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There are still issues with language and grammar. Please have the manuscript proofread.

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Comments to the Author

It is a good contribution using organic packing material for treatment of gas phase pollutant using biotrickling filters

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Characterization and evaluation of poplar and pine wood in twin biotrickling filters treating a mixture of NH_3, H_2S, butyric acid and ethylmercaptan

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Abstract

Biotrickling filters for waste gas treatment are often packed with expensive, inert packing materials. In this work, poplar and pine wood chips were evaluated as low-cost packing materials in two biotrickling filters for the simultaneous treatment of a mixture of organic and inorganic volatile compounds. Bioreactors were operated at gas contact times of 22-34 s. Inlet loading rates of 3.5±1.0 gN-NH_3 m^{-3}h^{-1} and 6.5±1.1 gS-H_2S m^{-3}h^{-1} were supplied, while ethylmercaptan (EM) and butyric acid were fed at loads of 3.6±1.2 g m^{-3}h^{-1} and 6.0±2.1 g m^{-3}h^{-1}, respectively. A thorough characterization of both ~~support media~~packing materials revealed some differences in the physical-chemical properties, mainly in their water retentivity and buffer capacity. Despite of ~~these~~ such differences, both bioreactors performed similarly. Bioreactors were able to achieve complete removal of NH_3 and butyric acid, while H_2S and EM removal efficiencies over 90% and 70%, respectively, were found. N-species analyses in the leachate proved high nitrification rates ~~for~~ in both ~~woods~~biotrickling filters. ~~The~~ Control of pH ~~control~~ was essential for maintaining nitrification activity. Other oxidation processes were hardly affected by pH changes. Both woods showed potentially attractive as ~~support media~~packing materials for biofiltration. Thus, availability and durability of woods are decisive factors to tip the balance.

Novelty or Significance. The work compares the performance of two biotrickling filters packed with two types of wood chips commonly used in biofilters. No previous works have directly compared the performance of two types of woods in biotrickling filters for the treatment of a range of organic and inorganic odorants because biotrickling filters are commonly packed with inert packing materials. Results indicated that the two types of woods tested behaved similarly and, more interestingly, showed equivalent treatment capacities than

that of inert packing materials in the removal of a range of typical pollutants in odorant waste gases. Research is of particular interest for improving biofiltration knowledge~~ of biofiltration~~. In addition, ~~since inorganic packing materials commonly used in biotrickling filters are much more expensive than organic packing materials,~~ this research has large practical implications in the cost-benefit of full-scale biotrickling filtration systems becasue inorganic packing materials commonly used in biotrickling filters are much more expensive than organic packing materials.

Keywords: Biotrickling filters, Organic media; packing characterization; odorants treatment, twin bioreactors

1 INTRODUCTION

The use of bioreactors for gaseous effluents treatment is a widely recognized biotechnology that has been successfully applied during the last decades in a wide range of industries for the abatement of a wide spectrum of pollutants. Among ~~the~~ different configurations, biotrickling filters have demonstrated their capabilities to remove odorant pollutants in processes such as the treatment of gaseous emissions from wastewater treatment plants (WWTPs) or composting processes. However, biotrickling filters use inorganic packing materials such as plastic or ceramic beds because of the presence of a continuously flowing water phase over the packed bed. Such conditions could potentially damage organic packing materials and cause reactor flooding [1]. Regarding organic materials, the use of different types of wood chips has been reported in conventional biofilters, a bioreactor configuration without a continuous water phase flowing over the packing material [2-4]. The main advantages of wood chips as packing material are their low purchasing price, their capacity to act as water reservoir due to a high water holding capacity~~,~~ as well as their capacity to avoid packing material compaction ~~of the material~~ [1]. Specifically, ~~their~~ water retentivity and water holding capacity of wood chips, which are favorable in comparison to inorganic packing materials, could be beneficial during unexpected situations such as a liquid phase recirculation failure or during the treatment of extremely dry streams at high temperatures, which could end up in ~~drying out~~ the packing material dry out. However, an organic material can be more rapidly exhausted and biodegraded under high water content conditions, which may hinder its use in biotrickling filters. The number of studies with biotrickling filters packed with wood chips is scarce in literature [5-6]. Chen et al. [7]~~,~~ studied the performance of two wood chips-based biofilters to reduce odor, H_2S and NH_3 from swine barn ventilation air distinguishing two kinds of woods: western cedar and oak wood. However, to the authors' knowledge there is no study indicating if a particular kind of wood is more effective ~~than others~~ when used in biotrickling filters~~ to the authors knowledge~~. However, little attention has been paid to the specific characteristics of different types of woods in relation to biotrickling filters performance in terms of removal efficiency (RE)~~, even l~~Less attention has been paid in trying to find evidences of advantages/disadvantages of using pine or poplar wood chips as packing materials [8]. The use of poplar and pine wood chips ~~results~~ is highly interesting from an economical perspective due to their affordability and low price (45-60 € m^{-3} and 40-50 € m^{-3}, respectively). Thus, it is interesting to study wood chips performance as packing material in-depth~~,~~ since it is an easy-to-get media, landfill disposable and a ~~proven~~ cost-effective material ~~as confirmed in previous studies~~ [9]. In this sense, the present work is the first work that ~~to~~ compared twin biotrickling filters packed with two different ~~kinds of~~ woods by an exhaustive evaluation in terms of media characterization and bioreactors performance for the treatment of a multi-component gaseous stream.

Regarding pollutants usually treated ~~by~~ in ~~biofiltration~~biofilters, NH_3 and H_2S are common ~~inorganic~~ volatile inorganic compounds widely studied due to their presence in a range of ~~processes~~ sites such as composting plants, livestock facilities, fish processing industries or WWTPs among others. NH_3 concentrations up to 120 ppmv and H_2S

concentrations in the range of 10-60 ppmv are often found in ~~those~~ such industries [1]. EM and butyric acid are volatile organic compounds mainly present at low concentrations, which may only lead to a ~~malodorous~~ bad odor problem. Butyric acid has a sour, sweaty smell and belongs to hydrophilic volatile fatty acids group typically generated when organic matter is decomposed under anaerobic conditions [10]. In turn, volatile organic sulfur compounds such as ethylmercaptan (EM) and dimethyldisulfide (DMDS) have lately received intensive attention because of their very low odor threshold, high toxicity, and potential corrosive effect [11]. Specifically, EM is a moderately soluble in water and toxic organic compound with an odor threshold as low as 0.7 µg L^{-1} (0.28 ppm_v) [12]. It has been also classified as one of the most annoying compounds in odor emissions [13]. Overall, the complex mixture used herein comprises some of the most typical and most annoying pollutants released in real emissions. It is important to highlight that the oxygen content might not limit microbial biodegradation at the pollutants load typically encountered in these facilities [1].

Based on the promising results obtained in a previous study [9], the present work focused on the evaluation of several properties of poplar and pine wood susceptible to affect the biofiltration ~~process~~ process. In addition, this work focused ~~and~~ on the ~~to~~ comparison~~e~~ of the behavior of both materials under identical conditions in a biotrickling filter configuration~~,~~ treating a mixture of H_2S, NH_3, EM and butyric acid during a period of more than three months.

2 MATERIALS AND METHODS

2.1 Experimental setup and operating conditions of the bioreactors

The experimental setup consisted of two parallel PVC biotrickling filters ~~made in PVC~~ with a height of 70 cm and an internal diameter of 8.6 cm. Reactors were packed with poplar and pine wood chips, respectively, up to a height of 50 cm, resulting in a packed bed volume of 2.9 L per biofilter. The polluted air was supplied in up-flow mode. Inlet H_2S and NH_3 concentrations were provided from pure gas cylinders and mixed with fresh air using digital mass flow controllers (Bronkhorst, The Netherlands). EM was fed by means of a double-head peristaltic pump (Mod. 403 U/VM2, Watson Marlow, England) that pumped air into glass bubblers containing liquid EM ~~97%~~ (97% purity, Sigma Aldrich, United States). Pure butyric acid was fed by means of a microburette Multiburette 2S (Crison Inst. S.A., Spain). The liquid level in both bioreactors was kept constant by means of two peristaltic pumps (Mod. 302 S, Watson Marlow, England) controlled by a home-made LabWindows^{TM} ~~CVI~~ application. ~~More d~~Detailed characteristics of the biofiltration setup can be found elsewhere [6].

Inoculation at ambient temperature (18 - 23ºC) was carried out during 48 hours in both reactors ~~at ambient temperature (18 - 23ºC)~~ by continuous recirculation ~~during 48 hours~~ of an activated sludge mixture at an initial concentration of 1.5 g VSS L^{-1} containing i) enriched ~~ammonium~~ ammonium-oxidizing bacteria (AOB) ~~taken~~ withdrawn from a pilot plant where partial nitrification was ~~achieved~~ taking place and ii) aerobic sludge from a urban WWTP (Manresa, Spain). Use of aerobic sludge from WWTPs for inoculation is widely accepted since a wide spectrum of microorganisms is encountered [14-15]. A more detailed description of packing materials characteristics as well as the inoculation procedure of the reactors is provided in the Supplementary Material section S1. Several samples were extracted along the experimental period in order to identify ~~sulfur~~ sulfur-oxidizing and nitrifying bacteria. However, the organic nature of ~~the~~ wood chips made difficult to obtain DNA from biofilm samples to produce reliable results. Thus, ~~it was not possible to characterize~~ characterization of~~the~~ microbial communities in the biotrickling filters was not possible. Either way, ~~to carry out~~ an in-depth ~~-~~microbial characterization of biotrickling filters was not the scope of this work.

Inlet concentrations of 48.5 ± 9.4 ppm$_v$ of NH_3, 40.2 ± 3.1 ppm$_v$ of H_2S, 11.7 ± 3.8 ppm$_v$ of EM and 13.3 ± 3.4 ppm$_v$ of butyric acid were kept constant throughout the experimental period, corresponding to loads of 3.5 ± 1.0 g N-NH_3 m^{-3} h^{-1} ~~of N-NH_3~~, ~~-~~6.5 ± 1.1 g S-H_2S m^{-3} h^{-1} ~~of S-H_2S~~, 3.6 ± 1.2 g EM m^{-3} h^{-1} ~~of EM~~ and 6.0 ± 2.1 g butyric acid m^{-3} h^{-1} ~~of butyric acid~~, respectively. Those are typical concentrations susceptible to be found at industrial facilities such as composting, food processing or WWTPs among others [1-2, 16]. During the experimental period, ~~-~~a constant gas flow rate of 310 L h^{-1} was fed to each biofilter, corresponding to an initial empty bed residence time (EBRT) of 34 s. However, ~~due to operational failures~~ this initial value was significantly reduced in the poplar wood reactor (PPWR) due to operational failures. Bioreactors were operated at a room temperature of 22 ± 2ºC and the recirculation flow rate was set at 130 mL min^{-1}. The liquid phase was continuously renewed by the automated supply of tap water. Make-up water flow rate varied between 600 and 2520 mL day^{-1}, corresponding to a~~n~~ hydraulic residence time (HRT) between 1.00 and 0.24 day. Thus, the Gas/Liquid ratio defined as the inlet gas flow rate divided by ~~the renovation of~~of the fresh liquid renewal varied from 12400/1 to 2953/1. The pH control was set ~~on~~ from day 28 onwards by means of the permanent addition of NaOH (0.02 g L^{-1}) in the make-up water flow.

2.2 Analytical methods

H_2S concentration was measured using an electrochemical H_2S sensor (Sure-cell, Euro-Gas Management Services LTD, England) with a detection limit of 1 ppm$_v$. NH_3 concentration was determined after bubbling the gas stream in acidified water and ~~later on~~ passed through an ammonium flow analyzer later on [17]~~,~~ with a detection limit of 5 mg N-NH_4^+ L^{-1}. ~~For EM and butyric acid determination, a~~ A calibrated Gas Chromatograph (6890N, Agilent Tech. S.A., Spain) was ~~employed~~used for EM and butyric acid determination~~,~~ with a detection limit of 2 ppm_v for both compounds. Chloride, N-ammonium, N-nitrite, N-nitrate, S-sulfate and P-phosphate ions concentration in leachate samples were determined in an ICS-1000 Ion Chromatograph (Dionex Corp., United States) equipped with an IonPac AS9-HC column with a detection limit of 5 mg L^{-1} for all species. Leachate pH and conductivity were measured by means of a pH 28 sensor and a MicroCM 2100 sensor (Crison Instr. S.A., Spain), respectively. According to the specifications of the instrumentation employed in this work, the following standard deviations were considered: 10% for EM and butyric acid RE, 1.5% for H_2S RE, 1-2% for species measured by ionic chromatography and 1% for the continuous flow analyzer. Regarding packing materials characterization, methods employed to evaluate materials properties are described elsewhere [18]. Finally, sulfur oxidation ~~process~~in ~~of~~ bioreactors was verified through S-SO_4^{2-} production rates, which were calculated through mass balances as detailed in the Supplementary Material section S2.

3 RESULTS

Packing materials characterization

The suitability of poplar and pine wood as packing material for biofiltration was evaluated by means of different physical-chemical parameters commonly studied in biofiltration (Tables 1 and 2). Among the natural carriers used in biofiltration, woods are the most extensively used together with compost, peat and soil [19]. However, the comparison of the behavior of different woods in biotrickling filters is still unexplored. Elementary analyses were performed to identify the capacity of each packing material to potentially provide macronutrients such as nitrogen and phosphorous necessary for biomass growth. Both materials presented a similar nutrient content: 46-49% C, 0.3% N, less than 0.1% S and 0.05% P. Concerning the specific surface area, which was measured by the BET technique (Table 1), ~~wood~~ wood-based materials showed a slightly lower specific surface area ~~value~~ (~~inferior to~~below 1.3 m^2 g^{-1}) ~~than materials like~~compared to compost and coconut fiber ~~but~~. A much lower specific surface area was found compared to porous materials ~~like~~ such as carbons (up to 950 m^2 g^{-1}). The ~~Packing materials~~ pH of packing materials was ~~close to neutral or~~ slightly acid (pH ≈ 6.7 for pine wood chips) while their buffer capacity was between 35 and 50 mL SO_4^{2-} L^{-1} (Table 1). Sorption capacities were determined for both dry and wet materials to obtain information ~~regarding~~ about the interactions nature between the contaminant, the packing materials and the aqueous phase. Poplar wood adsorption capacities of 0.05 and 0.06 mg toluene g^{-1} packing material were achieved under dry and wet conditions, respectively, according to the procedure detailed in Dorado et al. [17]. Pine wood showed a 30% decrease in its adsorption capacity (from 0.06 to 0.04 mg toluene g^{-1} packing material) under wet conditions, which ~~can be considered~~are the ~~common~~ normal operating conditions in biofilters. Larger reductions ~~of~~ in the adsorption capacity under wet conditions have been reported in other ~~common media~~packing materials [20]. In the materials presented herein, a lower water holding capacity and a similar porosity of both materials (0.88) could explain a minor reduction of such adsorption capacity. Moreover, the water retentivity measured, expressed as the water percentage lost per hour, revealed that both materials ~~can~~ retain ~~their~~ water ~~content~~ efficiently. In any case, the maximum sorption capacity of the materials was less than 0.10 mg toluene g^{-1} material. The water holding capacity and water retentivity are related to packing materials ~~structural configuration. Depending on the material specific~~ structure~~,~~. water

Despite the fact that water molecules can be more or less time retained in the material, ~~but after a certain period of time without the supply of extra water,~~ all ~~media~~ packing materials ~~might~~ lose most of ~~its~~ their water content after a certain period of time without the supply of extra water. For instance, when dealing with a dry moisture stream, it would be interesting to operate with materials with a large water retentivitiy ~~in order~~ to avoid packing material desiccation and allow microorganisms maintaining their activity. In the case of wood chips as unique packing material, several studies employing conventional biofilters achieved the highest reduction efficiencies for odor concentration and NH_3 removal when keeping the filter media moisture content over 60% (wet basis) [7,21]. Thus, both parameters~~, among others,~~ were considered key factors to take into account when choosing the most suitable packing material for a specific scenario.

Regarding pressure drop through the packed bed (ΔP), intrinsic ΔP for dry packing materials was below 1 cm water column per meter of packing material height in both cases (Table 2). Results agreed with typical ΔP ranges for ~~pressure drop through~~ packing materials [20]. Interestingly, ΔP slightly increased with the presence of water inside the packing material even if this influence was more remarkable at higher superficial velocities (data not shown). In the case of poplar wood, the ΔP ~~achieved~~ was twice that obtained for pine wood, which ~~is a sign of~~indicated a higher resistance to air flow due to the superficial rugosity of the material. Both materials were evaluated ~~at~~ under the same water content. ΔP ~~increases~~ increased between 5 and 30% ~~over~~ compared with that under dry conditions, which did not have a significant impact in terms of energy consumption costs as shown in Table 2. Besides punctual episodes, ΔP in both reactors never exceeded 7 cm of water column per meter of packing material height (figure S1 in Supplementary Material) during the entire operational period. The electricity consumption was calculated ~~considering a kilowatt-hour cost of 0.08 € kWh^{-1} and~~ by means of a previously reported empirical expression P(kW) = 3.64·10^{-4} ~~x~~ · Q (m^3 h^{-1}) [22] considering a kilowatt-hour cost of 0.08 € kWh^{-1}~~]~~. The increase in the electrical consumption due to the ΔP was estimated according to a mechanical energy balance: P(W) = ΔP (N m^{-2}) ~~x~~ · Q (m^3 s^{-1}) where P is the consumption power, ΔP is the pressure drop and Q is the flowrate circulating through the packing material.

Regarding energy costs associated to blow the air through the packing material, a difference of 2.5% between materials was found (Table 1 and 2). Therefore, the main difference between packing materials laid in their purchase cost ~~of the support materials~~ and ~~their~~ durability. The purchase cost, which is directly related with the availability of each wood, had a significant impact in the overall costs~~,~~ not only because of the large volumes usually required for biofilter construction but also because of packing materials replacement due to their limited durability~~ caused by a low mechanical and chemical resistance~~. Table 1 shows the purchase price of both packing materials according to prices of year 2014, Spanish market. The durability was estimated according to previous experiences of suppliers (Melcourt, UK).

Sulfur compounds removal

Regarding H$_2$S removal, both bioreactors maintained analogous trends. Initial REs around 50% were measured, which increased gradually up to REs above 85% on day 13 and remained that high the rest of the study (Figure 1a and b). Both reactors were able to biodegrade H$_2$S to SO$_4^{2-}$ from the beginning of the experimental period~~ on~~ (Figure 2). Since unexpected situations are likely to occur during real operation, some malfunctioning episodes were used to evaluate the resilience capacity of wood chip-based biotrickling filters. Thus, EM RE varied significantly during the fluidization of the packing material due to a flooding episode, denoting a low capacity to face such unexpected failure.

Both bioreactors startup took around 20 days until achieving REs above 85% (Figure 1c and d). Nevertheless, after reinoculation of both reactors on day 34 to reactivate the nitrification process, EM REs were lower than ~~those~~ before reinoculation. Two weeks before reinoculation, EM REs of 94 ± 5% and 88 ± 8% were measured for PPWR and pine wood reactor (PNWR), respectively~~, while a~~. After day 34~~ onwards~~, average REs decreased down to 75 ± 13% and 83 ± 16% for PPWR and PNWR, respectively. It is likely that flooding episodes in PPWR on days 37 and 58 negatively affected the EM elimination, leading to ~~these~~ such significant differences in EM REs in comparison with PNWR.

Both the startup period and unexpected operational changes lead to a significant dispersion of results. Despite of such variability, a similar trend was found in terms of EC of sulfur compounds (figure S2 in Supplementary Material). Both reactors performed similarly showing that the maximum EC was not reached for H_2S removal. However, from day 13 onwards, a pseudo-stationary period was achieved and RE values of 96 ± 4% and 97% ± 2 were measured for PPWR and PNWR, respectively, corresponding to maximum EC values of 6.5 ±0.9 and 5.6 ± 0.6 g m^{-3} h^{-1}. A plateau in the EC vs LR profile (figure S2b and S2d) was found at around 2 g EM m^{-3} h^{-1}, particularly in the case of the PPWR reactor.

Moreover, oxidation of reduced sulfur compounds was verified by assessing the S-SO_4^{2-} production rates (S-$SO_4^{2-}r_p$) along the time course of the experimental period (Figure 3) as well as a function of the total S load (figure S3a and S3b in Supplementary Material). The S-$SO_4^{2-}r_p$ increased 30% between days 9 and 18 of operation. During the startup of both bioreactors S-$SO_4^{2-}r_p$ progressively increased until day 24~~, where r_p was stabilized~~

~~at around~~ up to 6.5 g $S\text{-}SO_4^{2-}$ m^{-3} h^{-1}. Besides punctual episodes, no significant impact of pH was observed on $S\text{-}SO_4^{2-}r_p$, even in the case of a pH drop to pH 5 during startup (days 14 to 18). On the contrary, $S\text{-}SO_4^{2-}r_p$ was clearly affected in PPWR on days 37 and 58 due to a flooding/fluidization episode (arrow A in figure 2). Finally, it is important to mention that the $S\text{-}SO_4^{2-}r_p$ drop observed in both reactors on day 64 was due to an experiment performed to evaluate the effect of an EM feeding interruption (arrow B in figure 2). ~~So~~Consequently, the expected $S\text{-}SO_4^{2-}r_p$ drops of ~~, which were~~ around 13 and 42% in PPWR and PNWR, respectively, were caused by a decrease in the $S\text{-}SO_4^{2-}$ production.

It is worth mentioning that the $S\text{-}SO_4^{2-}r_p$ in both reactors were lower than the total S loaded as H_2S and EM (figures S3a and S3b in Supplementary Material), indicating that a fraction of the S was not recovered and that was probably converted to other S species such as elemental sulfur or thiosulfate. The impact of such S unbalance was more noticeable in the case of the PPWR reactor in which the percentage of $S\text{-}SO_4^{2-}$ recovered was around 75-80%.

Ammonia removal

No significant differences were observed between reactors in terms of NH_3 RE, which remained close to 100% all over the experimental period because of the large solubility of NH_3. However, N-species concentration in PPWR showed no evidences of nitrifying activity during the first month of operation, while slight ~~signs of~~ nitrification ~~were~~ was noticed in PNWR. Simultaneously, during the first two operational weeks, a pH decrease from neutral to pH below 5 occurred in both reactors. On days 13 and 18, the HRT was reduced from 1 day to 5.7 hours (indicated in Figure 3a and 3b with arrows). Moreover, from day 28 on, pH was controlled at 7 by the permanent addition of a NaOH 0.02 g L^{-1} solution to the make-up water line (indicated in both figures with an arrow).

Even though neutral pH was reestablished, nitrifying activity remained almost negligible. Hence, both reactors were reinoculated on day 34 to reactivate nitrification. ~~Right after~~Then, a gradual increase on NO_3^- production was observed~~. Simultaneously,~~ while NH_4^+ concentration progressively decreased. In less than 15 days, both bioreactors were capable to oxidize almost all the NH_3 supplied to N-NO_3^- (Figure 3a and 3b). The rest of the experimental period almost full NH_3 conversion to nitrate was achieved, besides punctual days that operational failures occurred resulting in slight accumulations of NH_4^+ in the liquid phase (e.g. on day 46, PNWR suffered a partial flooding of the upper part of the bioreactor due to a pump pipe blockage). Besides punctual failure episodes suffered on days 59 and 80, a very similar behavior was observed in the PPWR (Figure 3a). Nitrogen mass balances were assessed for both reactors (figure S4 in Supplementary Material) showing that deviations in the N recovery oscillated between 20 and 55% in both reactors, with a larger dispersion in the case of the PPWR.

Butyric acid removal

Butyric acid was removed almost completely ~~right~~ after the startup of both bioreactors. As discussed in the next section, the high solubility of this pollutant allowed achieving complete elimination during the whole experimental period.

4 DISCUSSION

Regarding ~~to~~ NH_3 removal, the nitrification capacity in both bioreactors remained almost negligible during the startup phase, which was attributed to the progressive acidification of the liquid phase due to SO_4^{2-} production, which led to pH values below 5 after 12 days of operation in both bioreactors. Characterization of packing materials showed a slightly acidic leachate, which was consistent with Lou and Lindsey [23] who reported a pH between 4.5-5 for pine wood. Slightly acid pH of woods can be related with resin acids content [24]. Often, buffering capacities of packing materials are not enough to compensate the production of acidic by-products from microbial oxidation in the biofiltration of waste gases containing significant loads of pollutants such as H_2S or VOCs. In this sense, several studies have proved that the acidification of the liquid phase can negatively affect the nitrification process [6, 25-27]. Park et al. [26] proved that ~~working at pH above 6.5~~ the maximal nitrification rate ~~could be~~was reduced to a half working at pH above 6.5~~, while~~. Jiang et al. [28] observed that the N-NH_4^+ fraction in the leachate (between 50 and 75%) was substantially superior than that of N-NO_2^- and N-NO_3^- at pH ~~values~~ equal or above 6 due to a probable NH_4^+ elimination by absorption and reaction to $(NH_4)_2SO_4$. Similarly, Rabbani et al. [29] ~~achieved~~ reached REs over 90% for H_2S and NH_3 in an acidified bioreactor~~, since~~ because the ~~stream ratio~~ H_2S/NH_3 ratio permitted an effective removal of both pollutants by biological oxidation of H_2S to sulfate and a subsequent chemical reaction of ammonium ~~with~~ and sulfate to form $(NH_4)_2SO_4$.

Moreover, free ammonia (FA) and/or free nitrous acid (FNA) accumulation can inhibit AOB [30]. During the first two weeks of operation FA and FNA concentrations in PNWR never exceeded 1.3 mg N-FA L^{-1} and $2 \cdot 10^{-5}$ mg N-FNA L^{-1}, respectively. ~~Considering i~~Inhibitions thresholds have been reported by Jubany et al. [31] ~~of~~ as 5.8 mg N-FA L^{-1} for AOB, 0.16 mg N-FNA L^{-1} for AOB, 0.78 mg N-FA L^{-1} for NOB and 0.02 mg N-FNA L^{-1} for NOB. Consequently,~~,~~ ~~it is likely that AOB and NOB were inhibited by~~ FA and/or FNA inhibited AOB and NOB, particularly in ~~these~~ biofilter sections ~~of the bioreactors~~ close~~r~~ to the inlet~~,~~ where loads ~~are~~ were higher. However, no significant impact on the overall nitrification process was observed. Nevertheless, in order to decrease the FA concentration and to increase the pH, the HRT was stepwise decreased twice on days 13 and 18 from 24 to 5.7 hours ~~and the~~while a permanent addition of a NaOH solution (0.02 g L^{-1}) was performed. These actions permitted a decrease of the N-NH_4^+ concentration from 200 ~~mg N-NH_4^+ L^{-1}~~ to 55 mg N-NH_4^+ L^{-1} during the following 14 days of operation, while pH ~~values~~ reached neutral values. During the first 10 days of operation, where pH was kept at 6.5-7.0, nitratation rates of 0.04 g N m^{-3} h^{-1} were calculated [32] denoting ~~a certain~~some nitrifying activity. However, ~~right after the pH decay,~~ N-NO_3^- production was interrupted right after the pH decay (days 13-20). The efforts to reestablish neutral pH in the bioreactors ~~could~~ did not recover the nitrifying activity ~~for~~ of PPWR, while the slight evidence~~s~~ of PNWR nitrification capacity ~~were~~ was not enough to avoid a restart of both reactors. Hence, both reactors were reinoculated on day 34. Thereafter, N-NO_3^- concentration was progressively increased. In approximately 15 days, most of the NH_3 supplied (3.5 ± 1.0 g N-NH_3 m^{-3} h^{-1}) was oxidized to NO_3^- reaching concentrations up to 50 mg N-NO_3^- L^{-1}. In general, N-NO_3^- production was similar in both reactors. Slight differences in pH observed on day 25 onwards were attributed to the lower buffer capacity of PNWR (51 and 35 mL SO_4^{2-} L^{-1} for poplar and pine wood, respectively), as well as to the presence of resin acids in pine wood [24]. ~~However, the pH in a bioreactor is strongly influenced by the acid/basic character of the pollutants supplied.~~ Furthermore, similar nitrogen recoveries around 40% were found in previous studies [33-35]. These deviations from ideality can be attributed to several facts, mainly biological processes such as denitrification or biomass growth. Moreover, butyric acid presence could favor denitrification. It is important to mention that a nitrogen mass balance carried out during the entire experimental period (figure S4 in Supplementary Material) confirmed that almost all the ammonia supplied was biodegraded to nitrate after 30 days of operation.

Thus, NH_3 elimination by mere adsorption onto the packing material was negligible considering the low loads supplied and the fact that the system operated more than 100 days. In addition, the low adsorption capacity of packing materials under wet operating conditions [17] ensured that, in the long-term operation under constant loading rates, bioreactors were in equilibrium after a few days in terms of ad/absorption considering such low adsorption capacities.

In contrast with the nitrification process, sulfide oxidation showed a higher stability. The SO_4^{2-} production increased from the beginning of the experimental period. Concentrations close to 400 mg S-SO_4^{2-} L^{-1} after 14 days of operation were found in both reactors without ~~the necessity~~ needing ~~of~~ a selective inoculation. This fact confirmed that the presence of sulfur-oxidizing bacteria in an aerobic sludge from a WWTP used as inoculum, which was estimated to be around 1.5% [36], was adequate to biodegrade H_2S to SO_4^{2-}~~,~~ as previously observed by Fortuny et al. [37] in a biotrickling filter treating high H_2S loads. Previous works performing specific inoculation and treating mixtures of H_2S and NH_3 ~~at~~ under similar loads ~~and performing specific inoculation~~ required between 5 and 10 days to oxidize most of the H_2S to SO_4^{2-} [38-39]. In the work presented herein, the low specific surface area ~~found for~~of both materials (1.3 m^2 g^{-1}) was a handicap if compared with porous materials such as activated carbon (950 m^2 g^{-1}) [40]. It is worth noticing that specific surface areas in Table 1 are referred to the total surface area including micropores, which may be hardly available under normal operating conditions of a biotrickling filter due to biomass growth and to the presence of a water layer over the biofilm. Taking into account these data and considering that no ~~selective~~ specific inoculation was carried out in this study, the 7-8 days ~~duration~~ required ~~observed~~ for ~~sulfur~~ sulfide oxidation to occur ~~process, which last around 7-8 days,~~ were~~can be~~ considered as a relatively short startup period.

Figure 2 shows that the S-SO_4^{2-} production rate did not reach the maximal production during the days that the HRT was reduced although both materials showed high capacity to keep suitable wet conditions, thus ~~and~~ avoiding dry areas that would lead to poor growth and~~, thus,~~ reduced REs. Although water holding capacities of poplar and pine wood are not significantly different, the water retentivity~~,~~ ~~indicates~~ indicated that poplar wood retains water more effectively, which beneficiate wet conditions inside the packing material for microorganisms maintenance (the drying rate was half of that for ~~the~~ pine wood). However, although this is interesting in terms of water preservation in poorly watered biofilters it can be detrimental for adsorption and absorption of more hydrophobic pollutants such as ethylmercaptan. It is likely that ~~this~~ the latter ~~could be one~~ was the ~~reason~~ factor ~~for which~~that ~~PPWR was more~~ affected biofilters performance during~~by~~ flooding episodes.

Furthermore, ~~and leaving aside punctual episodes,~~ S-SO_4^{2-} production in both bioreactors was stabilized with the HRT set at 5.7 hours and the pH controlled in the range 5.9 - 7.7. In this sense, Jiang et al. [28] studied the pH effect on sulfur oxidation stability in a range of 4 to 8.5~~. It was proved~~ showing that~~, under all the pHs studied,~~ over 90% of the final product was SO_4^{2-} under all the pHs studied~~, proving the robustness of this process~~. It is important to highlight that sulfur oxidizing species able to develop at pHs from 1 (i.e. *Acidithiobacillus caldus* bacteria) to 10 (i.e. *Thioalcalivibrio* spp.) have been reported in literature [41], proving the robustness of this process.

Regarding EM elimination, REs over 85% were reached after day 20 of operation, while butyric acid was almost completely removed ~~right after~~from the beginning of the experimental period. Probably, ~~the~~ a ~~difference of~~ 5-fold ~~times in order of magnitude~~difference in their Henry constant (H_{EM}: $1.6\cdot10^{-1}$ g aq^{-1} (gas/aqueous) and

$H_{Butyric\ acid}$: $8.7 \cdot 10^{-6}$ g aq^{-1} [9, 42])~~,~~ favored butyric acid absorption in the liquid phase. Total organic carbon measurements were carried out to quantify the amount of butyric acid removed by mere absorption in the liquid phase or by biological activity. However, ~~Measurements~~ measurements were not reliable since the detachment of the organic media disguised the results. It is important to highlight that the EM removal robustness is directly related to the first degradation step in which the C-S bond is broken and metabolized by heterotrophic biomass. After that, the degradation pathway is the same than that corresponding to the H_2S oxidation [43]. Moreover, the acidification of both bioreactors during the startup phase had surely a negative effect on EM absorption, which is favored under alkaline conditions [44]. However, such an effect was not observed in the present study. Arellano-García et al. [44] observed that EM solubility was enhanced by around 80% by increasing the pH from 7.0 to 10.0. They considered that the EC of their system was limited by the low oxidation activities of their alkaliphilic microbial culture and that a pH control system was a must in order to set the most suitable pH to favor the elimination of the pollutants to be treated. Furthermore, EBRT studies (data not shown) suggested that the main responsible for the incomplete EM elimination was ~~the~~ a mass transfer limitation, since pollutants such as mercaptans require large EBRTs [12].

In both bioreactors no nutrients were added to the make-up water solution, since it is widely accepted that most of natural organic media have enough nitrogen and phosphorous content for developing a process culture [1]. Similarly, the organic matter content detected (around 95% by weight) constituted an alternative substrate source for biofilter microorganisms which could be used during starvation periods such as process shut-downs, process rotation or intermittent loads [17].

Since physical-chemical properties of both woods do not underscore a significant different behavior in terms of RE, ~~economic~~ costs associated to the ~~acquisition~~ purchase and ~~use~~ maintenance of packing materials become a ~~differentiating~~ key factor. Woods ~~are a promising packing material for biofiltration because it is~~ a largely available and cost-effective resource, thus becoming a promising packing material for biofiltration. Moreover, current forest management practices provide huge amounts of low-quality wood, which could be used in the construction of biofilters [45]. While estimated ~~PNWR shows an~~ annual material costs for PNWR were between 10 and 16 € m^{-3} y^{-1}~~, the PPWR~~ represent a 25% ~~decrease of the~~lower cost was estimated for the PPWR ~~around 25%~~ at the local prices of the present study (Table 1). Considering the energy to blow the air through the packing material in relation to the pressure drop, the use of pine or poplar wood chips represents a difference in the annual total cost of 7.3 % (Table 2). Thus, ~~according to market prices in relation to materials accessibility in the zone of implantation,~~since elimination capacities reached were similar for both woods, the use of a kind of wood can be more attractive just ~~for~~ because of economical reasons according to market prices in relation to materials accessibility in the zone of implantation~~without affecting the elimination capacities reached~~. In this sense, further research is needed to establish materials durability based on long-term studies, which would be useful to perform ~~more~~ accurate suitability and economical studies with both packing materials.

4. CONCLUSIONS

The co-treatment of a complex mixture of NH_3, H_2S, EM and butyric acid was successfully achieved in biotrickling filters~~reactors~~ packed with poplar and pine wood as an alternative to inorganic materials. Overall, taking all the evaluated properties into consideration, poplar and pine wood are support media potentially suitable to keep active ~~the~~ biomass growing on their surface and, subsequently, show a good performance in the abatement of a wide range of compounds. ~~Even though~~Despite of the differences observed in the materials characterization, no significant variations in the REs were observed under biofiltration conditions for the two different ~~kinds of~~ woods. Thus, only economical aspects such as durability and material cost, according to material availability, become relevant to choose the most suitable organic ~~support media~~packing material in the case of wood supports.

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LIST OF ABBREVIATIONS

AOB - Ammonium oxidizing bacteria
BET - Brunauer Emmett and Teller
DMDS - Dimethyldisulfide
EBRT - Empty bed residence time
EC - Elimination capacity
EM - Ethylmercaptan
FA - Free ammonia

FNA - Free nitrous acid

HRT - Hydraulic residence time

LR - Loading rate

NOB - Nitrite oxidizing biomass

PNWR - Pine wood reactor

PPWR - Poplar wood reactor

PVC - Polyvinyl chloride

RE - Removal efficiency

rp - Production rates

VOC - Volatile organic compound

VSS - volatile suspended solids

WWTP - wastewater treatment plant

ΔP - pressure drop

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Characterization and evaluation of poplar and pine wood in twin biotrickling filters treating a mixture of NH_3, H_2S, butyric acid and ethylmercaptan

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Abstract

Biotrickling filters for waste gas treatment are often packed with expensive, inert packing materials. In this work, poplar and pine wood chips were evaluated as low-cost packing materials in two biotrickling filters for the simultaneous treatment of a mixture of organic and inorganic volatile compounds. Bioreactors were operated at gas contact times of 22-34 s. Inlet loading rates of 3.5±1.0 gN-NH_3 $m^{-3}h^{-1}$ and 6.5±1.1 gS-H_2S $m^{-3}h^{-1}$ were supplied, while ethylmercaptan (EM) and butyric acid were fed at loads of 3.6±1.2 g $m^{-3}h^{-1}$ and 6.0±2.1 g $m^{-3}h^{-1}$, respectively. A thorough characterization of both packing materials revealed some differences in the physical-chemical properties, mainly in their water retentivity and buffer capacity. Despite of such differences, both bioreactors performed similarly. Bioreactors were able to achieve complete removal of NH_3 and butyric acid, while H_2S and EM removal efficiencies over 90% and 70%, respectively, were found. N-species analyses in the leachate proved high nitrification rates in both biotrickling filters. Control of pH was essential for maintaining nitrification activity. Other oxidation processes were hardly affected by pH changes. Both woods showed potentially attractive as packing materials for biofiltration. Thus, availability and durability of woods are decisive factors to tip the balance.

Novelty or Significance. The work compares the performance of two biotrickling filters packed with two types of wood chips commonly used in biofilters. No previous works have directly compared the performance of two types of woods in biotrickling filters for the treatment of a range of organic and inorganic odorants because biotrickling filters are commonly packed with inert packing materials. Results indicated that the two types of woods tested behaved similarly and, more interestingly, showed equivalent treatment capacities than that of inert packing materials in the removal of a range of typical pollutants in odorant waste

gases. Research is of particular interest for improving biofiltration knowledge. In addition, this research has large practical implications in the cost-benefit of full-scale biotrickling filtration systems becasue inorganic packing materials commonly used in biotrickling filters are much more expensive than organic packing materials.

Keywords: Biotrickling filters, Organic media; packing characterization; odorants treatment, twin bioreactors

1 INTRODUCTION

The use of bioreactors for gaseous effluents treatment is a widely recognized biotechnology that has been successfully applied during the last decades in a wide range of industries for the abatement of a wide spectrum of pollutants. Among different configurations, biotrickling filters have demonstrated their capabilities to remove odorant pollutants in processes such as the treatment of gaseous emissions from wastewater treatment plants (WWTPs) or composting processes. However, biotrickling filters use inorganic packing materials such as plastic or ceramic beds because of the presence of a continuously flowing water phase over the packed bed. Such conditions could potentially damage organic packing materials and cause reactor flooding [1]. Regarding organic materials, the use of different types of wood chips has been reported in conventional biofilters, a bioreactor configuration without a continuous water phase flowing over the packing material [2-4]. The main advantages of wood chips as packing material are their low purchasing price, their capacity to act as water reservoir due to a high water holding capacity as well as their capacity to avoid packing material compaction [1]. Specifically, water retentivity and water holding capacity of wood chips, which are favorable in comparison to inorganic packing materials, could be beneficial during unexpected situations such as a liquid phase recirculation failure or during the treatment of extremely dry streams at high temperatures, which could end up in the packing material dry out. However, an organic material can be more rapidly exhausted and biodegraded under high water content conditions, which may hinder its use in biotrickling filters. The number of studies with biotrickling filters packed with wood chips is scarce in literature [5-6]. Chen et al. [7] studied the performance of two wood chips-based biofilters to reduce odor, H_2S and NH_3 from swine barn ventilation air distinguishing two kinds of woods: western cedar and oak wood. However, to the authors' knowledge there is no study indicating if a particular kind of wood is more effective when used in biotrickling filters. However, little attention has been paid to the specific characteristics of different types of woods in relation to biotrickling filters performance in terms of removal efficiency (RE)Less attention has been paid in trying to find evidences of advantages/disadvantages of using pine or poplar wood chips as packing materials [8]. The use of poplar and pine wood chips is highly interesting from an economical perspective due to their affordability and low price (45-60 € m^{-3} and 40-50 € m^{-3}, respectively). Thus, it is interesting to study wood chips performance as packing material in-depth since it is an easy-to-get media, landfill disposable and a cost-effective material [9]. In this sense, the present work is the first work that compared twin biotrickling filters packed with two different woods by an exhaustive evaluation in terms of media characterization and bioreactors performance for the treatment of a multi-component gaseous stream.

Regarding pollutants usually treated in biofilters, NH_3 and H_2S are common volatile inorganic compounds widely studied due to their presence in a range of sites such as composting plants, livestock facilities, fish processing industries or WWTPs among others. NH_3 concentrations up to 120 ppmv and H_2S concentrations in the range of 10-60 ppmv are often found in such industries [1]. EM and butyric acid are volatile organic compounds mainly present at low concentrations, which may only lead to a bad odor problem. Butyric acid has a sour, sweaty smell and belongs to hydrophilic volatile fatty acids group typically generated when organic matter is decomposed under anaerobic conditions [10]. In turn, volatile organic sulfur compounds such as ethylmercaptan (EM) and dimethyldisulfide (DMDS) have lately received intensive attention because of their very low odor threshold, high toxicity, and potential corrosive effect [11]. Specifically, EM is a moderately soluble in water and toxic organic compound with an odor threshold as low as 0.7 µg L^{-1} (0.28 ppm_v) [12]. It has been also classified as one of the most annoying compounds in odor emissions [13]. Overall, the complex mixture used herein comprises some of the most typical and most annoying pollutants released in real emissions. It is important to highlight that the oxygen content might not limit microbial biodegradation at the pollutants load typically encountered in these facilities [1].

Based on the promising results obtained in a previous study [9], the present work focused on the evaluation of several properties of poplar and pine wood susceptible to affect the biofiltration process. In addition, this work focused on the comparison of the behavior of both materials under identical conditions in a biotrickling filter configuration treating a mixture of H_2S, NH_3, EM and butyric acid during a period of more than three months.

2 MATERIALS AND METHODS

2.1 Experimental setup and operating conditions of the bioreactors

The experimental setup consisted of two parallel PVC biotrickling filters with a height of 70 cm and an internal diameter of 8.6 cm. Reactors were packed with poplar and pine wood chips, respectively, up to a height of 50 cm, resulting in a packed bed volume of 2.9 L per biofilter. The polluted air was supplied in up-flow mode. Inlet H_2S and NH_3 concentrations were provided from pure gas cylinders and mixed with fresh air using digital mass flow controllers (Bronkhorst, The Netherlands). EM was fed by means of a double-head peristaltic pump (Mod. 403 U/VM2, Watson Marlow, England) that pumped air into glass bubblers containing liquid EM (97% purity, Sigma Aldrich, United States). Pure butyric acid was fed by means of a microburette Multiburette 2S (Crison Inst. S.A., Spain). The liquid level in both bioreactors was kept constant by means of two peristaltic pumps (Mod. 302 S, Watson Marlow, England) controlled by a home-made LabWindows^{TM} application. Detailed characteristics of the biofiltration setup can be found elsewhere [6].

Inoculation at ambient temperature (18 - 23ºC) was carried out during 48 hours in both reactors by continuous recirculation of an activated sludge mixture at an initial concentration of 1.5 g VSS L^{-1} containing i) enriched ammonium-oxidizing bacteria (AOB) withdrawn from a pilot plant where partial nitrification was taking place and ii) aerobic sludge from a urban WWTP (Manresa, Spain). Use of aerobic sludge from WWTPs for inoculation is widely accepted since a wide spectrum of microorganisms is encountered [14-15]. A more detailed description of packing materials characteristics as well as the inoculation procedure of the reactors is provided in the Supplementary Material section S1. Several samples were extracted along the experimental period in order to identify sulfur-oxidizing and nitrifying bacteria. However, the organic nature of wood chips made difficult to obtain DNA from biofilm samples to produce reliable results. Thus, characterization of microbial communities in the biotrickling filters was not possible. Either way, an in-depth microbial characterization of biotrickling filters was not the scope of this work.

Inlet concentrations of 48.5 ± 9.4 ppm_v of NH_3, 40.2 ± 3.1 ppm_v of H_2S, 11.7 ± 3.8 ppm_v of EM and 13.3 ± 3.4 ppm_v of butyric acid were kept constant throughout the experimental period, corresponding to loads of 3.5 ± 1.0 g N-NH_3 m^{-3} h^{-1}, 6.5 ± 1.1 g S-H_2S m^{-3} h^{-1}, 3.6 ± 1.2 g EM m^{-3} h^{-1} and 6.0 ± 2.1 g butyric acid m^{-3} h^{-1} , respectively. Those are typical concentrations susceptible to be found at industrial facilities such as composting, food processing or WWTPs among others [1-2, 16]. During the experimental period, a constant gas flow rate of 310 L h^{-1} was fed to each biofilter, corresponding to an initial empty bed residence time (EBRT) of 34 s. However, this initial value was significantly reduced in the poplar wood reactor (PPWR) due to operational failures. Bioreactors were operated at a room temperature of 22 ± 2ºC and the recirculation flow rate was set at 130 mL min^{-1}. The liquid phase was continuously renewed by the automated supply of tap water. Make-up water flow rate varied between 600 and 2520 mL day^{-1}, corresponding to a hydraulic residence time (HRT) between 1.00 and 0.24 day. Thus, the Gas/Liquid ratio defined as the inlet gas flow rate divided by of the fresh liquid renewal varied from 12400/1 to 2953/1. The pH control was set from day 28 onwards by means of the permanent addition of NaOH (0.02 g L^{-1}) in the make-up water flow.

2.2 Analytical methods

H_2S concentration was measured using an electrochemical H_2S sensor (Sure-cell, Euro-Gas Management Services LTD, England) with a detection limit of 1 ppm_v. NH_3 concentration was determined after bubbling the gas stream in acidified water and passed through an ammonium flow analyzer later on [17] with a detection limit of 5 mg $N\text{-}NH_4^+$ L^{-1}. A calibrated Gas Chromatograph (6890N, Agilent Tech. S.A., Spain) was used for EM and butyric acid determination with a detection limit of 2 ppm_v for both compounds. Chloride, N-ammonium, N-nitrite, N-nitrate, S-sulfate and P-phosphate ions concentration in leachate samples were determined in an ICS-1000 Ion Chromatograph (Dionex Corp., United States) equipped with an IonPac AS9-HC column with a detection limit of 5 mg L^{-1} for all species. Leachate pH and conductivity were measured by means of a pH 28 sensor and a MicroCM 2100 sensor (Crison Instr.

S.A., Spain), respectively. According to the specifications of the instrumentation employed in this work, the following standard deviations were considered: 10% for EM and butyric acid RE, 1.5% for H_2S RE, 1-2% for species measured by ionic chromatography and 1% for the continuous flow analyzer. Regarding packing materials characterization, methods employed to evaluate materials properties are described elsewhere [18]. Finally, sulfur oxidation in bioreactors was verified through S-SO_4^{2-} production rates, which were calculated through mass balances as detailed in the Supplementary Material section S2.

3 RESULTS

Packing materials characterization

The suitability of poplar and pine wood as packing material for biofiltration was evaluated by means of different physical-chemical parameters commonly studied in biofiltration (Tables 1 and 2). Among the natural carriers used in biofiltration, woods are the most extensively used together with compost, peat and soil [19]. However, the comparison of the behavior of different woods in biotrickling filters is still unexplored. Elementary analyses were performed to identify the capacity of each packing material to potentially provide macronutrients such as nitrogen and phosphorous necessary for biomass growth. Both materials presented a similar nutrient content: 46-49% C, 0.3% N, less than 0.1% S and 0.05% P. Concerning the specific surface area, which was measured by the BET technique (Table 1), wood-based materials showed a slightly lower specific surface area (below 1.3 $m^2\ g^{-1}$) compared to compost and coconut fiber. A much lower specific surface area was found compared to porous materials such as carbons (up to 950 $m^2\ g^{-1}$).

The pH of packing materials was slightly acid (pH ≈ 6.7 for pine wood chips) while their buffer capacity was between 35 and 50 mL SO_4^{2-} L^{-1} (Table 1). Sorption capacities were determined for both dry and wet materials to obtain information about the interactions nature between the contaminant, the packing materials and the aqueous phase. Poplar wood adsorption capacities of 0.05 and 0.06 mg toluene g^{-1} packing material were achieved under dry and wet conditions, respectively, according to the procedure detailed in Dorado et al. [17]. Pine wood showed a 30% decrease in its adsorption capacity (from 0.06 to 0.04 mg toluene g^{-1} packing material) under wet conditions, which are the normal operating conditions in biofilters. Larger reductions in the adsorption capacity under wet conditions have been reported in other packing materials [20]. In the materials presented herein, a lower water holding capacity and a similar porosity of both materials (0.88) could explain a minor reduction of such adsorption capacity. Moreover, the water retentivity measured, expressed as the water percentage lost per hour, revealed that both materials retain water efficiently. In any case, the maximum sorption capacity of the materials was less than 0.10 mg toluene g^{-1} material. The water holding capacity and water retentivity are related to packing materials structure. Despite the fact that water molecules can be more or less time retained in the material, all packing materials lose most of their water content after a certain period of time without the supply of extra water. For instance, when dealing with a dry moisture stream, it would be interesting to operate with materials with a large water retentivitiy to avoid packing material desiccation and allow microorganisms maintaining their activity. In the case of wood chips as unique packing material, several studies employing conventional biofilters achieved the highest reduction efficiencies for odor concentration and NH_3 removal when keeping the filter media moisture content over 60% (wet basis) [7,21]. Thus, both parameters were considered key factors to take into account when choosing the most suitable packing material for a specific scenario.

Regarding pressure drop through the packed bed (ΔP), intrinsic ΔP for dry packing materials was below 1 cm water column per meter of packing material height in both cases (Table 2). Results agreed with typical ΔP ranges for packing materials [20]. Interestingly, ΔP slightly increased with the presence of water inside the packing material even if this influence was more remarkable at higher superficial velocities (data not shown). In the case of poplar wood, the ΔP was twice that obtained for pine wood, which indicated a higher resistance to air flow due to the superficial rugosity of the material. Both materials were evaluated under the same water content. ΔP increased between 5 and 30% compared with that under dry conditions, which did not have a significant impact in terms of energy consumption costs as shown in Table 2. Besides punctual episodes, ΔP in both reactors never exceeded 7 cm of water column per meter of packing material height (figure S1 in Supplementary Material) during the entire operational period. The electricity consumption was calculated by means of a previously reported empirical expression $P(kW) = 3.64\cdot10^{-4} \cdot Q\ (m^3\ h^{-1})$ [22] considering a kilowatt-hour cost of 0.08 € kWh^{-1}. The increase in the electrical consumption due to the ΔP was estimated according to a mechanical energy balance: $P(W) = \Delta P\ (N\ m^{-2}) \cdot Q\ (m^3\ s^{-1})$ where P is the consumption power, ΔP is the pressure drop and Q is the flowrate circulating through the packing material.

Regarding energy costs associated to blow the air through the packing material, a difference of 2.5% between materials was found (Table 1 and 2). Therefore, the main difference between packing materials laid in their purchase cost and durability. The purchase cost, which is directly related with the availability of each wood, had a significant impact in the overall costs not only because of the large volumes usually required for biofilter construction but also because of packing materials replacement due to their limited durability. Table 1 shows the purchase price of both packing materials according to prices of year 2014, Spanish market. The durability was estimated according to previous experiences of suppliers (Melcourt, UK).

Sulfur compounds removal

Regarding H_2S removal, both bioreactors maintained analogous trends. Initial REs around 50% were measured, which increased gradually up to REs above 85% on day 13 and remained that high the rest of the study (Figure 1a and b). Both reactors were able to biodegrade H_2S to SO_4^{2-} from the beginning of the experimental period (Figure 2). Since unexpected situations are likely to occur during real operation, some malfunctioning episodes were used to evaluate the resilience capacity of wood chip-based biotrickling filters. Thus, EM RE varied significantly during the fluidization of the packing material due to a flooding episode, denoting a low capacity to face such unexpected failure.

Both bioreactors startup took around 20 days until achieving REs above 85% (Figure 1c and d). Nevertheless, after reinoculation of both reactors on day 34 to reactivate the nitrification process, EM REs were lower than before reinoculation. Two weeks before reinoculation, EM REs of 94 ± 5% and 88 ± 8% were measured for PPWR and pine wood reactor (PNWR), respectively. After day 34, average REs decreased down to 75 ± 13% and 83 ± 16% for PPWR and PNWR, respectively. It is likely that flooding episodes in PPWR on days 37 and 58 negatively affected the EM elimination, leading to such significant differences in EM REs in comparison with PNWR.

Both the startup period and unexpected operational changes lead to a significant dispersion of results. Despite of such variability, a similar trend was found in terms of EC of sulfur compounds (figure S2 in Supplementary Material). Both reactors performed similarly showing that the maximum EC was not reached for H_2S removal. However, from day 13 onwards, a pseudo-stationary period was achieved and RE values of 96 ± 4% and 97% ± 2 were measured for PPWR and PNWR, respectively, corresponding to maximum EC values of 6.5 ±0.9 and 5.6 ± 0.6 g m^{-3} h^{-1}. A plateau in the EC vs LR profile (figure S2b and S2d) was found at around 2 g EM m^{-3} h^{-1}, particularly in the case of the PPWR reactor.

Moreover, oxidation of reduced sulfur compounds was verified by assessing the S-SO_4^{2-} production rates (S-$SO_4^{2-}r_p$) along the time course of the experimental period (Figure 3) as well as a function of the total S load (figure S3a and S3b in Supplementary Material). The S-$SO_4^{2-}r_p$ increased 30% between days 9 and 18 of operation. During the startup of both bioreactors S-$SO_4^{2-}r_p$ progressively increased until day 24 up to 6.5 g S-SO_4^{2-} m^{-3} h^{-1}. Besides punctual episodes, no significant impact of pH was observed on S-$SO_4^{2-}r_p$, even in the case of a pH drop to pH 5 during startup (days 14 to 18). On the contrary, S-$SO_4^{2-}r_p$ was clearly affected in PPWR on days 37 and 58 due to a flooding/fluidization episode (arrow A in figure 2). Finally, it is important to mention that the S-$SO_4^{2-}r_p$ drop observed in both reactors on day 64 was due to an experiment performed to evaluate the effect of an EM feeding interruption (arrow B in figure 2). Consequently, the expected S-$SO_4^{2-}r_p$ drops of around 13 and 42% in PPWR and PNWR, respectively, were caused by a decrease in the S-SO_4^{2-} production.

It is worth mentioning that the S-$SO_4^{2-}r_p$ in both reactors were lower than the total S loaded as H_2S and EM (figures S3a and S3b in Supplementary Material), indicating that a fraction of the S was not recovered and that was probably converted to other S species such as elemental sulfur or thiosulfate. The impact of such S unbalance was more noticeable in the case of the PPWR reactor in which the percentage of S-SO_4^{2-} recovered was around 75-80%.

Ammonia removal

No significant differences were observed between reactors in terms of NH_3 RE, which remained close to 100% all over the experimental period because of the large solubility of NH_3. However, N-species concentration in PPWR showed no evidences of nitrifying activity during the first month of operation, while slight nitrification was noticed in PNWR. Simultaneously, during the first two operational weeks, a pH decrease from neutral to pH below 5 occurred in both reactors. On days 13 and 18, the HRT was reduced from 1 day to 5.7 hours (indicated in Figure 3a and 3b with arrows). Moreover, from day 28 on, pH was controlled at 7 by the permanent addition of a NaOH 0.02 g L^{-1} solution to the make-up water line (indicated in both figures with an arrow). Even though neutral pH was reestablished, nitrifying activity remained almost negligible. Hence, both reactors were reinoculated on day 34 to reactivate nitrification. Then, a gradual increase on NO_3^- production was observed while NH_4^+ concentration progressively decreased. In less than 15 days, both bioreactors were capable to oxidize almost all the NH_3 supplied to N-NO_3^- (Figure 3a and 3b). The rest of the experimental period almost full NH_3 conversion to nitrate was achieved, besides punctual days that operational failures occurred resulting in slight accumulations of NH_4^+ in the liquid phase (e.g. on day 46, PNWR suffered a partial flooding of the upper part of the bioreactor due to a pump pipe blockage). Besides punctual failure episodes suffered on days 59 and 80, a very similar behavior was observed in the PPWR (Figure 3a). Nitrogen mass balances were assessed for both reactors (figure S4 in Supplementary Material) showing that deviations in the N recovery oscillated between 20 and 55% in both reactors, with a larger dispersion in the case of the PPWR.

Butyric acid removal

Butyric acid was removed almost completely after the startup of both bioreactors. As discussed in the next section, the high solubility of this pollutant allowed achieving complete elimination during the whole experimental period.

4 DISCUSSION

Regarding NH_3 removal, the nitrification capacity in both bioreactors remained almost negligible during the startup phase, which was attributed to the progressive acidification of the liquid phase due to SO_4^{2-} production, which led to pH values below 5 after 12 days of operation in both bioreactors. Characterization of packing materials showed a slightly acidic leachate, which was consistent with Lou and Lindsey [23] who reported a pH between 4.5-5 for pine wood. Slightly acid pH of woods can be related with resin acids content [24]. Often, buffering capacities of packing materials are not enough to compensate the production of acidic by-products from microbial oxidation in the biofiltration of waste gases containing significant loads of pollutants such as H_2S or VOCs. In this sense, several studies have proved that the acidification of the liquid phase can negatively affect the nitrification process [6, 25-27]. Park et al. [26] proved that the maximal nitrification rate was reduced to a half working at pH above 6.5. Jiang et al. [28] observed that the N-NH_4^+ fraction in the leachate (between 50 and 75%) was substantially superior than that of N-NO_2^- and N-NO_3^- at pH equal or above 6 due to a probable NH_4^+ elimination by absorption and reaction to $(NH_4)_2SO_4$. Similarly, Rabbani et al. [29] reached REs over 90% for H_2S and NH_3 in an acidified bioreactor because the H_2S/NH_3 ratio permitted an effective removal of both pollutants by biological oxidation of H_2S to sulfate and a subsequent chemical reaction of ammonium and sulfate to form $(NH_4)_2SO_4$.

Moreover, free ammonia (FA) and/or free nitrous acid (FNA) accumulation can inhibit AOB [30]. During the first two weeks of operation FA and FNA concentrations in PNWR never exceeded 1.3 mg N-FA L^{-1} and $2\cdot10^{-5}$ mg N-FNA L^{-1}, respectively. Inhibitions thresholds have been reported by Jubany et al. [31] as 5.8 mg N-FA L^{-1} for AOB, 0.16 mg N-FNA L^{-1} for AOB, 0.78 mg N-FA L^{-1} for NOB and 0.02 mg N-FNA L^{-1} for NOB. Consequently, FA and/or FNA inhibited AOB and NOB, particularly in biofilter sections close to the inlet where loads were higher. However, no significant impact on the overall nitrification process was observed. Nevertheless, in order to decrease the FA concentration and to increase the pH, the HRT was stepwise decreased twice on days 13 and 18 from 24 to 5.7 hours while a permanent addition of a NaOH solution (0.02 g L^{-1}) was performed. These actions permitted a decrease of the N-NH_4^+ concentration from 200 to 55 mg N-NH_4^+ L^{-1} during the following 14 days of operation, while pH reached neutral values. During the first 10 days of operation, where pH was kept at 6.5-7.0, nitratation rates of 0.04 g N m^{-3} h^{-1} were calculated [32] denoting some nitrifying activity. However, N-NO_3^- production was interrupted right after the pH decay (days 13-20). The efforts to reestablish neutral pH in the bioreactors did not recover the nitrifying activity of PPWR, while the slight evidence of PNWR nitrification capacity was not enough to avoid a restart of both reactors. Hence, both reactors were reinoculated on day 34. Thereafter, N-NO_3^- concentration was progressively increased. In approximately 15 days, most of the NH_3 supplied (3.5 ± 1.0 g N-NH_3 m^{-3} h^{-1}) was oxidized to NO_3^- reaching concentrations up to 50 mg N-NO_3^- L^{-1}. In general, N-NO_3^- production was similar in both reactors. Slight differences in pH observed on day 25 onwards were attributed to the lower buffer capacity of PNWR (51 and 35 mL SO_4^{2-} L^{-1} for poplar and pine wood, respectively), as well as to the presence of resin acids in pine wood [24]. Furthermore, similar nitrogen recoveries around 40% were found in previous studies [33-35]. These deviations from ideality can be attributed to several facts, mainly biological processes such as denitrification or biomass growth. Moreover, butyric acid presence could favor denitrification. It is important to mention that a nitrogen mass balance carried out during the entire experimental period (figure S4 in Supplementary Material) confirmed that almost all the ammonia supplied was biodegraded to nitrate after 30 days of operation. Thus, NH_3 elimination by mere adsorption onto the packing material was negligible considering the low loads supplied and the fact that the system operated more than 100 days. In addition, the low adsorption capacity of packing materials under wet operating conditions [17] ensured that, in the long-term operation under constant loading rates, bioreactors were in equilibrium after a few days in terms of ad/absorption considering such low adsorption capacities.

In contrast with the nitrification process, sulfide oxidation showed a higher stability. The SO_4^{2-} production increased from the beginning of the experimental period. Concentrations close to 400 mg S-SO_4^{2-} L^{-1} after 14 days of operation were found in both reactors without needing a selective inoculation. This fact confirmed that the presence of sulfur-oxidizing bacteria in an aerobic sludge from a WWTP used as inoculum, which was estimated to be around 1.5% [36], was adequate to biodegrade H_2S to SO_4^{2-} as previously observed by Fortuny et al. [37] in a biotrickling filter treating high H_2S loads. Previous works performing specific inoculation and treating mixtures of H_2S and NH_3 under similar loads required between 5 and 10 days to oxidize most of the H_2S to SO_4^{2-} [38-39]. In the work presented herein, the low specific surface area of both materials (1.3 m^2 g^{-1}) was a handicap if compared with porous materials such as activated carbon (950 m^2 g^{-1}) [40]. It is worth noticing that specific surface areas in Table 1 are referred to the total surface area including micropores, which may be hardly available under normal operating conditions of a biotrickling filter due to biomass growth and to the presence of a water layer over the biofilm. Taking into account these data and considering that no specific inoculation was carried out in this study, the 7-8 days required for sulfide oxidation to occur were considered as a relatively short startup period.

Figure 2 shows that the S-SO_4^{2-} production rate did not reach the maximal production during the days that the HRT was reduced although both materials showed high capacity to keep suitable wet conditions, thus avoiding dry areas that would lead to poor growth and reduced REs. Although water holding capacities of poplar and pine wood are not significantly different, the water retentivity indicated that poplar wood retains water more effectively, which beneficiate wet conditions inside the packing material for microorganisms maintenance (the drying rate was half of that for pine wood). However, although this is interesting in terms of water preservation in poorly watered biofilters it can be detrimental for adsorption and absorption of more hydrophobic pollutants such as ethylmercaptan. It is likely that the latter was the factor that affected biofilters performance during flooding episodes.

Furthermore, S-SO_4^{2-} production in both bioreactors was stabilized with the HRT set at 5.7 hours and the pH controlled in the range 5.9 - 7.7. In this sense, Jiang et al. [28] studied the pH effect on sulfur oxidation stability in a range of 4 to 8.5 showing that over 90% of the final product was SO_4^{2-} under all the pHs studied. It is important to highlight that sulfur oxidizing species able to develop at pHs from 1 (i.e. *Acidithiobacillus caldus* bacteria) to 10 (i.e. *Thioalcalivibrio* spp.) have been reported in literature [41], proving the robustness of this process.

Regarding EM elimination, REs over 85% were reached after day 20 of operation, while butyric acid was almost completely removed from the beginning of the experimental period. Probably, a 5-fold difference in their Henry constant (H_{EM}: $1.6 \cdot 10^{-1}$ g aq^{-1}

(gas/aqueous) and $H_{Butyric\ acid}$: $8.7\cdot10^{-6}$ g aq^{-1} [9, 42]) favored butyric acid absorption in the liquid phase. Total organic carbon measurements were carried out to quantify the amount of butyric acid removed by mere absorption in the liquid phase or by biological activity. However, measurements were not reliable since the detachment of the organic media disguised the results. It is important to highlight that the EM removal robustness is directly related to the first degradation step in which the C-S bond is broken and metabolized by heterotrophic biomass. After that, the degradation pathway is the same than that corresponding to the H_2S oxidation [43]. Moreover, the acidification of both bioreactors during the startup phase had surely a negative effect on EM absorption, which is favored under alkaline conditions [44]. However, such an effect was not observed in the present study. Arellano-García et al. [44] observed that EM solubility was enhanced by around 80% by increasing the pH from 7.0 to 10.0. They considered that the EC of their system was limited by the low oxidation activities of their alkaliphilic microbial culture and that a pH control system was a must in order to set the most suitable pH to favor the elimination of the pollutants to be treated. Furthermore, EBRT studies (data not shown) suggested that the main responsible for the incomplete EM elimination was a mass transfer limitation, since pollutants such as mercaptans require large EBRTs [12].

In both bioreactors no nutrients were added to the make-up water solution, since it is widely accepted that most of natural organic media have enough nitrogen and phosphorous content for developing a process culture [1]. Similarly, the organic matter content detected (around 95% by weight) constituted an alternative substrate source for biofilter microorganisms which could be used during starvation periods such as process shut-downs, process rotation or intermittent loads [17].

Since physical-chemical properties of both woods do not underscore a significant different behavior in terms of RE, costs associated to the purchase and maintenance of packing materials become a key factor. Woods a largely available and cost-effective resource, thus becoming a promising packing material for biofiltration. Moreover, current forest management practices provide huge amounts of low-quality wood, which could be used in the construction of biofilters [45]. While estimated annual material costs for PNWR were between 10 and 16 € m^{-3} y^{-1} represent a 25% lower cost was estimated for the PPWR at the local prices of the present study (Table 1). Considering the energy to blow the air through the packing material in relation to the pressure drop, the use of pine or poplar wood chips represents a difference in the annual total cost of 7.3 % (Table 2). Thus, since elimination capacities reached were similar for both woods, the use of a kind of wood can be more attractive just because of economical reasons according to market prices in relation to materials accessibility in the zone of implantation. In this sense, further research is needed to establish materials durability based on long-term studies, which would be useful to perform accurate suitability and economical studies with both packing materials.

4. CONCLUSIONS

The co-treatment of a complex mixture of NH_3, H_2S, EM and butyric acid was successfully achieved in biotrickling filters packed with poplar and pine wood as an alternative to inorganic materials. Overall, taking all the evaluated properties into consideration, poplar and pine wood are support media potentially suitable to keep active biomass growing on their surface and, subsequently, show a good performance in the abatement of a wide range of compounds. Despite of the differences observed in the materials characterization, no significant variations in the REs were observed under biofiltration conditions for the two different woods. Thus, only economical aspects such as durability and material cost, according to material availability, become relevant to choose the most suitable organic packing material in the case of wood supports.

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LIST OF ABBREVIATIONS

AOB - Ammonium oxidizing bacteria

BET - Brunauer Emmett and Teller

DMDS - Dimethyldisulfide

EBRT - Empty bed residence time

EC - Elimination capacity

EM - Ethylmercaptan

FA - Free ammonia

FNA - Free nitrous acid

HRT - Hydraulic residence time

LR - Loading rate

NOB - Nitrite oxidizing biomass

PNWR - Pine wood reactor

PPWR - Poplar wood reactor

PVC - Polyvinyl chloride

RE - Removal efficiency

rp - Production rates

VOC - Volatile organic compound

VSS - volatile suspended solids

WWTP - wastewater treatment plant

ΔP - pressure drop

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Table 1 Physical properties, estimated prices, durabilities and annual material cost of poplar and pine wood.

Parameter	Poplar wood	Pine wood
Water-holding capacity ($g\ g^{-1}$)	1.16	1.35
Water retentivity ($\%\ h^{-1}$)	- 0.67	-1.52
Surface area ($m^2 g^{-1}$)	1.21	0.99
pH	7.2	6.7
Buffer capacity ($mL\ SO_4^{2-}\ l^{-1}$)	51	35
Material cost (€ m^{-3})	45-60	40-50
Estimated durability (years)	5	3-4
Annual material cost (€ $m^{-3}\ y^{-1}$)	9-12	10-16

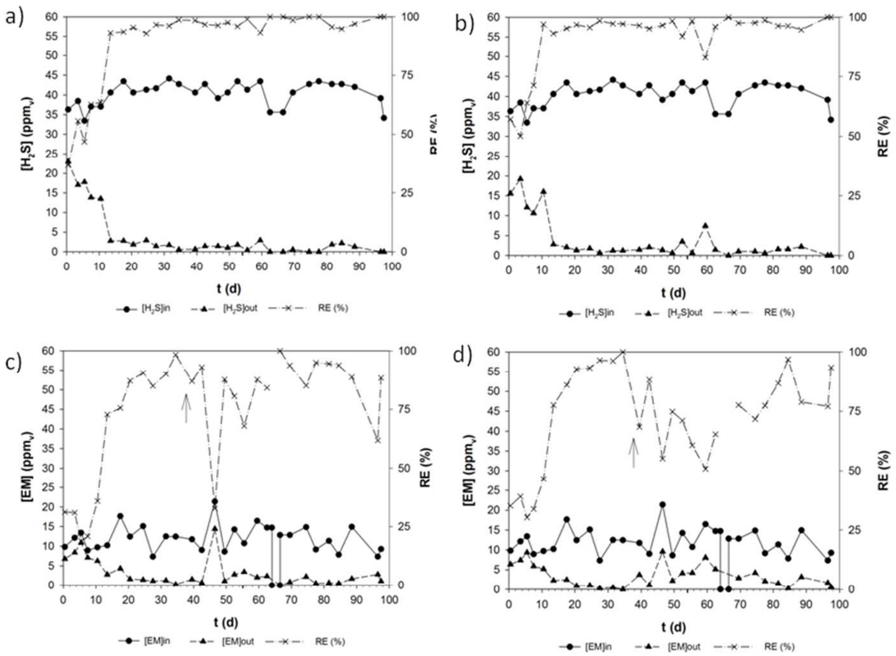

Fig. 1 Inlet and outlet H2S concentrations and removal efficiency (RE) in the gas phase for PNWR (a) and PPWR (b). Inlet and outlet EM concentrations and removal efficiency (RE) in the gas phase in PNWR (c) and PPWR (d). Arrows indicate the reinoculation day.
Figure 1
254x190mm (96 x 96 DPI)

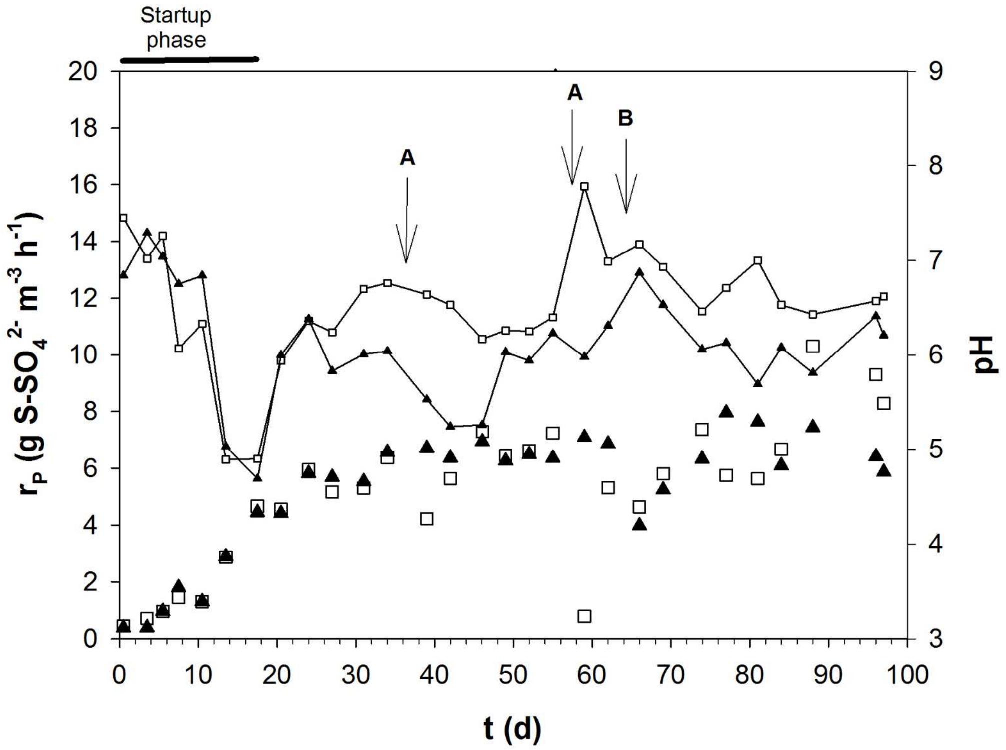

Fig. 2 Evolution of S-sulphate production rate, rP (PPWR, □; PNWR, ▲) and pH in both bioreactors (PPWR, -□-; PNWR, -▲-). A and B arrows are related to punctual episodes concerning PPWR and PPWR/PNWR, respectively.
Figure 2
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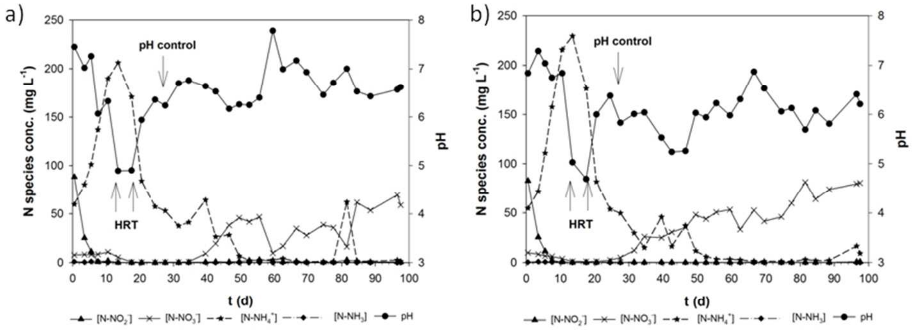

Fig. 3 Profiles of nitrogen species and pH in the liquid phase in PPWR (a) and PNWR (b).
Figure 3
254x190mm (96 x 96 DPI)