Performances of a semi-passive field-pilot for bioremediation of As-rich Acid Mine Drainage at the Carnoulès mine (France)

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Abstract

Passive and semi-passive treatment systems show great potential to treat AMD originating from abandoned mines. However, these methods still have operational shortcomings that limit their use at field scale, particularly dealing with arsenic rich effluents. The aim of this study was to determine iron and arsenic removal yields of two field treatment devices, which were designed to optimize the natural process of bio-oxidation and co-precipitation to clean-up the mine waste water from the ancient Carnoulès mine. Almost one year of monitoring showed the efficiency and the stability of the treatment under environmental and operational variations. Using assisted aeration and bacterial support in the devices, average arsenic (As) and iron (Fe) removals of 67% and 43% were achieved from an effluent containing up to 111 mg/L As and 1067 mg/L Fe. Additional steps will be considered to reach water quality and sludge disposal requirements.

Keywords: mine wastes, arsenic removal, bio-oxidation, field-pilot

Introduction

Arsenic is very common in Acid Mine Drainage (AMD) and represents a threat for aquatic ecosystems and human health. The development of passive or semi-passive effective, sustainable and affordable process for the treatment of As-rich AMD is essential. However, most of these processes are still running at laboratory scale only. The present study focused on the evaluation in field conditions of two semi-passive treatment devices for arsenic (As) and iron (Fe) removal from high-As AMD, at the abandoned Carnoulès mine in Southern France. These devices exploit bacterial Fe and As oxidation followed by As co-precipitation with ferric(hydroxy)sulfates. The present study is in continuity with previous laboratory and field scale trials carried out since 2014, within the framework of the projects "IngECOST-DMA" (Fernandez-Rojo et al. 2017, 2018, 2019; Laroche et al. 2018) and "COMPAs" (ongoing project) From this previous .

Methods

Two devices of 1 m^3 each were installed next to the source of the AMD stream, at the base of the Carnoulès tailing dam. The devices were both directly fed with AMD water by a pump. Devices worked in down-flow conditions and were equipped with two-air diffusers at their bottom to ensure sufficient oxygen supply (Fig. 1). The outlet effluent was discharged in the AMD downstream. Two support media were compared. One device was filled with plastic support Biofill® (device "PS") and the other with a mixture 80/20 (mass ratio) of wood and pozzolana (device "WP"). Plastic support had a porosity of 98% and a specific surface area of 160 m^2/m^3. The wood and pozzolana mixture had a porosity of 62% and an estimated specific surface area of 333 m^2/m^3. The working volumes were 263 L for PS and 290 L for WP. The treatment was carried out under controlled flow rates (15 L/h or 30 L/h) in discontinuous operation during

seven periods (A-G) from August 2019 to September 2020. Periods were defined based on changes in the inflow rate and/or undesired interruptions.

Table 1 *Duration of each working period, flow rate and corresponding theoretical hydraulic retention time.*

Period	Duration (days)	Start and end date for each period	Flow rate (L/h)	HRT (h) PS device	HRT (h) WP device
A	33	July 25 to August 28	15	17.5	19.3
B	13	December 6 to December 19	15	17.5	19.3
C	36	January 16 to February 21	15	17.5	19.3
D	19	February 21 to Mars 12	30	8.8	9.7
E	29	May 20 to June 18	30	8.8	9.7
F*	27	July 9 to August 5	30	8.8	9.7
G*†	43	August 5 to September 18	15	17.5	19.3

**Accumulation of the sludge in the bottom of the devices caused clogging of the aeration systems during period F and beginning of period G; † Cleaning of the air diffusers was done in mid-period G.*

The physico-chemistry of inlet and outlet waters were monitored at least once a week. Analysis included pH, temperature, dissolved oxygen concentration (DO), conductivity and redox potential (converted to standard hydrogen electrode (SHE)). These parameters were measured in-situ by a portable multi meter. Analysis of total dissolved Fe, As and S were carried out by ICP-MS. Redox Fe species (Fe(II), Fe(III)) were analyzed by colorimetry. Redox As species (As(III), As(V)) were analyzed using HPLC-ICP-MS. The methods are detailed in Fernandez-Rojo et al. (2017). The results were used to calculate the saturation index of As and Fe solid phases using the geochemical modeling software CHESS (van der Lee et al. 2003). Additional water samples were occasionally taken for Total Organic Carbon (TOC) analysis by catalytic oxidation (method NF EN 1484).

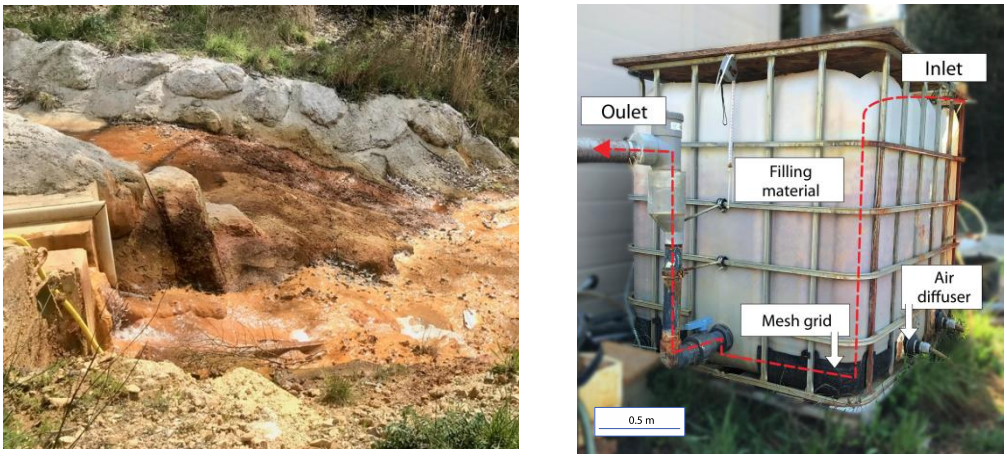


Figure 1. *AMD stream and treatment device in-situ (polyethylene container).*

A sludge sampling campaign was conducted in period F (July 27). The sludge that had accumulated onto the support media was recovered from two sections of each device. The first section corresponded to the first 50 cm from the top of the device. The second section corresponded to the remaining 50 cm until the bottom of the device. The composition of the sludge (mineralogy, As/Fe molar ratio, As redox speciation) was determined using X-Ray Diffraction and ICP-MS or HPLC-ICP-MS after appropriate dissolution (Fernandez-Rojo et al. 2017). A leaching test (ISO 17294-2:2016) was carried out on a subsample of the mixture of

upper and lower section of the sludge from the PS device, it was evaluated the sludge of PS due to the similarity of the sludge composition between the devices. We applied a solid to liquid ratio of 1:10. The analysis was run by the external laboratory WESSLING (France).

Data were analyzed by non-parametric test Mann-Whitney; the p-values were obtained at the level of $p < 0.05$. The statistical analyses and graphs were performed with the R free software.

Results and discussion

Inlet water

The knowledge of the variability of the physico-chemistry of the AMD is important in the perspective of future sizing of a real-scale treatment. During the one-year monitoring period, the water temperature varied from 7 to 31 °C (Table 2). The Fe and As concentrations during the coldest and rainiest months (430 and 42 mg/L, respectively, from December to April) were almost half of the concentration measured during the driest and hottest months (1000 and 102 mg/L, respectively, from July to August). Both elements were mostly in reduced forms Fe(II) and As(III). In general, pH and redox potential variation reflected the dissolved Fe concentration variation. The pH ranged from 3.2 to 5, with the lowest values during periods of highest concentration of Fe and As. The redox potential ranged from 224 to 628mV SHE, with lowest values during periods of lowest concentration of Fe and As. This was related to the common origin of Fe, As and protons in the Carnoulès AMD (dissolution of As-rich pyrite) and the control of AMD redox status by the Fe(III)/Fe(II) couple as generally observed (España et al. 2005). The DO of the inlet water ranged from 1 to 11 mg/L, the lowest values being observed during the hottest periods. The average TOC value in the inlet water was 3.65 ± 1.5 mg/L, indicator of a low organic content effluent. These results confirmed some variability of the Carnoulès AMD physico-chemistry (Casiot et al. 2006; Elbaz-Poulichet et al. 2006; Egal et al. 2010). However, the continuous supply of high concentration of Fe(II) ensures the sustainability of the treatment based on biological Fe(II) oxidation.

Table 2 *General characterization of the inlet water physico-chemistry, the values were estimated with all the data obtained during the seven monitoring periods (n=58).*

	pH	T (°C)	DO (mg/L)	Eh (mV)	Fe(II) (mg/L)	Fe (mg/L)	S (mg/L)	As (mg/L)	As(III) (%)	As(V) (%)	TOC (mg/L)
Minimum	3.2	7.1	1	224	326	427	587	42	50	14	2.8
Maximum	5.1	32.0	11	628	1079	1067	1109	111	86	50	7.1
Median	4.2	20.7	6	443	705	768	889	86	74	26	2.4

General performances

The concentrations of dissolved Fe(II), total dissolved Fe and total dissolved As in the inlet and outlet waters allowed to calculate the oxidation and removal yields in each device. The theoretical hydraulic retention time (HRT) and devices performances are presented in Fig. 1 and Fig. 2. The oxidation and removal percentages were slightly higher (Mann-Whitney, p-value <0.05) for the WP device than for the PS device (Fig. 2). However, no significant differences were evidenced for Fe and As removal rates (Mann-Whitney, p-value >0.05) considering the one hour residence time difference between the two devices (WP had a bigger working volume).

Variation of the performances along the different periods differed substantially between the two devices. The average Fe(II) oxidation efficiency remained at a maximum from period A to period E with the WP device, while the PS device showed a progressive increase of the average Fe(II) oxidation efficiency among these periods. This reflected a faster adaptability and stability of the WP device illustrated by the smaller standard deviation of the oxidation yields within each period (Fig. 2A).

No significant performances variation (Mann-Whitney, p-value >0.05) was observed between the two HRT (≈ 9h and ≈ 18 h) evaluated among the Fe oxidation, Fe removal and As removal for each device. For both devices, the highest performances obtained during the monitoring period reached 92 ± 6 % for iron oxidation, 43 ± 11 % for iron removal and 67 ± 10 % for arsenic removal for a HRT of 9h.

The lowest performances for iron oxidation and iron removal in both systems were observed during periods F and G (Fig. 2A and Fig. 2B), which corresponded to periods of poor oxygen supply caused by the clogging of the aeration systems. However, the decrease of iron removal did not impact the arsenic removal, which reached 60 to 75 % during periods F and G (Fig. 2.C). This may be related to the sorption of arsenic onto Fe-As solid phases that had already accumulated in the devices during the previous periods and/or to the co-precipitation of As with the low amount of newly formed Fe(III). In this respect, arsenic removal reaching 5-97% had been observed in the previous field pilot that only oxidized 20% of Fe(II) (Fernandez-Rojo et al. 2019).

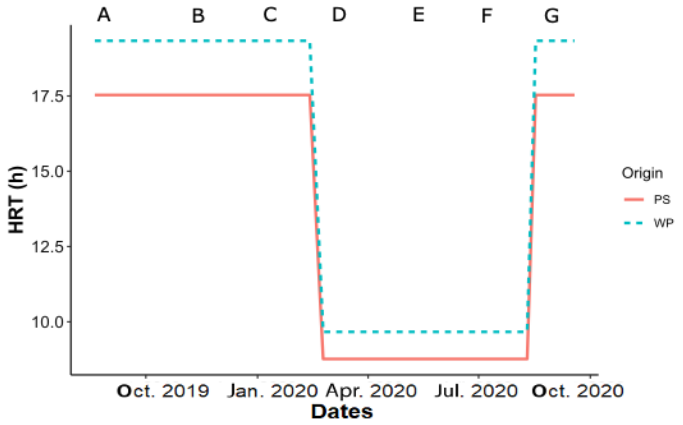


Figure 1. *Variation of the hydraulic retention time (HRT) across the monitoring periods.*

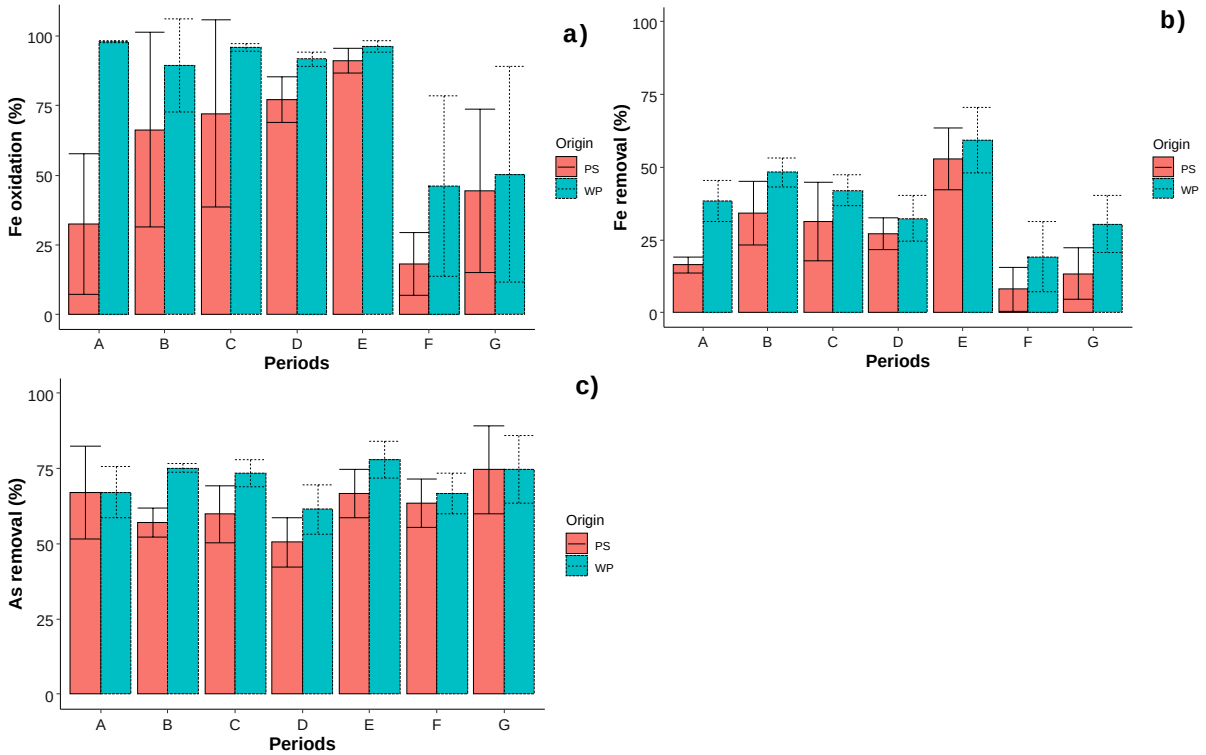


Figure 2. *Performance of PS and WP devices (a) percentage of iron oxidation, (b) percentage of iron removal and c) percentage of arsenic removal.*

Comparison with previous laboratory and field pilot experiments

In our previous field pilot (Fernandez-Rojo et al. 2019), the clogging of the sand bed and insufficient oxygen supply using simple diffusion at the air/water interface were important limitations. In the present study, forced aeration and the use of a support of higher porosity (>60% versus < 40% for the sand) improved the performances compared to our previous passive field-scale experiment. Indeed, the present devices exhibited higher Fe oxidation and removal and higher As removal than our previous field pilot at similar HRT values, these performances were close to the yields of our laboratory bioreactor (Fig. 3).

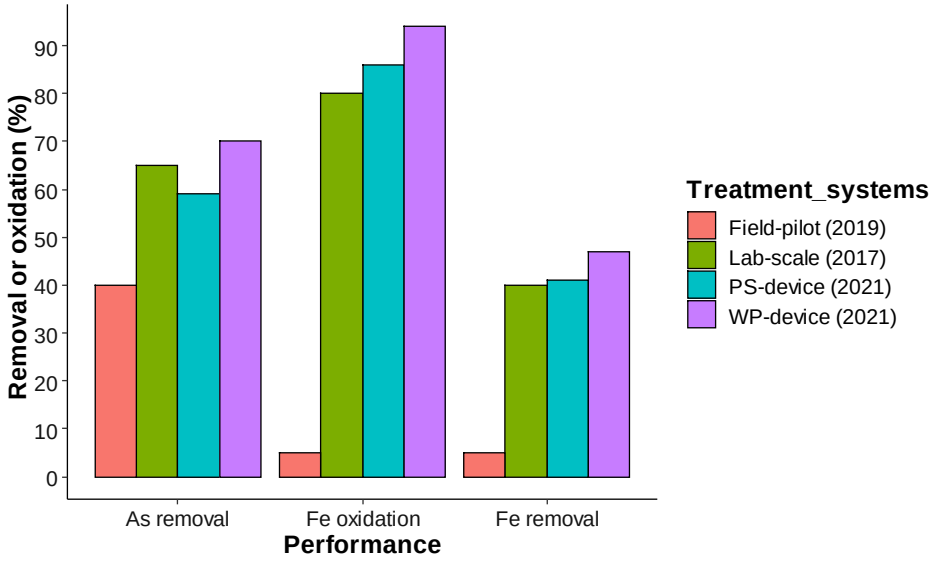


Figure 3. *Performances (in term of Fe(II) oxidation, Fe removal and As removal) obtained for the WP and PS devices (present study), previous field-scale pilot (Fernandez-Rojo et al. 2019) and laboratory-scale reactor* (Fernandez-Rojo et al. 2017) *with hydraulic retention times of 10±1h, 9±1h, 9±1 and 8±1h, respectively.*

Sludge characterization

Sludge recovery and characterization in the upper and lower sections inside each device (Table 3) provided an evaluation of the homogeneity of the biological treatment inside the devices. During the dismantling of the devices, we observed that the PS sludge was more compacted and strongly attached to the filling material contrary to the WP sludge that was waterier and thus easily transported to the bottom of the system. Consequently, the PS precipitates were more homogenously distributed inside the device than the WP precipitates. The average Fe, As and S contents of the sludge were similar for the PS and WP devices. However, the As/Fe molar ratio of the PS sludge was slightly higher than the one of the WP sludge.

Table 3 Characterization of the sludge accumulated at the PS and WP supports, sampled from the upper and lower section.

Device		**As (g/kg dry wt.)**	**Fe (g/kg dry wt.)**	**S (g/kg dry wt.)**	**As/Fe (molar)**	**As(III) (%)**	**As(V) (%)**
PS	top	82.5	306.4	45.4	0.36	17	83
	bottom	68.2	275.9	39.8	0.33	19	81
	average	75 ± 10	291 ± 22	43 ± 4	0.35 ± 0.02	18 ± 1	82 ± 1
WP	top	49.9	254.2	45.5	0.26	17	83
	bottom	67.2	316.0	55.2	0.28	17	83
	average	58 ± 12	285 ± 43	50 ± 7	0.27 ± 0.01	17 ± 0	83 ± 0

Only one crystallized Fe phase jarosite was identified by XRD, in both the PS and WP devices. This was in agreement with the positive value of jarosite saturation index calculated from outlet water chemistry. The sludge contained up to 83 g/kg (dry wt.) of arsenic mainly under As(V) form (81-83%) whatever the section and the device, which is advantageous for sludge management since As(V)-bearing solid phases are more stable than As(III)-bearing ones.

Perspectives for the sludge disposal

Leaching tests provide guidance on the compatibility of the sludge with storage in landfill waste facilities. The leachate from the PS sludge showed values below most thresholds for storage in Class 1 (hazardous industrial waste). The pH was the only parameter that exceeded the standard (Table 4). Therefore, addition of a neutralization agent to increase the pH would be necessary in the perspective of long-term storage. This should deserve additional trial.

Table 4 *Amount of element leached from the sludge of the PS device (in mg per kg of dried material) and pH of the leachate during leaching test*

Parameters	**As**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**SO_4^{2-}**	**COT**	**pH**
Class 1[1]	25	5	70	100	40	50	200	--	1000	4 <pH< 13
PS sludge[2]	4.7	0.09	0.26	0.23	0.97	0.14	23	5500	20	2.7

[1]Classification of the European Council Directive 1999/31/ EC of April 26. 1999 on the landfill of waste; class 1: reserved for special industrial. [2]Sludge sample from July 27of 2020.

Conclusions

These results demonstrated that our semi-passive devices achieving biological iron oxidation can function in real field conditions and exhibit stable performances with low maintenance during several months, under variable AMD physico-chemistry. The present devices combined the forced aeration and high porosity filling material, which appeared to be key factors to increase the performances compared to our previous field pilot. The wood and pozzolana mixture showed a better stability of Fe(II) oxidation yield than the plastic support. Our study provided fundamental and technical advances for a full-scale treatment facility adapted for an As-rich AMD. Additional stages are in progress to improve the quality of the treated water.

Acknowledgements

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