Research collaboration between Saint-Gobain Leca International and the Institute of Sustainable Processes at Universidad de Valladolid

Phase I - Comparative Evaluation of Filtralite AIR 10-20 and Filtralite AIR AC with conventional packing materials during malodorous emissions abatement

1. Description of the experimental set-up

The experimental set-up built for malodorous air treatment consists of three identical PVC biotrickling filters (internal diameter = 0.1 m, height = 1 m, total working volume = 3.5 L) packed with three different materials: Filtralite AIR 10-20 mm (BTF-F), FILTRALITE AIR AC (BTF-FILTRALITE AIR AC) and Kaldnes K2 plastic rings (BTF-K) (Images 1 and 2). The air stream entering the system is first pumped through an activated carbon filter, where any residual pollutant of atmospheric air is eliminated. The air is then humidified (parameter not measured) in a water column, entering afterwards a mixing chamber. In the mixing chamber, the clean air stream is mixed with a synthetic mixture of H_2S, toluene and methyl mercaptan in N_2 (purchased from Abelló Linde, Spain). The resulting polluted stream is divided into three identical streams of 1 L/min by means of rotameters. The individual streams are then fed at the bottom of each biotrickling filter. The clean air exiting the biotrickling filters is discharged outside de room using an extraction fan. Figure 2 shows a schematic of the biotrickling filters and sampling ports for H_2S and VOCs.

Image 1 Picture of the biotrickling filters

Image 2 Picture of the experimental set-up

Three 1-L holding tanks magnetically stirred are used as liquid mineral salt medium (MSM) reservoirs, containing the required nutrients for the microbial community with the following composition. The composition of the MSM is depicted in Table 1. This composition does not contain biodegradable organic matter (TOC), similarly to the effluent from a wastewater treatment plant.

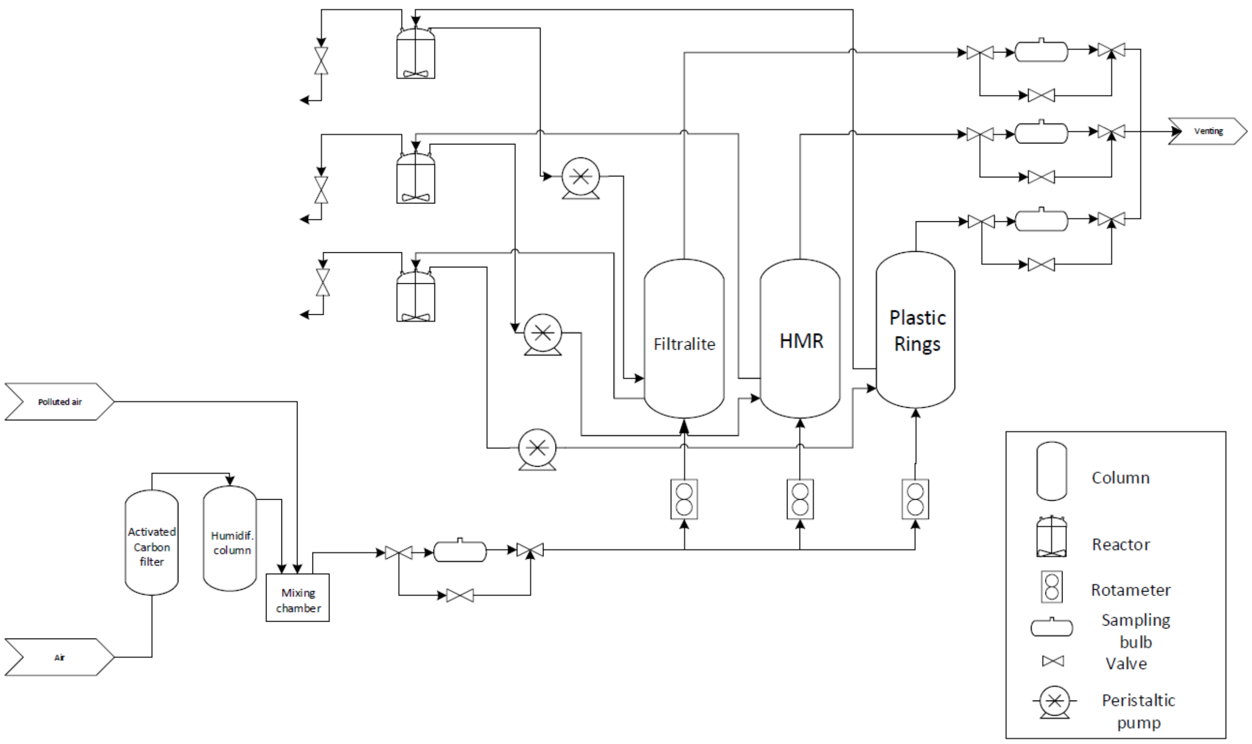

Figure 2. Schematic diagram of the experimental set-up.

Table 1 Composition of the mineral salt medium

Reagent	**Concentration (g/L)**
KH_2PO_4	0.7
$K_2HPO_4 \cdot 3H_2O$	0.917
KNO_3	3
NaCl	0.2
$MgSO_4 \cdot 7H_2O$	0.345
$CaCl_2 \cdot 2H_2O$	0.026
Trace Solution	2 (mL/L)

The trace element solution is prepared as shown in Table 2:

Table 2 Composition of the trace element solution

Reagent	**Concentration (g/L)**
EDTA	0.5
$FeSO_4 \cdot 7H_2O$	0.2
$ZnSO_4 \cdot 7H_2O$	0.01
$MnCl_2 \cdot 4H_2O$	0.003
H_3BO_3	0.345
$CoCl_2 \cdot 6H_2O$	0.02
$CuCl_2 \cdot 2H_2O$	0.001
$NiCl_2 \cdot 6H_2O$	0.002
$NaMoO_4 \cdot 6H_2O$	0.003

The liquid is continuously recycled through the packed beds at a flowrate of 0.15 L/min countercurrently with the polluted stream.

2. Analytical procedure

Pollutants concentration is measured periodically both at the inlet and outlet of the biotrickling filters. Toluene is analyzed in a gas chromatograph equipped with a flame ionization detector and a HP-5-MS (30 m × 0.25 mm × 0.25 µm) column (Image 3). Solid-phase microextraction (SPME) is used as a pre-concentration technique using 250 glass bulbs as sampling ports. On the other hand, H_2S and methylmercaptan are analyzed using portable detectors with specific sensors: Dräger X-am 5000 (Image 3) and Dräger X-am 7000 (Image 3), respectively.

Liquid samples are also withdrawn periodically from the holding tanks in order to determine pH, total organic carbon, inorganic carbon, total nitrogen and sulfate concentrations. The pH is measured daily using a pHmeter Eutech Cyberscan pH 510 (Eutech Instruments, Netherlands). Both the inorganic carbon, the total organic carbon and the total nitrogen are measured in a TOC-VCSH analyzer coupled with a TNM-1 chemiluminescence module (Shimadzu, Japan). Finally, the pressure drop across the columns is also periodically determined using a U-meter filled with water as the manometric fluid.

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Image 3 Picture of the GC-FID for toluene analysis (left figure), XAM 500 for H_2S analysis and XAM 7000 for methylmercaptan analysis.

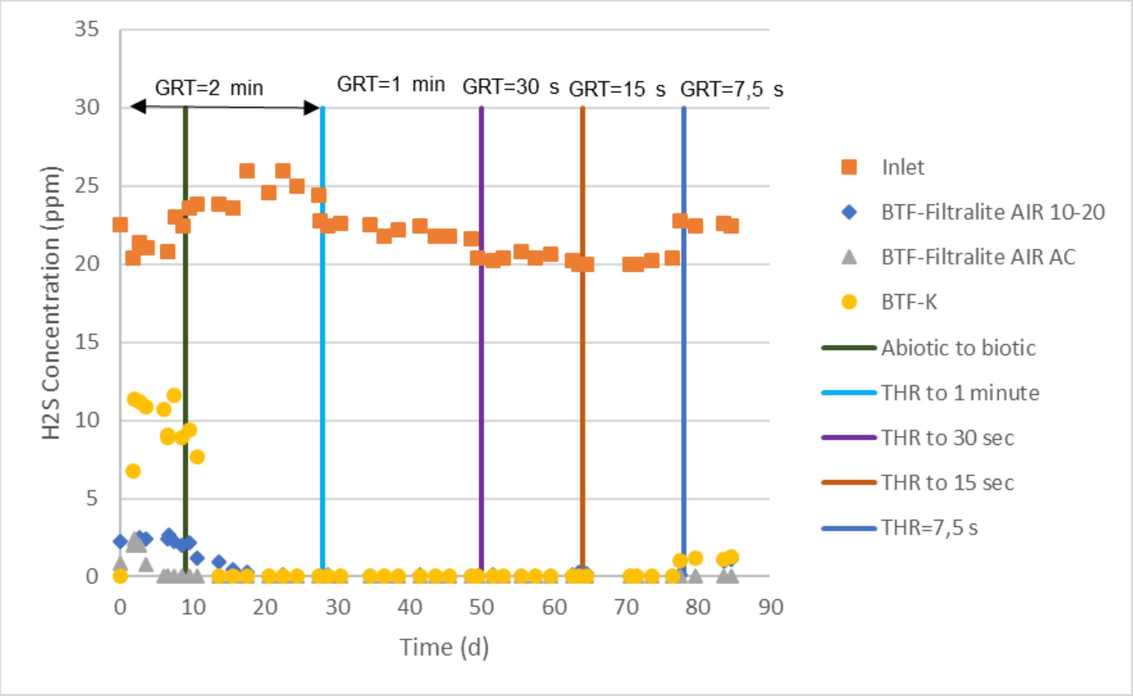
3. Preliminary results

A 9-days abiotic test was performed prior inoculation of the BTFs in order to evaluate the possibility of physical-chemical removal of the target pollutants by the packing materials. Under abiotic conditions, Filtralite AIR AC supported a complete removal of H_2S, while FILTRALITE AIR 10-20 mm removed more than 90%. The performance of Saint-Gobain SAINT-GOBAIN LECA INTERNATIONAL International material without inoculation outcompeted the removal efficiency of conventional plastic rings, which supported a 50 % removal of H_2S. The BTFs were then inoculated with activated sludge from Valladolid wastewater treatment plant. Thus, three bottles with 200 mL of sludge were centrifuged for 10 minutes at 10,000 rpm. The supernatant was removed, and the biomass was resuspended in 100 ml of fresh MSM. The inoculum was then added to the holding tanks and recycled through the bed. After the inoculation period, 150 mL of the cultivation medium were daily taken and used for analysis, and replaced with fresh MSM. This MSM renewal also maintained the pH above inhibitory levels.

The BTFs were initially operated at a gas residence time (GRT) of 2 min until day 27, decreasing afterwards the GRT to 30, 15 and 7.5 s by days 50, 63 and 77, respectively. The GRT is calculated using the universally accepted equation: *Empty volume of the reactor divided by the gas flowrate*. The mineral salt medium exchange rate increased when decreasing the gas residence time, following an exchange ratio of 2.5 L H_2O/g H_2S fed. The measurement of the Total Nitrogen concentration revealed similar concentrations in the waste MSM than in the fresh MSM.

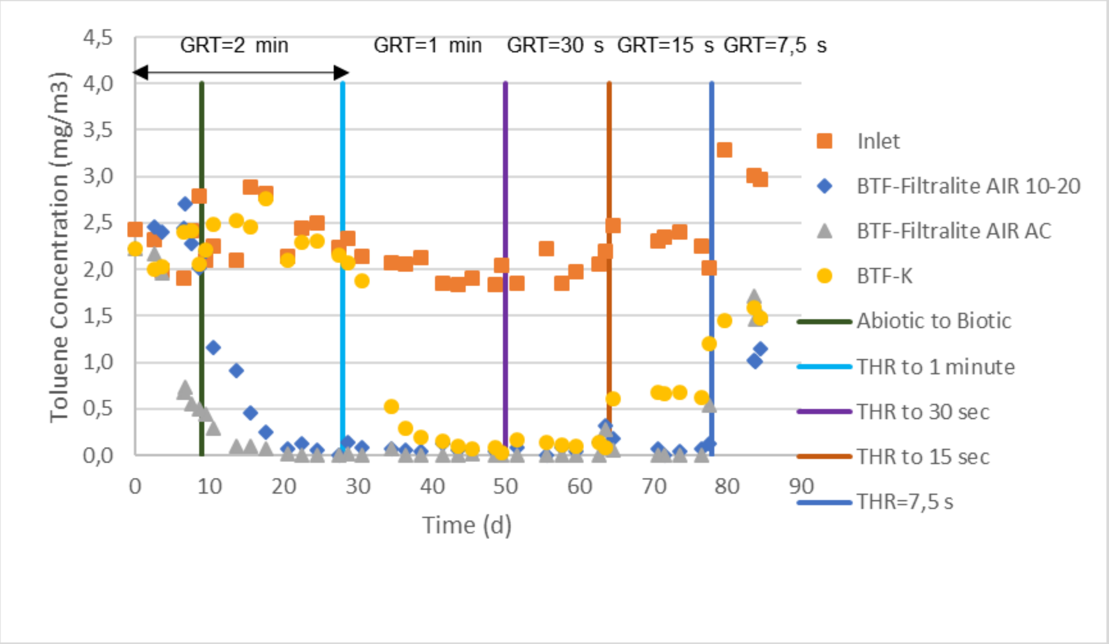
The results showed that the three BTFs were capable of degrading inlet H_2S concentrations of ~25 ppm at GRT of 2 min and 1 min (Graph 1). The BTF-FILTRALITE AIR AC completely removed the H_2S before inoculation of the systems, while the BTF-F and the BTF-K rapidly achieved a complete H_2S removal 2 and 4 days after inoculation, respectively. The residence time was reduced to 30 and 15 s by days 50 and 64, respectively, with no concomitant deterioration of the H_2S removal performance observed in any of the BTFs. Nevertheless, a further reduction of the GRT to 7.5 s resulted in an increase in the outlet H_2S concentration in the BTF-F and the BTF-K to 1.2 ppm (corresponding to a removal efficiency of 95 %), while the BTF-FILTRALITE AIR AC was able to sustain a complete H_2S

removal. At this point it should be stressed that biotrickling filters are typically operated at gas residence times of 7-15 s at commercial scale.



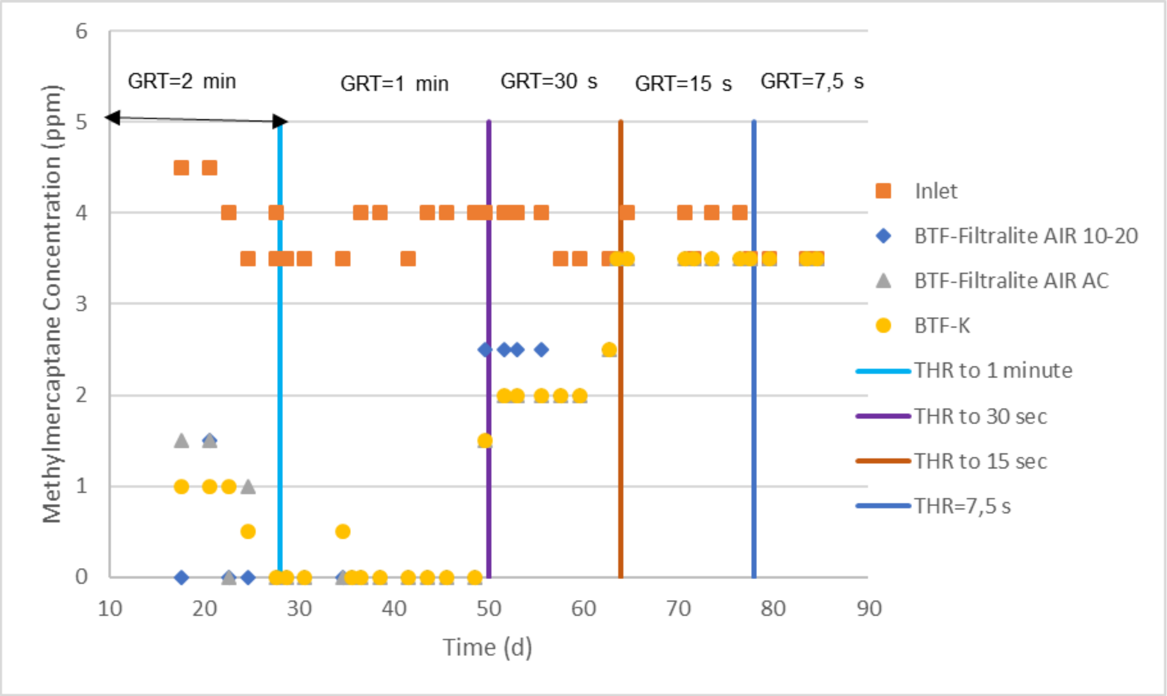
Graph 1. Time course of H_2S concentration in the inlet (■) and outlet of the three biotrickling filters: BTF-F (♦), BTF-FILTRALITE AIR AC (▲) and BTF-K (●)

In the particular case of toluene, no removal was observed for the BTF packed with Kaldnes plastic rings during the first 27 days of operation, despite this biotrickling filter was inoculated with activated sludge by day 9 (Graph 2). On the contrary, both the BTF-FILTRALITE AIR AC and the BTF-F reached toluene removal efficiencies of >99 % within 11 and 15 days after inoculation at a GRT of 2 min. Surprisingly, a decrease in the residence time to 1 min promoted the abatement of toluene in the BTF-K, likely due to a higher turbulence and therefore an improved transfer of the pollutant to the liquid phase (which ultimately triggered the establishment of an effective toluene degrading community, whose growth was likely limited by the low pH of the trickling solution), achieving removals of >99 % from day 37 onwards at this GRT. The high toluene removal was also maintained in the three BTFs at a GRT of 30 s. However, a further reduction in the GRT to 15 s lead to a decrease in the toluene removal performance of BTF-K, increasing the outlet toluene concentration up to 0.65 mg/m^3 (which corresponded to a removal efficiency of 72 %). On the contrary, both the BTF-F and the BTF-FILTRALITE AIR AC were able to maintain toluene removal efficiencies > 99 %, which highlights the good performance of SAINT-GOBAIN LECA INTERNATIONAL packing materials. Finally, the reduction in the GRT to 7.5 s resulted in a deterioration in the toluene removal performance regardless of the BTF, with average toluene outlet concentrations of 1.5 mg/m^3 (corresponding to removal efficiencies of 50 %) for BTF-K and BTF-FILTRALITE AIR AC and 1 mg/m^3 for BTF-F (corresponding to a removal efficiency of 67%).



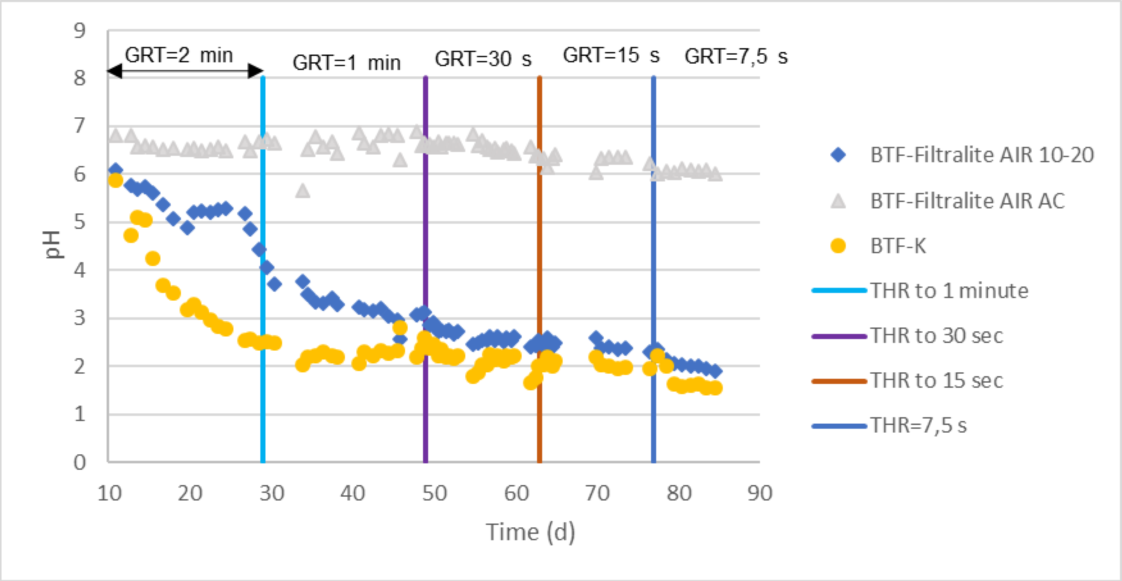
Graph 2. Time course of toluene concentration in the inlet (■) and outlet of the three biotrickling filters: BTF-F (♦), BTF-FILTRALITE AIR AC (▲) and BTF-K (●)

Methylmercaptan was only analyzed from day 17 onwards of the experiment due to analytical issues in the optimization of the method by GC-FID at the initial stages of the project. No methylmercaptan was observed in the outlet gas stream of any BTF at GRTs of 2 and 1 min. However, when the GRT was reduced to 30 seconds, the outlet concentration of methylmercaptan increased to 2.5 mg/m^3 in BTF-F and 2 mg/m^3 in the BTF-K and BTF-FILTRALITE AIR AC, resulting in removal efficiencies of 28 % and 42 %, respectively. In the last operating stages, at GRTs of 15 and 7.5 s, no methylmercaptan removal was recorded in any of the BTFs (Graph 3). At this point it should be highlighted that the Henry's law constants of H_2S, toluene and methyl mercaptan are 1×10^{-3}, 1.5×10^{-3} and 3.5×10^{-3} mol/(m^{3}Pa), which rules out a potential mass transfer limitation causing the deterioration of methylmercaptan removal based only on the mass transfer gradient. The gas-liquid mass transfer in BTF depends, not only on the gas-liquid concentration gradient, but also on the mass transfer coefficient (K_La), which itself is a function of the pollutant. Indeed, K_La is proportional to the (molar volume of the pollutant)^0.4, where the molar volume for H_2S, toluene and methyl mercaptan are 33, 106 and 55 mL/mol. The results suggest that FILTRALITE AIR AC was able to support better methylmercaptan removal efficiencies due to the higher metabolic activity of the microbial community as a result of the higher pH values provided by FILTRALITE AIR AC compared to plastic rings.



Graph 3. Time course of methylmercaptan concentration in the inlet (■) and outlet of the three biotrickling filters: BTF-F (♦), BTF-FILTRALITE AIR AC (▲) and BTF-K (●)

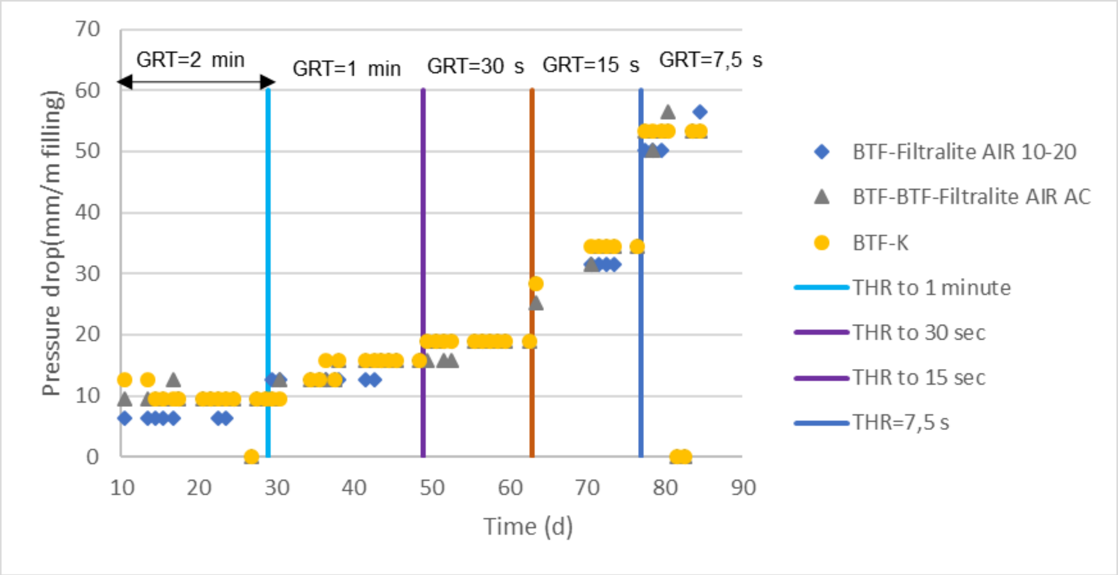
The pH measurements started during the biotic phase of the process in the recycling liquid. The pH remained roughly stable in the BTF-FILTRALITE AIR AC, with initial values of 6.4 ± 0.0 and a final value of 6.1 ± 0.0 in the last operating stage at a GRT of 7.5 s (Graph 4). On the contrary, a significant pH drop was observed in the BTF packed with plastic rings, reaching minimum values of 2.8 after 15 days of operation. This low pH was detrimental for microbial activity and might explain the lower pollutant removal performance observed in the filter with plastic rings. After this initial drop, the pH in the BTF-K stabilized at ~ 2-2.2, slightly decreasing in the last operating stage to average values of 1.7 ± 0.3. In the case of the BTF-F, after the initial pH stabilization by day 20, a sharp drop was recorded along with the increase in H_2S load, reaching values of ~ 3.3 by day 36. From this day onwards, a steady decrease was observed in the pH of the recycling liquid, reaching values of 2.0 ± 0.1 when operating at a GRT of 7.5 s. At this point it should be stressed that the aerobic oxidation of H_2S to sulphate was responsible for this decrease in pH in the recirculation liquid solution.



Graph 4. Time course of the pH in the trickling liquid of the three biotrickling filters: BTF-F (♦), BTF-FILTRALITE AIR AC (▲) and BTF-K (●)

The pressure drop remained stable in the three systems at values of ~9 mmH_2O/m_{bed} in the FILTRALITE AIR AC and plastic rings BTFs and was slightly lower in the Filtralite AIR 10-20 mm BTF at ~6 mmH_2O/m_{bed} when working at a GRT of 2 min. Concomitant increases in the pressure drop were recorded when decreasing the GRT, reaching values of 15 mmH_2O/m_{bed} at 1 min, 19 mmH_2O/m_{bed} at 30 s, 35 mmH_2O/m_{bed} at 15 s and ~55 mmH_2O/m_{bed} at 7.5 s regardless of the BTF (Graph 5). Interestingly, SAINT-GOBAIN LECA INTERNATIONAL materials provided pressures drops at low as classical plastic rings, which foresees a good performance of these materials in terms of energy demand during odour abatement. The reason for this similarity needs to be further investigated.

Finally, a stable sulphate concentration of ~1650 mg SO_4^{-2}/L was recorded in the trickling liquid of the BTF packed with Filtralite AIR 10-20 mm for the first 22 days of operation. Then, sulphate concentration fluctuated from a minimum value of 1186 mg SO_4^{-2}/L on day 51 to a maximum of 1811 mg SO_4^{-2}/L on day 36. This value increased from 796 to 1605 mg SO_4^{-2}/L and from 264 to 753 mg SO_4^{-2}/L from days 9 to 16 of operation in the BTF-FILTRALITE AIR AC and the BTF-K, respectively. Then, the concentrations of SO_4^{-2} gradually increased reaching a maximum of 1897 mg SO_4^{-2}/L in BTF-FILTRALITE AIR AC by day 71 of operation and 1672 mg SO_4^{-2}/L by day 64 in BTF-K. These concentrations were far below inhibitory concentrations of sulphate for H_2S degrading bacteria.



Graph 5. Time course of the pressure drop in the three biotrickling filters: BTF-F (♦), BTF-FILTRALITE AIR AC (▲) and BTF-K (●)

4. Biomass extraction

By day 84, the experiment was concluded and samples of the three packing materials were withdrawn and sent for DNA analysis (Image 3).

Image 3. Packing materials from BTF-K, BTF-FILTRALITE AIR AC and BTF-F by the end of operation

5. Conclusions

The results from Phase I collaboration between SAINT-GOBAIN LECA INTERNATIONAL and Valladolid University confirmed the superior performance of SAINT-GOBAIN LECA INTERNATIONAL materials as packing materials in biotrickling filters. Both FILTRALITE AIR AC and Filtralite AIR 10-20 mm supported higher H_2S and toluene removal efficiencies than conventional plastics rings, and a significantly better process start-up. The benefits of SAINT-GOBAIN LECA INTERNATIONAL materials during biotrickling filtration derive from its superior ability to favor the development of biofilms and to maintain higher pH values in the trickling solution. SAINT-GOBAIN LECA INTERNATIONAL materials can provide an outstanding odour removal at gas residence times of 7.5 to 15 s at pressure drops comparable to conventional plastic rings.