk, 2003). In a constructed wetland, the main surfaces which have been found to sorb arsenic include: (1) the medium (or substrate), (2) mineral particles or colloids -particularly (oxy)(hydr)oxides-, and (3) organic matter.

Gravel is the most common supporting medium that has been used for arsenic removal (Buddhawong et al., 2005; Kröpfelová et al., 2009; Singhakant et al., 2009a). However, Buddhawong et al. (2005) reported that the As adsorption capacity of gravel was low (in the range of up to $4.3 \mu\text{g kg}^{-1}$), and therefore it was likely that other processes, such as binding with the Fe content of the gravel media, were responsible for the removal of As. The type and chemical composition of the supporting media should therefore be considered for improving the efficiency of metal removal in a wetland (Ye et al., 2003). However, from the available literature, it appears that the use of an adequate or specific sorbent media to enhance the removal of As in constructed wetlands has been poorly studied, despite the fact that it has been recommended by several researchers (refer to Section 4.6).

Arsenate sorption onto most metals (hydr)oxides and clay minerals (Inskeep et al., 2002), especially onto Fe and Mn oxyhydroxides, is well known and has been reported by a number of researchers (e.g., Kneebone et al., 2002; Pastén et al., 2006). Furthermore, it has been reported that Fe oxides have greater sorption capacity for As than do clay minerals (Gräfe and Sparks, 2006), aluminium (Al) oxides (Pfeifer et al., 2004) and Mn oxides (Mucci et al., 2000). On the other hand, arsenite can be sorbed mostly onto Fe hydroxides (Inskeep et al., 2002). Several authors attribute this sorption property as an important source of metal removal in con-

structed wetlands if Fe and/or Mn oxides are present (Sjöblom, 2003).

Organic matter is able to sorb arsenite and arsenate (Redman et al., 2002), inhibiting As mobility by serving as a binding agent and/or by forming insoluble complexes (Wang and Mulligan, 2006). On the other hand, it has been reported that organic matter can enhance As release from sediments and soils, mainly through competition for available adsorption sites, the formation of soluble organic matter–arsenic complexes, and the change of redox chemistry in site surfaces and As species (Wang and Mulligan, 2006). Organic matter can also compete with As for sorption sites on metallic oxides (Redman et al., 2002). In addition, during the mineralisation of organic matter, arsenate can serve as an electron acceptor, being reduced to arsenite (Ackermann et al., 2008). Hence, organic matter can remove arsenic from water, but also release it from solid phases and therefore increase As concentration in the aqueous phase. In the case of constructed wetlands, Singhakant et al. (2009a) concluded that organic matter enhanced the adsorption capacity in the wetland bed: humic and fulvic acids from plants root decomposition could associate with As by metal-bridging mechanisms and ligand exchange-surface complexation (Singhakant et al., 2009a). Buddhawong et al. (2005) concluded that organic compounds released by root activity could be used by microorganisms as carbon sources. This decreased the redox potential, which caused the dissolution of crystalline Fe; but due to partly oxic conditions, Fe was precipitated, coprecipitating As. Despite the fact that little research has been conducted on the As binding capability of organic matter (Wang and Mulligan, 2006), the effect of organic matter on As mobility depends partly on the solubility of organic matter itself (Sharma and Sohn, 2009). Dissolved organic matter tends to mobilise As, whereas particulated organic matter tends to immobilise As.

Arsenic sorption is a complex process that can occur in different surfaces in a constructed wetland and is affected by different factors, such as pH, redox potential, Fe and organic matter. Sorption onto Fe oxides is favoured by oxidising conditions and near-neutral to acidic pH (Section 4.1). As such, specific conditions must be provided to promote sorption in a wetland.

3.4. Methylation

Methylation followed by volatilisation of metalloids such as mercury (Hg), selenium (Se) and As is a well known phenomenon that takes place in aquatic environments (Kosolapov et al., 2004). Under highly reducing and anoxic conditions, As can be converted to gaseous arsines, which are highly toxic compounds (Frankenberg Jr. and Arshad, 2002). Examples of volatile arsines are arsine (AsH_3), methylarsine ($\text{CH}_3(\text{AsH}_2)$), dimethylarsine ($(\text{CH}_3)_2\text{AsH}$) and trimethylarsine ($(\text{CH}_3)_3\text{As}$). The formation of methylarsines is a biological process that can be mediated by different organisms, such as fungi and bacteria. Sulphate-reducing bacteria are the main Hg methylating agent in soil and aquatic sediments (Bright et al., 1994). King et al. (2002) studied Hg methylation by sulphate-reducing bacteria in constructed wetlands, but no evidence of As methylation by sulphate-reducing bacteria was reported, despite the fact that it has been found that these bacteria are able to methylate As in other environments (Bright et al., 1994; Michalke et al., 2000). As such, arsenic methylation is not believed to significantly contribute to As removal in constructed wetlands. Furthermore, the relevance of this process in constructed wetlands has not been well studied (Buddhawong et al., 2005).

3.5. Plant uptake

Direct uptake and accumulation of As in plants appear to play a very minor role in As removal (García et al., 2010). For example, Ye

et al. (2003) reported that only 2% of the total As input was accumulated into the plant tissues, and they highlighted the minor role of plant uptake. The same conclusion was drawn by Singhakant et al. (2009a), who reported that only 0.5–1% of the total As input was accumulated into the plant tissues.

The accumulation of As depends on the type of plant (Zhao et al., 2010). In *Lemna gibba* L. (duckweed) (Mkandawire and Dudel, 2005) and *Spirodela polyrhiza* L. (great duckweed) (Rahman et al., 2007), accumulation of As increased as concentration of As in water increased. Harvesting could be an option for bioaccumulation, but this has been considered unsuccessful in treatment wetlands (Kadlec and Wallace, 2009). However, Adhikari et al. (2010) suggested annual harvesting based on their reported As uptake, which fluctuated between 0.05 and 0.53 kg As ha⁻¹ y⁻¹. No other harvesting recommendations have been found in the available literature. If the above-ground biomass is not harvested, leaves and stems are eventually returned to the surface of the medium. Decaying plant biomass may act as a source, but it can also act as a sink for metals (García et al., 2010). It has been found that leaves tissues can release metals such as mercury, copper and zinc (Weis and Weis, 2004), but apparently this phenomenon has not been investigated for As.

Different studies have shown that roots accumulate more As than do shoots (e.g., Qian et al., 1999; Ye et al., 2003; Barley et al., 2005; Vymazal et al., 2009; Adhikari et al., 2010). In the study of Ye et al. (2003), As concentrations in roots were 2 to 10-fold greater than those of the shoots. Mean values in roots fluctuated between 5 and 30 mg kg⁻¹ depending on the type of plant. The values reported by Buddhawong et al. (2005) in the roots of *Juncus effusus* were within that range: between 0.3 and 7.2 mg kg⁻¹.

Arsenic is taken up by plant roots (Zhao et al., 2010) and different reasons may explain why As remains there: limited translocation of As from roots to shoots (Wang et al., 2002) and the presence of Fe and S (Zhao et al., 2010). In addition, As speciation plays a relevant role in the uptake mechanism and further translocation: there is enough evidence to affirm that arsenate is taken up by the same transporters of phosphate in the roots, but it is not known what form of As is translocated from roots to shoots and how this translocation occurs. Whilst arsenate and phosphate are similar, arsenate and arsenite are not, therefore their uptake mechanisms may differ (Dhankher, 2005).

It should be noted that some studies reporting As accumulation were performed in hydroponic systems (e.g., Qian et al., 1999; Rahman et al., 2007) or in plants growing in mine waters (e.g., Mkandawire and Dudel, 2005), therefore the results may not be comparable with those in wetland systems (e.g., Ye et al., 2003; Barley et al., 2005; Buddhawong et al., 2005; Vymazal et al., 2009; Adhikari et al., 2010). Furthermore, Comino et al. (2009) found that As accumulation by *Poa annua* reached its minimum when they were planted in 100% zeolite (instead of 100% gravel, or other combinations of gravel and zeolite) due to the high As absorption capacity of zeolite. Therefore, the presence of a suitable substrate, in this case zeolite, may decrease the As uptake by plants, increasing the overall removal capacity.

Despite their minor role in As uptake, wetland plants can play an indirect but important role, because the plants: (1) stimulate the growth of metal-oxidising bacteria by oxygen transfer into the rhizosphere (Cooper et al., 1996); (2) provide organic matter as a carbon source for sulphate-reducing bacteria and metal-oxidising bacteria (National Rivers Authority, 1992), as organics released from plant roots help release sulphides to precipitate As or co-precipitate As with Fe (Singhakant et al., 2009a); (3) provide a surface for microorganisms in the wetland (National Rivers Authority, 1992; Nuttal et al., 1995); (4) use their roots as surfaces for iron plaque, which is mostly iron (hydr)oxides precipitates, to retain As (Blute et al., 2004); and (5) oxygenate the

substrate by their roots, to provide an extensive region where aerobic and anaerobic conditions are adjacent (National Rivers Authority, 1992), thereby facilitating coupled aerobic–anaerobic processes.

It would appear that the role of wetland algae in the removal of As is negligible. Buddhawong et al. (2005) reported that an algae pond (operated in parallel with constructed wetlands) did not remove As at all. Even though the use of algae as an As biosorbent has been reported (Mohan and Pittman Jr., 2007), macrophytes are likely to be or become the dominant plants in treatment wetlands (Kadlec and Wallace, 2009). It therefore appears that future research to assess the role of wetland vegetation in As removal should be focused primarily on macrophytes.

4. The effect of environmental factors on arsenic removal

A variety of environmental factors can affect the removal of As in constructed wetlands, and changes in one factor often affects another (such as pH and alkalinity; temperature and dissolved oxygen). However, many of these factors can be controlled during the design/operation of the wetlands or during any pretreatment process, such as through varying the type of wetland substrate, providing an additional carbon source, or adjusting the pH of either the influent water or of the wetland substrate.

4.1. pH

The speciation of As is significantly affected by pH. As detailed in Section 2, As(III) is mostly found as an uncharged species at neutral pH, whilst As(V) is mostly found as negative species under conditions of pH higher than 2.3. Likewise, changes in the speciation of As can affect pH, as the oxidation of As(III) to As(V) decreases the pH value, whereas the precipitation of arsenosulphides increases it.

The sorption of As to metal (oxy)(hydr)oxides depends on pH. Metal ions on the oxide surface complete their coordination shell with OH groups in the presence of water. Depending on pH, these OH groups can release or bind H^+ , developing a surface charge. As such, the sorption properties of iron and other metal (oxy)(hydr)oxides are controlled through ion exchange involving OH_2^+ , OH and O^- surface functional groups (Stollenwerk, 2003). This type of adsorption requires As to be in the form of anions (such as $H_2AsO_4^-$) to provide a proton for complexation with the OH group, forming H_2O (Hingston et al., 1972; cited by Stollenwerk (2003)). Therefore, pH is one of the most important factors controlling the adsorption of As(III) and As(V) due to its influence on As speciation and on the composition of surface functional groups. At near-neutral to acidic pH, As (V) tends to be strongly sorbed to oxide minerals. At alkaline pH, As desorption is promoted by the negative charge of the mineral surface (Mukherjee et al., 2009).

The microbial activity of sulphate-reducing bacteria is influenced by pH; these bacteria prefer neutral environments, although sulphate reduction has been observed in acidic conditions (pH 3–4) (Hao, 2003). In addition, sulphate-reducing bacteria control their pH environment by generating alkalinity (Eq. (7)).

Despite the fact that constructed wetlands have been most widely used for acid mine drainage treatment, they generally have limited capacity to raise pH (Kadlec and Wallace, 2009). The wetland substrate may be used to adjust pH: zeolite and blast furnace slag are used to raise pH, but the effect may be transitory (Kadlec and Wallace, 2009). For coal mine waters, the incorporation of anoxic limestone drains or alkali-dosing for pH adjustment is recommended where the influent has $pH < 5.5$. The use of Reducing and Alkalinity Producing Systems (RAPS, or Successive Alkalinity Producing Systems SAPS), or compost-based wetlands are recom-

mended for $4 < pH < 5.5$ (Mayes et al., 2009). Compost-based wetlands are constructed with a ~ 0.5 m thick substrate of organic waste material which promotes bacterial sulphate reduction in addition to increasing alkalinity.

4.2. Alkalinity

High alkalinity provides a buffer to prevent resolubilisation of non-dissolved As, because an abrupt change in pH can release sorbed or particulated As by solubilisation. Carbonate alkalinity is generally desirable, as carbonated species are likely to precipitate. Bacterial production of bicarbonate by sulphate reduction, or the presence of limestone in the medium, can lead to sufficiently high bicarbonate levels to form precipitates with metals (García et al., 2010). Changes in alkalinity can indicate changes in the speciation of As and sulphate-reducing bacteria activity, since sulphate-reducing bacteria provide alkalinity to the water (Eq. (7)) and affect its pH (Sjöblom, 2003; Cohen, 2006). As detailed in Section 4.1, the adjustment of pH in wetland systems is achieved by increasing alkalinity, generated by carbonated minerals and/or by bacterial activity.

4.3. Temperature

Biochemical processes are affected by temperature. The optimum temperature for sulphate-reducing bacteria ranges between 28 °C and 32 °C (Hao, 2003). Sulphate reduction rates decrease as temperature decreases (Sobolewski, 1999; Sjöblom, 2003), while the solubility of oxygen increases as temperature decreases. Therefore, if As is going to be removed by sulphide precipitation, high temperature is required.

Temperature cannot realistically be controlled in real-scale wetland systems. However, it may be controlled indirectly by controlling water depth (Lee et al., 2009). When water levels are reduced to their lowest mark, the water temperature is often elevated (Kadlec and Wallace, 2009), enhancing bacterial activity. The degree of temperature variation with depth will of course depend on season, with the greatest ability to control temperature during the warmer season.

4.4. Dissolved oxygen

Oxygen slowly oxidises As(III) in water (Bissen and Frimmel, 2003). In an oxygenated environment As can be removed by coprecipitation/sorption by Fe(III) oxyhydroxides, which are the dominant form of Fe (at $pH \geq 6.5$ and $Eh > 0$) (Faulkner and Richardson, 1989).

Dissolved oxygen also affects microbial activity. Sulphate-reducing bacteria are obligate anaerobes, but they may survive a temporary exposure to oxygen and become active again under anaerobic conditions (Hao, 2003). The critical dissolved oxygen concentration below which sulphate reduction can occur is $0.1\text{--}1\text{ mg L}^{-1}$ (US EPA, 1985). The type of flow affects oxygen availability: vertical flow wetland systems tend to have good performance in oxygen transfer, favouring aerobic microbial populations; whilst horizontal flow wetland systems tend to be oxygen-limited and therefore will typically favour anaerobic microbial populations (Kadlec and Knight, 1996; Faulwetter et al., 2009). The method of distributing inflow also affects the availability of oxygen: batch feeding favours more aerobic processes, whilst continuous feeding favours more anaerobic processes (Faulwetter et al., 2009). Vegetation also plays a role by transferring oxygen into the rhizosphere and subsequently into the substrate.

4.5. Competing species

The sorption of arsenic oxyanions is very sensitive to the presence of competing anions, particularly phosphate (PO_4^{-3} , HPO_4^{-2} , $\text{H}_2\text{PO}_4^{-}$), sulphate (SO_4^{-2}), carbonate (CO_3^{-2}), bicarbonate (HCO_3^{-}) and chloride (Cl^{-}) (Mukherjee et al., 2009). Phosphate and silicate (SiO_4^{-4}) have the same tetrahedral configuration as arsenate, and therefore can desorb As(V) from different surfaces (Henken, 2009c). It was found that As(V) bound to a soil (which consisted of quartz, clay minerals, Fe and Al oxides) was effectively mobilised by the presence of phosphate in solution. The ability of anions in mobilising As from soil particles follows the order $\text{PO}_4^{-3} \gg \text{CO}_3^{-2} > \text{SO}_4^{-2} \approx \text{Cl}^{-}$ (Goh and Lim, 2005). In addition, the sorption of carbonate on ferrihydrite (hydrated ferric oxide) decreases the sorption capacity of As(V) significantly (Appelo et al., 2002). The effect of similar anion species in the removal of As in constructed wetlands has not been reported. However, this effect may be controlled by encouraging different removal mechanisms, depending on the type of polluted water and the levels of relevant anions. For example, in groundwater, sulphate concentrations are low while phosphate and carbonate are high (Cheng et al., 2009); whereas in acid mine drainage sulphate concentrations can be several orders of magnitude higher than that of arsenate (Cheng et al., 2009), while phosphate is not present in mine-contaminated water (National Rivers Authority, 1992). One way to improve the treatment of these waters would be encouraging sulphide precipitation (sulphate reduction by sulphate-reducing bacteria) instead of sorption: the presence of sulphate will enhance the removal of As, instead of prevent it as in the case of sorption. In the case of groundwater, a source of sulphate would be required.

4.6. Supporting media

Wetland media provide support to vegetation and microorganisms, and create differing environmental conditions, such as oxic and anoxic zones. The substrates which positively influence sulphate reduction have an important role in acid mine drainage treatment, because sulphide minerals have been found in a number of wetland sediments (Sheoran and Sheoran, 2006), and therefore in wetland media. Moreover, the media offers surfaces to allow direct sorption of metal ions, and/or other particles which can sorb them. The use of alternative media to improve the removal of metals has been suggested by some researchers but not extensively studied, even though it has been recommended to improve metal removal, not only for As (e.g., Stark et al., 1996; Ye et al., 2003).

Gravel has been found to have a limited As removal capability (Lizama A. et al., in press; Singhakant et al., 2009a). Organic substrates such as peat have been found to effectively retain As in natural peat bogs and peatlands due to its affinity to organic matter (González et al., 2006; Cloy et al., 2009). However, Kalmykova et al. (2009) did not recommend peat columns to sorb As at neutral or alkaline pH due to the diminished removal capability of iron hydroxides occurring in peat (Kalmykova et al., 2009), as presented in Section 4.1. Natural and synthetic zeolites have been found to remove As (Elizalde-González et al., 2001; Payne and Abdel-Fattah, 2005; Chutia et al., 2009). However, from the literature it appears that zeolite has been used as a supporting medium in only one study of constructed wetlands aiming to remove As (Lizama A. et al., in press), even though it has been successfully employed to remove organic matter (e.g., Stefanakis et al., 2009; Stefanakis and Tsihrintzis, 2009), nitrogen (Saeed and Sun, 2011), phosphorous (Sakadevan and Bavor, 1998), and zinc (Sarafraz et al.,

2009). The study of Lizama A. et al. (in press) confirmed the ability of zeolite for removing As. Limestone has been used as a supplementary medium in wetlands (Duncan, 2002; Groudev et al., 2008), but barely as the main medium (Lizama A. et al., in press), therefore its effectiveness as the main wetland substrate for the removal of As has not been thoroughly investigated, even though it appears that it has capability to enhance the removal (Lizama A. et al., in press).

4.7. Sulphate and iron

The removal of As can be achieved by arsenosulphides precipitation. This process requires a source of sulphide (such as sulphide produced from sulphate reduction by sulphate-reducing bacteria). In wetlands that treat acid mine drainage, sulphate is usually available due to the exposure of sulphide-containing minerals to water and oxygen, which results in the generation of sulphate (National Rivers Authority, 1992). If sulphate is unavailable, arsenic precipitation will be limited to the formation of other minerals instead of sulphide minerals.

The removal of dissolved Fe often coincides with the removal of As, mainly via the same precipitation/coprecipitation processes, whereas the presence of Fe oxyhydroxides facilitates the removal of As by sorption, depending on the pH and the presence of competing species.

4.8. Carbon source

Sulphate-reducing bacteria and metal-oxidising bacteria require organic carbon for synthesis, which can be provided by vegetation, organic pollutants, or the organic portion of wetland media. A carbon source is essential to stimulate sulphate reduction, and this can be provided by organic materials such as mulch and wood chips (Lloyd et al., 2004). Supplemental carbon sources have been introduced in several wetlands to increase the rate of sulphate reduction (Sheoran and Sheoran, 2006).

5. Synthesis of As removal pathways

The main removal pathways of As in constructed wetlands are precipitation, coprecipitation and sorption. Even though these are chemical processes, they can be microbially-mediated. Depending on environmental conditions, arsenic can precipitate mainly as arsenosulphides (reduced species) and as arsenates (oxidised species), coprecipitate with sulphides or Fe oxides, or it can be sorbed onto the wetland substrate, metal oxides and/or organic matter.

The most important factors that affect the removal of As are pH and the presence of Fe and S. Other factors such as temperature, the presence of a carbon source and dissolved oxygen become more important in the presence of microorganisms.

It is possible to enhance particular removal processes by controlling/mediating their corresponding triggering factors. If there is sulphate, a carbon source can be added, therefore leading to the precipitation of arsenosulphides. If there is dissolved Fe, raising the pH will precipitate it, therefore As will coprecipitate. The design of wetland systems should consider the control of these key factors.

6. Design and modelling of constructed wetlands for As removal

Currently, there is no official guideline on how a wetland should be designed specifically for the removal of arsenic. Information about the design of wetlands for metals removal is also rare, but some tentative design guidelines have been proposed using simple pollutant removal models such as the zero-order model or the first-order kinetic decay models (Kadlec and Wallace, 2009). Before sufficient experiment data are collected for As removal, the design

for lab- or pilot-scale experimental wetland targeting As can be based on these relatively simple design guidelines. The zero-order model fixes the removal rate per unit area of the wetland, assuming that the concentration decays at a constant rate toward the final outlet concentration, and that this decay rate is proportional to the hydraulic loading (design flow/area) of the wetland (Eq. (8)):

$$R_A = \frac{Q}{A}(C_i - C_o) \quad (8)$$

where A is the wetland area, m^2 ; C_i the inlet concentration, $g L^{-1}$; C_o the outlet concentration, $g L^{-1}$; Q the flow rate, $L d^{-1}$; and R_A is the area-adjusted contaminant removal rate, $g m^{-2} d^{-1}$.

One study has provided a tentative areally-adjusted As removal rate of $18 g m^{-2} d^{-1}$ (PIRAMID Consortium, 2003); however this value represents a single treatment system consisting of ponds and wetlands in the Carnoulès mine, France; and the rate was obtained from aerobic ponds rather than from an anaerobic wetland. According to Kadlec and Wallace (2009), the reported values for R_A vary considerably in different studies (Fe–Mn removal); therefore, the model cannot be widely extrapolated without detailed site-specific calibration. They also suggested that the zero-order model does not accurately represent the metal removal process in wetlands.

The first-order model, which assumes plug-flow, is also widely used for a range of wetland types (Wong et al., 2006). The model assumes a first-order exponential decay of the pollutant concentration towards the final outlet concentration, again with the decay rate proportional to the hydraulic loading of the system (Eq. (9)):

$$K = \frac{Q}{A}(\ln C_i - \ln C_o) + C^* \quad (9)$$

where K is the areal constant rate, in $m d^{-1}$, and C^* is the equilibrium concentration.

Goulet et al. (2001) tested the suitability of this model to predict the retention of dissolved As (among other metals) in different seasons. The model failed to fit summer, autumn and winter data for almost every metal investigated, including As. The first-order model only considers hydraulic retention time, but other variables – such as biological and hydrological conditions – may need to be included in removal models (Goulet et al., 2001). In addition, a first-order model considering water losses or gains (Kadlec and Knight, 1996) did not represent the removal of arsenic in free surface flow constructed wetlands due to poor mass removal (Dombeck et al., 1998).

The first step in developing more useful and reliable design models for As removal is to collect reliable data on the influence of key design/operating parameter (including As loading, hydraulic loading, pH, availability of organic matter, etc.), with the ultimate aim of using the data to develop an improved set of algorithms to predict performance and to allow designers to size and design systems.

7. Key research needs

It is apparent from the literature that constructed wetlands have the potential to remove metals and metalloids. However, little is known about their efficiency, nor about means of optimising arsenic retention. Most studies describing the application of constructed wetlands in the removal of metals and metalloids come from studies on the treatment of acid mine drainage using surface flow systems. The efficiency of subsurface flow wetlands has not been sufficiently studied, since wetlands with conventional soil (surface flow systems) or gravel (subsurface flow systems) media have been most-commonly employed. Little is known about how the use of alternative substrates may affect As removal.

Microorganisms potentially play a key role in the mobility, toxicity and availability of metals in wetlands, but understanding of their removal mechanisms is still unclear (Kosolapov et al., 2004). From the available literature, it appears that under the presence of sulphate and reducing conditions (and therefore the possible presence of sulphate-reducing bacteria), As is primarily removed by sulphide precipitation; whereas under the presence of Fe and oxidising conditions (and therefore the presence of sulphate-reducing bacteria is unlikely), As is mainly removed by coprecipitation/sorption with Fe. However, Fe precipitation and As oxidation can be mediated by bacteria (Section 3.1). More evidence is required to confirm the relevance of the role of microorganisms in the removal of As. Different microbial communities can be involved in As removal, but they have not been extensively studied in constructed wetlands. In general, it does not seem necessary to inoculate wetlands with the desired microorganisms; however, they cannot establish immediately (Kadlec and Wallace, 2009). An initial seeding followed by the providing of the required environmental conditions for their growth could enhance the removal of As, but no studies have yet tested this hypothesis.

Since few studies have focused on investigating As, the removal mechanisms for As in constructed wetlands are not well understood. Nevertheless, in order to assess As speciation in the solid phase, different techniques have been used and they could be potentially applied in constructed wetlands.

To quantify the removal of As driven by the different wetlands components, a mass balance is usually carried out by quantifying the content of As in the plants, in the media/sediments and in the outlet water. However, with this conventional mass balance approach, it is difficult to distinguish whether the As retained in the wetland components is sorbed, precipitated, or both. Advanced techniques, such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and synchrotron-based techniques such as X-ray spectroscopy (Landrum et al., 2009; Lombi and Susini, 2009), can be used to find out the speciation of arsenic in the solid phase and identify As species. Such information can be very useful for enhancing As removal processes in wetlands, as well as in other treatment systems. Some studies have used these techniques to examine the speciation of arsenic in aquatic environments or natural wetlands. For example, Gräfe et al. (2008) studied the co-sorption products of arsenate and copper on iron minerals with extended X-ray absorption fine structure (EXAFS), whereas Blute et al. (2004) characterised the association of arsenic and iron in the roots of *Typha latifolia* (cattail) using X-ray absorption near-edge spectroscopy (XANES). The plants, however, were obtained from a natural wetland, which contained arsenic from industrial sources, rather than from a constructed wetland (Blute et al., 2004). Regarding X-ray diffraction techniques, X-ray powder diffraction was employed by Bauer et al. (2008) to identify As association in a wetland soil in contact with groundwater rich in As, whereas synchrotron-based micro X-ray diffraction (μ -XRD) and synchrotron-based micro X-ray fluorescence (μ -SXRF) were employed by Gao and Schulze (2010) to analyse As and metal-contaminated soils from a natural wetland. Despite the fact that X-ray diffraction has been employed to study the mineralogy of solids in constructed wetlands treating acid mine drainage (e.g., Karathanasis and Thompson, 1995; Gagliano et al., 2004), it appears that it has not been employed to study As-containing minerals. To date, only Duncan et al. (2004) have reported the use of synchrotron analysis to confirm the presence of As polysulphides in a wetland system in Trail, Canada, but details of the synchrotron technique were not provided, making it difficult to apply the synchrotron technique to other As-containing samples.

Current design guidelines to predict the removal of arsenic in wetland systems are based only on zero-order model and first-order model. Neither has been shown to be effective in predicting As

removal and neither takes into account important operating conditions or substrate type. Other more elaborate models for metal removal – such as the self-organising map (Lee and Scholz, 2006), and the Wheal Jane wetlands model (Whitehead et al., 2005) – may be applied to As. However, a better understanding of the main factors that affect As removal and the key processes involved is required in order to develop more reliable and useful models, which in turn, could be used to guide wetland design.

8. Conclusions

To date, the main application of constructed wetlands in the removal of metals and metalloids has been the treatment of acid mine drainage, where arsenic was not the priority pollutant. Arsenic, as a metalloid, presents differences in reactivity and therefore in the removal processes with metals such as Cu and Zn. The literature on As removal in treatment wetlands is very limited, and studies have showed that constructed wetlands have considerable potential to remove arsenic from contaminated waters.

Major As removal mechanisms in the wetlands include precipitation, coprecipitation and sorption. While methylation and plant uptake play a minor role, microorganisms such as sulphate-reducing bacteria, iron-oxidising bacteria, arsenite-oxidising bacteria and arsenate-reducing bacteria can mediate the removal mostly by oxidation/reduction reactions, followed by precipitation, coprecipitation or sorption depending on the environmental conditions. The main environmental factors that affect As removal in wetlands include pH, alkalinity, dissolved oxygen, the presence of iron and sulphate, competing chemicals, organic carbon, and the nature of the wetland media. Before reliable modelling and design equations or guidelines can be adopted, greater understanding is required of the processes affecting As removal in wetlands, taking into account the influence of the wetland characteristics and the operating conditions.

Overall, this review is the first to focus on, and integrate available literature regarding As removal in constructed wetlands. The review has identified major removal mechanisms and environmental factors that contribute to As removal. Before constructed wetlands can be confidently applied to remove As from contaminated waters, it is necessary to understand further about the roles of two main system components: supporting media and microorganisms. The role of macrophytes, both directly and in mediating microbial processes, may also be important.

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