Iron and arsenic removal rates in a continuous flow reactor treating As-rich acid mine drainage (AMD)

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Abstract

Arsenic is one of the most hazardous elements associated to acid mine drainage with concentrations ranging from ≤ 1 µg L^{-1} to hundreds of mg L^{-1} in these leachates. To date, there is no affordable method to efficiently treat As-rich AMD over the long term. Natural attenuation processes based on oxidation of iron and arsenic by autochthonous bacteria present in AMD promote precipitation of these elements. The exploitation of these processes offer a promising method for the treatment of As-rich acid mine drainage (AMD).

In the present study, the Fe(II) oxidation rates and Fe and As removal rates have been investigated in a laboratory pilot-scale system with a continuous circulation of AMD water under controlled conditions (temperature, light, water-height and residence time). The system was fed with AMD from the Carnoulès mine with a permanent acid character (pH 2-4), an average iron concentration of 0.5 g L^{-1} in the reduced form (Fe(II)) and an average arsenic concentration of 40 mg L^{-1} predominantly under As(III) oxidation state.

The efficiency and rates of Fe(II) oxidation and of Fe and As removal were determined in the pilot as a function of experiment duration and for a range of residence times, in presence or absence of a floating film that develops naturally at the surface of the water. The Fe- and As-rich biofilms formed in the pilot were characterized for their mineralogy, redox As speciation, and bacterial quantification.

During the early stage of experiment, results evidenced that the gradual coverage of the pilot channel bottom with an Fe-As precipitate, that contained $6 \pm 3 \times 10^6$ bacterial cell/g (dry wt.), increased the Fe(II) oxidation efficiency and the Fe and As removal by two orders of magnitude. At the steady state, $\sim 90\%$ Fe(II) was oxidized and $\sim 30\%$ Fe and $\sim 80\%$ As were precipitated within a residence time of 200 min. Rate values were slightly lower than those measured in the field in the natural AMD stream at Carnoulès. The development of a thin floating film at the surface of water in the pilot channel affected oxygen diffusion and retarded these rates. All these results improve our understanding of natural processes responsible for arsenic attenuation in AMD, and give some indications that might be considered when designing an Fe and As removal passive treatment in AMDs.

Key words: Acid mine drainage, arsenic removal, bioremediation, laboratory pilot

Introduction

Arsenic is an ubiquitous and toxic element associated to acid mine drainage (AMD) (Paikaray 2015; Williams 2001). Nowadays there is no treatment able to remove As efficiently over the long term without the need for expensive reactants and filter materials. In this context, bacterial oxidation of iron

followed by the precipitation of Fe-As minerals provide an opportunity to conceive a bioremediation system to effectively treat As-rich AMD. This natural attenuation process has been described in many mining sites around the world: France (Casiot et al. 2003; Egal et al. 2010), Spain (Asta et al. 2010), Japan (Fukushi et al. 2003), Australia (Gault et al. 2005), Cuba (Romero et al. 2010) or Taiwan (Chen and Jiang 2012). It could be exploited for the treatment of AMD waters containing arsenic. However, the factors controlling this natural process and the subsequent variations of As removal efficiency are still poorly understood. Therefore, it is essential to identify key parameters controlling the rates of Fe oxidation and As removal. For this purpose, experiments were conducted in a continuous flow reactor where natural attenuation of Fe and As takes place under controlled conditions of temperature, light, flow rate and water height. The effect of the gradual coverage of the bottom of the channel by a biofilm and the effect of residence time on Fe(II) oxidation and Fe- and As- removal efficiency was investigated in presence or absence of a thin film floating that formed at the water surface in low flow conditions in the pilot channel.

Materials and methods

The experiments were conducted in a laboratory continuous-flow reactor made of four channels of 1 m length and 6 cm large (Fig.1). Water is circulating through these channels by pumping through a 3.17 mm i.d. tygon tubing at the inlet and at the outlet in order to maintain a stable water height of 4 mm during the experiment. Accurate flow rate is obtained with peristaltic pumps (Gilson, Minipuls 3). Channels are illuminated (T5 Superplant 216W CROISSANCE 6500 K) in the 400-500 nm spectra with a day/night cycle of 12 h and thermo-regulated at 20 ± 0.5 ºC using a refrigerated-heating circulator (Julabo F34-EH) and circulation of thermostatic fluid in a double-envelope underneath the channels. The bottom of the channels is covered with a biodegradable canvas facilitating the natural attachment of the Fe- and As-rich deposit that forms during the experiments.
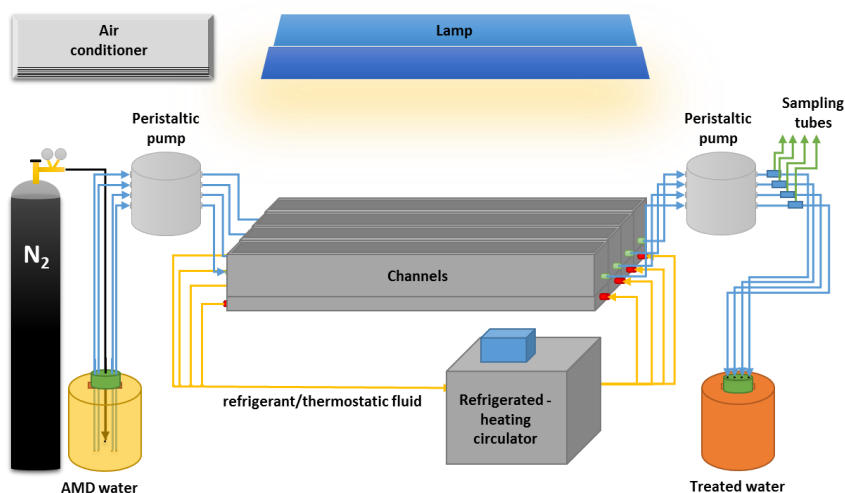
Figure 1. Laboratory continuous flow reactor treating As-rich AMD

The feeding water used in all experiments is AMD water from the Reigous creek (Carnoulès mine, France). On average, this water had a pH ~ 3, an Fe concentration of 0.5 g L^{-1} in the reduced form (Fe(II)) and an As concentration of 40 mg L^{-1}, predominantly under As(III) oxidation state. Natural attenuation processes leading to the partial removal of arsenic have been evidenced in Reigous Creek (Egal et al. 2010) and Fe- and As-oxidizing bacteria were identified (Bruneel et al. 2011). Once collected, the water was purged with N_2 and preserved under N_2 atmosphere in the laboratory until use. Nitrogen bubbling in the feeding AMD water was carried out during the whole experiment duration to limit Fe oxidation prior to channel inlet.

During the experiments, the main physicochemical parameters of the water (pH, Electrical Conductivity (EC) and Redox Potential (Eh)) were monitored at regular time intervals at the inlet and at the outlet of

the channels. Dissolved Oxygen (DO) profiles in the water column were performed with an oxygen microoptode (50 μm tip diameter, Unisense), coupled to a microoptode-meter and fixed in a micromanipulator. Water samples were taken at the inlet and outlet for analyses of Fe(II), total Fe (Fe(T)), As(III), As(V) and total As (As(T)). They were preserved using routine procedures as described elsewhere (Egal et al. 2010). Fe(II) and Fe(T) were analyzed by molecular absorption spectrophotometry at 510 nm wavelength, and As(III), As(V) and As(T) were analyzed by High Performance Liquid Chromatography ICP-MS (Héry et al. 2014).

In Exp 1a, the four channels were fed continuously during 13 days with a fixed water flow of 0.5 mL min^{-1} which set the residence time to 324 ± 30 min. During this experiment, the bottom of the channels gradually covered with an orange deposit while an iridescent floating film progressively formed at the surface of the water. Inlet and outlet water chemistry were monitored until reaching a steady state for Fe(II) oxidation in the channels. Then, a kinetic experiment was conducted; a range of residence times (from 24 to 366 min) were applied successively by regulating the flow rate. For each residence time, after a stabilization period corresponding to at least three times the residence time duration, inlet and outlet water chemistry were determined, allowing to calculate the proportion of Fe(II) oxidized and As removed for each residence time. After this kinetic experiment, the floating film was removed and the Fe-As deposits at the bottom of two of the four channels (which had an age of 17 days) were collected to analyze the mineralogy by X-Ray Diffraction (XRD), As speciation by X-ray Absorption Near Edge Structure (XANES) spectroscopy (Maillot et al. 2013), and bacteria cells counting by Gallios™ flow cytometer (Lunau et al. 2005). Then, a new kinetic experiment (Exp 1b) was conducted with the two remaining channels. The range of residence times applied to the channels was 30 - 252 min. At the end of Exp1b, 34 days after the start, the Fe-As deposits were collected and analyzed as in Exp 1a.

In each experiment, rates of Fe(II) oxidation, Fe and As removal were calculated with Eq. 1,

$$Rate\ (mol\ L^{-1}\ s^{-1}) = \frac{[X]inlet - [X]outlet}{\Delta t} \tag{1}$$

where [X] is the dissolved concentration of Fe(II), Fe(Total) or As(Total) in mol L^{-1}, and Δt is the residence time in seconds.

Results

Variation of iron oxidation and iron and arsenic removal as a function of experiment duration

At early stage of Exp 1a, during the first two days, the proportion of Fe(II) oxidized during the course of the water from the inlet to the outlet of the channel was lower than 1 %, corresponding to Fe(II) oxidation rate of 3 ± 2 x 10^{-9} mol L^{-1} s^{-1}. The proportion of Fe removed from the dissolved phase was also lower than 1 %. After this "lag time", the proportion of Fe(II) oxidized increased up to ~ 90 % within the first ~ 9 days, then stabilised (steady state) during the next 4 days. The proportion of Fe removed from the dissolved phase increased simultaneously up to 28 % (Fig. 2) and the accumulated amount of Fe precipitated inside the channel reached 0.9 mg cm^{-2}, corresponding to the gradual coverage of the bottom of the channel with an orange precipitate that looked like natural Fe-rich deposit in AMD streams. Once the steady state was reached, Fe oxidation rate averaged 3.3 ± 0.4 x 10^{-7} mol L^{-1} s^{-1},

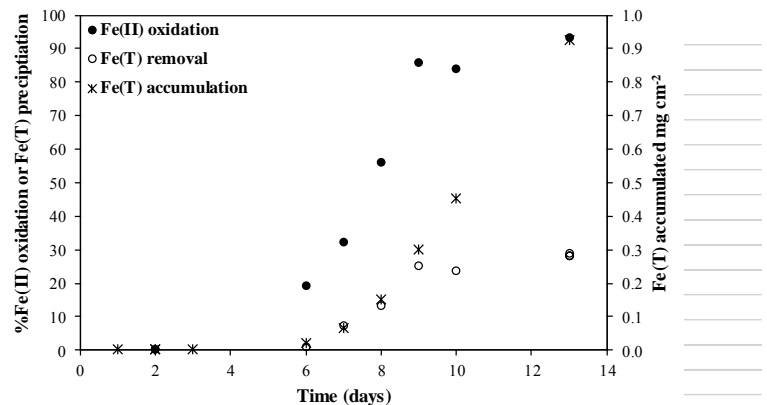*Fig 040 Variation of the proportion of Fe(II) oxidized, the proportion of Fe(T) precipitated between inlet and outlet of the channels as a function of experiment duration and the Fe(T) accumulated inside the channel per unit of area in Exp 1a and Exp 1b. Residence time was fixed at 324 ± 30 min. Physico-chemistry of the AMD water: pH = 3.01 ± 0.07; Fe(II) = 433 ± 28 mg L^{-1}; Fe(T) = 449 ± 13 mg L^{-1}; As(III) = 16 ± 14 mg L^{-1}; As(V) = 8 ± 2 mg L^{-1}; As(T) = 24 ± 17 mg L^{-1}.*

corresponding to a rate increase of approximately two orders of magnitude with respect to the rate value at the early stage of experiment, while Fe removal rate reached $1.1 \pm 0.1 \times 10^{-7}$ mol L^{-1} s^{-1} and As removal reached 65 %, corresponding to an As removal rate of $3.5 \pm 0.1 \times 10^{-9}$ mol L^{-1} s^{-1}.

Variation of iron oxidation and iron and arsenic removal as a function of residence time
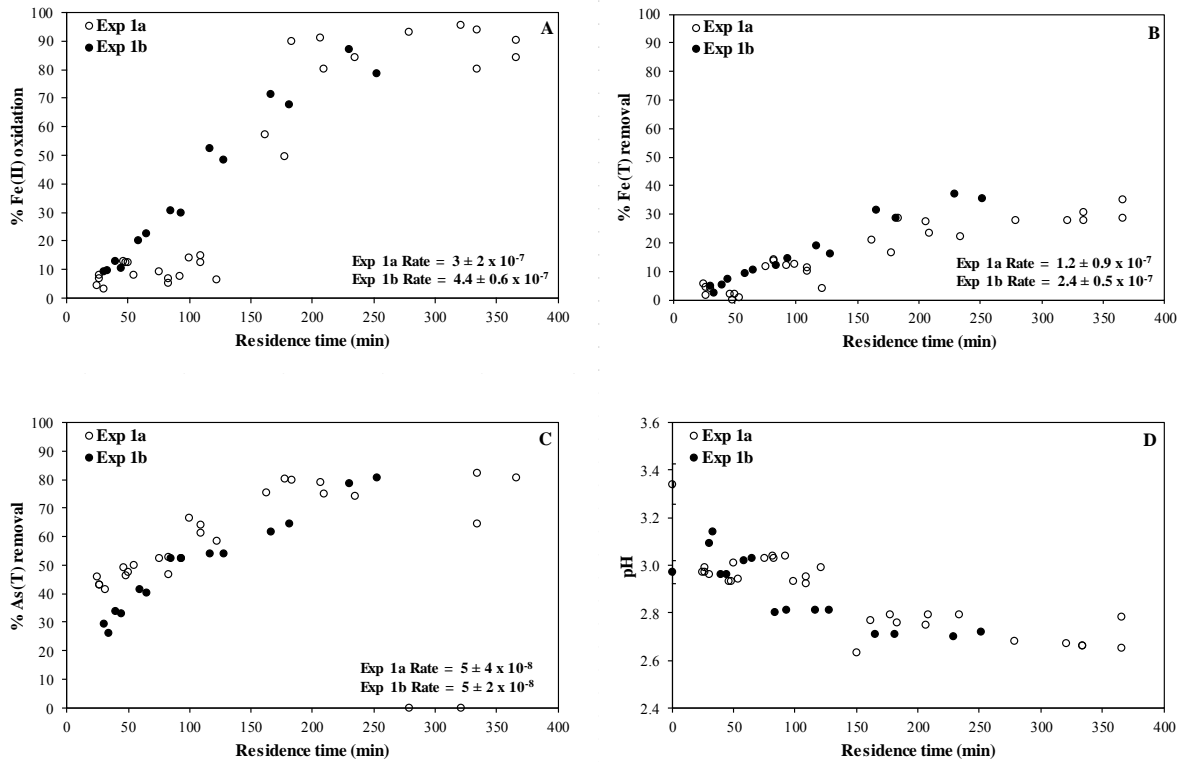
Fig. 050 *% Fe(II) oxidation (A), % Fe removal (B), % As removal (C), pH (D) as a function residence time in Exp 1a (with floating film) and Exp 1b (without floating film), and associated rates in mol L^{-1} s^{-1}. Physico-chemistry of the AMD water from Exp 1a: pH = 2.97 ± 0.05; Fe(II) = 447 ± 31 mg L^{-1}; Fe(T) = 460 ± 24 mg L^{-1} ; As(III) = 13 ± 4 mg L^{-1}; As(V) = 17 ± 6 mg L^{-1}; As(T) = 30 ± 9 mg L^{-1}. Physico-chemistry of the AMD water from Exp 1b: pH = 3.34 ± 0.08; Fe(II) = 414 ± 11 mg L^{-1}; Fe(T) = 419 ± 13 mg L^{-1} ; As(III) = 26 ± 3 mg L^{-1}; As(V) = 7 ± 2 mg L^{-1}; As(T) = 34 ± 2 mg L^{-1}.*

Kinetic experiments Exp 1a and Exp 1b showed an increase of Fe(II) oxidized by increasing the residence times from ~ 25 to 200 min, then, a plateau was reached with ~ 90 % of Fe(II) oxidized (Fig. 3A). The shape of the curve differed from Exp 1a to 1b; Fe(II) oxidation was delayed for residence times lower than ~ 120 min in Exp 1a compared with Exp 1b (Fig. 3A). Measurement of dissolved oxygen concentration along the water column showed a drastic decrease of this parameter until anoxic condition at 1 mm depth below the floating film that developed in Exp 1a (Fig. 4, Exp 1a). Such a drastic oxygen depletion was not observed in the absence of floating film in Exp 1b (Fig. 4, Exp 1b). Fe removal (Fig. 3B) was also delayed in Exp 1a for residence times lower than 120 min, as a consequence of retarded Fe(II) oxidation, but As removal did not seem to be affected (Fig. 3C). pH decreased up to ~ 0.5 units for residence times higher than ~ 200 min (Fig. 3D).
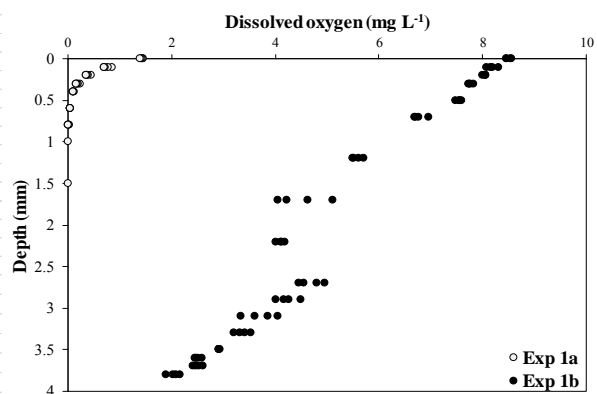
Fig. 060 *Dissolved oxygen profile along the water column (0 mm depth = water surface) in the channel. Profile Exp 1a corresponds to middle channel position under the floating film, experiment time = 21 days, residence time = 300 min. Profile Exp 1b corresponds to outlet channel position, experiment time*

Characterisation of the Fe-As rich deposit precipitated in the channels

The deposit that covered the channel bottom contained 348 mg Fe g^{-1} (dry wt.) and 67 mg As g^{-1} (dry wt.) in Exp 1a, and 334 mg Fe g^{-1} (dry wt.) and 70 mg As g^{-1} (dry wt.) in Exp 1b, with a corresponding As/Fe molar ratio of 0.14 and 0.16, respectively. XRD analyses showed that the dominant crystalline phase that precipitated in the channels was schwertmannite. XANES analyses indicated that the deposits contained both As(III) and As(V) species, with 16 ± 2 % As(III) and 85 ± 2 % As(V) in Exp 1a, and 24 ± 2 % As(III) and 78 ± 2 % As(V) in Exp 1b. Bacterial cell counting indicated 8.4 x 10^6 bacterial cell g^{-1} (dry wt.) in Exp 1a, and 4.5 x 10^6 bacterial cell g^{-1} (dry wt.) in Exp 1b.

Discussion

Increased efficiency of Fe(II) oxidation and Fe precipitation with time (Exp 1a) was associated to the gradual coverage of the bottom of the channel with an orange deposit made of iron and arsenic that also contained bacterial cells. Such deposits that naturally form in AMD streambeds were shown to contain Fe-oxidizing bacteria (Leblanc et al. 1996; Druschel et al. 2004). The formation of these bacterial rich deposits has been shown to increase the rate of Fe(II) oxidation in batch experiments with the AMD from Carnoulès mine (Casiot et al. 2003). It is well known that Fe(II) oxidation is mediated by bacterial catalysis at acid pH (Kirby and Kostak Jr 2002; Kirby et al. 1999). Results from this research show that this activity also takes place in our laboratory continuous flow channel reactor, where the presence of this bacterial rich deposit attached to the channel bottom increases Fe(II) oxidation rate by two orders of magnitude compared to the rate obtained with only free bacterial cells in the water. After ~ 9 days, a steady state was reached for Fe(II) oxidation, which seems to coincide with the complete coverage of the channel bottom with the bacteria rich deposit. DeSa et al. (2010) also observed improved Fe(II) oxidation in gutter reactors that contained iron mound sediment compared to the ones without any sediment as well as an improved Fe(II) oxidation over time as sediment aged. Fe(II) oxidation rates (~ 4 x 10^{-7} mol L^{-1} s^{-1}, Fig. 3A) obtained in the present study were close to those measured in the field in AMD from the Iberian Pyrite Belt (3.4 to 4.3 x 10^{-7} mol L^{-1} s^{-1}, in Asta et al. (2010) and 8 x 10^{-7} mol L^{-1} s^{-1} in Sánchez-España et al. (2007)) but were lower than those measured *in-situ* in the Reigous creek at the Carnoulès mine (3.8 x 10^{-6} mol L^{-1} s^{-1} in Egal et al. 2010). Lower rates were also observed in laboratory compared to the field by Sánchez-España et al. (2007). Differences in the amount of Fe(II) oxidizing bacteria and community distribution between laboratory reactors and field streams might explain such differences and will require further research.

As removal rate obtained in the present study (~ 5 x 10^{-8} mol L^{-1} s^{-1}) was ten-fold lower than in the field (3.58 x 10^{-7} mol L^{-1} s^{-1} in Egal et al., 2010), in accordance with lower Fe(II) oxidation rate in laboratory experiments. The Fe-As solids in the channel bottom resembled to those found in Carnoulès streambeds (Maillot et al., 2013), with the predominance of schwertmannite and the coexistence of both As(III) and As(V) species. Thus, the As removal in the pilot(~ 80 % within 200 min of residence time) is attributed to the natural attenuation of both As(III) and As(V) species, as a result of biological Fe(II) oxidation.

Comparison of kinetic experiments 1a and 1b showed the influence of the floating film, that develops naturally at the surface of low flow AMD water, on Fe(II) oxidation rates. Fe(II) oxidation was delayed for shorter residence times (<120 min) in presence of this floating film and this was ascribed to dissolved oxygen depletion along the water column. Elbaz-Poulichet et al. (2006) had previously observed a detrimental effect of the floating film on Fe and As removal in experimental pool at the Carnoulès mining site and suggested an oxygen diffusion inhibition.

The importance of water oxygenation for Fe(II) oxidation rate has been evidenced in many laboratory and field studies. Chen and Jiang (2012), in a field study at Chinkuashih mining area in Taiwan observed that AMD creek sections exhibited Fe(II) oxidation rates that were 1 to 2 orders of magnitude lower than in waterfall sections, where it reached 6.1 to 6.7 x 10^{-6} mol L^{-1} s^{-1}; and suggested that waterfall aeration was the main factor driving Fe(II) oxidation rate. Similarly, Sánchez-España et al. (2007) studied the Fe(II) oxidation rates in batch reactors with oxygenated/suboxic AMD, and showed that high DO concentration increased Fe(II) oxidation rates. These results suggest that oxygenation conditions

may strongly affect Fe(II) oxidation rates in laboratory and field conditions. However, the presence of the floating film did not appear to affect As removal efficiency, even at short residence times. A possible explanation is that As can be removed efficiently at low As/Fe molar ratios in the aqueous phase (< 0.1) (Maillot et al. 2013), and thus, only small amount of particulate Fe may be sufficient for As precipitation, since As(V) is effectively retained onto Fe solids at acid pH (Cheng et al. 2009). Additionally, it was found that arsenite can coprecipitate with amorphous phases, with schwertmannite, and/or be incorporated in tooeleite ($Fe_6(AsO_3)_4SO_4(OH)\cdot4H_2O$) in AMD. This last was observed in batch experiments carried out with strains of *A. ferrooxidans* in Carnoulès mine water (Egal et al. 2009).

Field and laboratory results agree with the predominant role of the Fe-bacterial-rich precipitates in the so called "natural attenuation" processes. Any human or natural activity (like heavy rains) that could remove these ochreous precipitates from AMD streambeds, would considerably affect the natural As removal efficiency. This is important to consider because the full recovering of this attenuation would probably need some time to be achieved, in accordance with the coverage of the whole riverbed with the bacterial-rich precipitates. Furthermore, the efficiency of the natural attenuation process can also be diminished at low stream flow rates, like in summer season, by standing waters that can limit oxygen diffusion along the water column. Therefore, the oxygenation has to be improved, by, for example, promoting the formation of cascades.

Conclusion

First experiments from this pilot showed the importance of some key factors affecting Fe and As removal that have to be considered in the conception of field bioremediation systems that aim to treat As-rich AMD. The deposits covering the channels bottom were found to improve Fe and As removal, due to the biotic Fe(II) oxidation. Water oxygenation was a key factor controlling the Fe(II) oxidation rate, which is the basis of natural attenuation process. This means that, for an efficient bioremediation system, the oxygenation of water has to be maximized and standing water should be avoided.

Acknowledgements

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