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Removal of a Mixture of Seven Volatile Organic Compounds (VOCs) Using an Industrial Pilot-Scale Process Combining Absorption in Silicone Oil and Biological Regeneration in a Two-Phase Partitioning Bioreactor (TPPB)

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Abstract: The treatment of a synthetic polluted gas containing seven volatile organic compounds (VOCs) was studied using a pilot plant in real industrial conditions. The process combined VOC absorption in silicone oil (PolyDiMethylSiloxane, i.e., PDMS), a biological regeneration of the PDMS in a two-phase partitioning bioreactor (TPPB), and a phase separation including settling and centrifugation. The TPPB was operated at a water/PDMS volume ratio of 75/25. The VOCs treatment performance was efficient during the entire test, corresponding to 10 PDMS regeneration cycles. The analysis of the content of the aqueous phase and PDMS confirmed that VOCs are progressively degraded until mineralization. The nitrogen consumption and the characterization of the microorganisms highlighted possible anoxic functioning of the biomass within the first decanter. Moreover, although the absorption and biodegradation performances were very satisfactory, the separation of all phases, essential for the PDMS recycling, was problematic due to the production of biosurfactants by the microorganisms, leading to the formation of a stable emulsion and foaming episodes. As a consequence, the packed column showed slight fouling. However, no significant increase in the pressure drop of the packed bed, as well as no significant impact on VOC absorption efficiency was observed.

Keywords: absorption; silicone oil; two-phase partitioning bioreactor; volatile organic compound; biological degradation; emulsion

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1. Introduction

Volatile Organic Compounds (VOCs) are hydrocarbons with potential heteroatoms (halogens, nitrogen, oxygen, sulfur . . .) with a vapor pressure higher than 10 Pa. These molecules are very diverse and are used in many different industrial sectors, as solvents or additives for example. One important characteristic of these compounds is their high volatility, leading to significant emissions into the air, which can be toxic towards human health, and also the environment. For example, VOCs can cause respiratory diseases and contribute to global warming through tropospheric ozone production [1]. Based on these considerations, some scientific and technological advances must be found to reduce these emissions. Some preventive solutions have been studied, but when reduction is not possible, curative processes must be developed. Thus, VOC treatment can be performed using several kinds of technologies; the main ones currently used at the industrial scale are

adsorption, thermal and catalytic oxidation, biofiltration, and condensation [2]. Condensation is suitable for low flow rates and high VOC concentrations with simple composition, while adsorption and thermal and catalytic oxidation can be addressed to larger flow rates. Nonetheless, these last processes are energy-consuming and not eco-friendly. Biofiltration is an eco-efficient solution that can be used to treat a large flow rate with low VOC concentrations, but preferentially for water-soluble VOC. To improve the performance of the biofiltration process, the introduction of a non-apolar phase, named non-aqueous phase (NAP), can be used to absorb hydrophobic VOCs before their degradation. This kind of biological reactor is called a Two-Phase Partitioning Bioreactor (TPPB) [1,3,4]. The selection of a NAP must satisfy several criteria [5]. Among the liquid phases tested (e.g., lubricant [6], vegetal oils [6,7], alkanes [8,9], ionic liquids [10]), silicone oils (i.e., PolyDiMethylSiloxane, PDMS) are the most adapted NAP to be implemented in a TPPB (mainly due to their low volatility and viscosity, high affinity for VOC, compatibility with biomass, and no bioavailability) [11–14].

Several reactor configurations for VOC biodegradation in TPPB, i.e., stirred tank bioreactors, airlift bioreactors, and packed bed bioreactors such as biofilters and biotrickling filters, have been studied at laboratory-scale, but no full-scale TPPB for actual polluted gas treatment has yet been implemented [15]. Elsewhere, only a few studies concerning TPPB at pilot-scale are reported in the literature. Aldric and Thonart [11] studied a 4.5 L pilot-scale TPPB for BTEX removal at high concentrations with successful performances (around 63% for isopropylbenzène). Daugulis and Janikowski [8], studying the degradation of PAH (Poly Aromatic Hydrocarbons, naphthalene and phenanthrene) with dodecane as the NAP in a 150 L bioreactor, demonstrated the degradation of 300 g of PAH in less than 21 h (95 g m^{-3} h^{-1}). Lalanne et al. [16] developed a large laboratory bioscrubber to study the influence of a cutting oil on the bioscrubber performance. The results showed that the addition of the NAP strongly increased the amount of absorbed aromatic compounds, with the removal efficiency of hydrophobic compounds increasing from 12% to 36%. Similarly, the influence of the cutting oil addition on the absorption and the biodegradation of toluene was studied in a large-scale bioscrubber by Nourmohammadi et al. [17]. The biocompatibility of the cutting oil and its ability to enhance the absorption and the biodegradation of toluene confirmed the results reported in Lalanne et al. [16]. Recently, Nourmohammadi et al. [18] replaced the cutting oil with silicone oil to assess the absorption and the biodegradation of toluene. The results confirmed the literature data demonstrating the positive influence of the silicone oil for the removal of hydrophobic VOCs such as toluene. However, the study of a TPPB treating a polluted gas in real conditions, including the absorption step, the biodegradation step, and the regeneration step of the NAP, is still lacking.

As a result, there is a need to demonstrate that TPPB can be implemented at a large scale to treat an industrial gas polluted by a mixture of various VOCs. Therefore, this work consisted of studying, for the first time to our knowledge, the complete operation of a large pilot-scale installation combining a first VOC absorption in silicone oil, then silicone oil biological regeneration in a TPPB, permitting simultaneously VOC degradation (in a 1250 L bioreactor), and finally phase separation (settling and centrifugation). The trials were monitored on an industrial site whose main activities are hazardous waste collection and valorization, aiming at the production of a complex VOC mixture of different hydrophobicities at low concentrations.

With the purpose of determining the ability of the studied process to be implemented in a full-scale installation for low VOC concentration and high flow rates, absorption experiments were first carried out in order to optimize the performances of the process through hydrodynamics and VOC removal efficiencies characterization. Secondly, the operation of the TPPB was monitored through carbon and nutrient concentrations, acclimated biomass, and produced biosurfactant effects.

2. Materials and Methods

The pilot-scale process was installed on an industrial site specializing in the collection and valorization of chemical waste. The objective of the plant is to produce a fuel that can be used by cement factories as well as by incinerators. The main VOC identified from the analysis of the gaseous emissions generated by the industrial site were n-heptane, ethyl acetate, propan-2-ol, methylisobutylketone, toluene, m-xylene, and 1,3,5-trimethylbenzene (1,3,5-TMB). The Henry's law constants of these molecules at 25 °C are given in Table 1 for systems air/water and air/PDMS, respectively [19]. As observed, some molecules are very hydrophobic, such as n-hexane, whereas others are hydrophilic and weakly soluble in PDMS, such as isopropanol.

Table 1. Henry's law constants at 25 °C (Pa m^3 mol^{-1}).

Molecules	Water	PDMS	Ratio water/PDMS
n-heptane	2.08 $\times 10^5$	2.34	88,888
Ethyl acetate	14.9	6.39	2.33
Isopropanol	0.31	19.93	0.016
Methylisobutylketone (MIBK)	21.1	1.78	11.8
Toluene	510.0	2.15	237
m-xylene	644.5	0.71	907
1,3,5-triméthylbenzène	714.3	0.22	3246

2.1. Pilot-Scale Installation

The pilot-scale process, shown in Figure 1, was designed and built by TC Plastic Company (Pontchâteau, France). A packed column (internal diameter of 0.15 m, height of 1.3 m) was fed by a regenerated PDMS stored in a 1000 L tank. The PDMS used was Rhodorsil 47 V20, provided by Bluestar Silicones Company, Beijing, China (molar mass 3000 g mol^{-1}; density 900 kg m^{-3}; dynamic viscosity 20 mPa s at 25 °C; surface tension 21 mN m^{-1}). The absorption column (counter-current mode) was filled (1.3 m height) with a random packing material, IMTP® 15 mm (INTALOX® Metal Tower Packing provided by Koch Glitsch France SA, Arles, France; hydraulic diameter: 1.28 $\times$ 10^{-2} m; specific surface area: 299 m^2 m^{-3}; porosity: 96%). After absorption, PDMS was collected in a 300 L tank, from which PDMS was circulated towards the TPPB of 1250 L, continuously aerated (bubbling system) and agitated with a Rushton turbine in order to be mixed with the aqueous phase, consisting of water, nutrients, and biomass from the waste water treatment plant of Fougères (France). The volume ratio of PDMS and the aqueous phase in the TPPB was 25/75 (*v*/*v*), corresponding to the optimal volume ratio [20]. The design of the TPPB and the flow rates operated led to a PDMS residence time of 3 h. Once PDMS was biologically regenerated, the liquid phase (PDMS/aqueous phase) was transferred to a non-aerated settling tank (decanter #1) for a first separation step by means of an automatic valve. Theoretically, PDMS should be separated from the top of this settling tank, and the aqueous phase containing biomass should be drained from its bottom. However, because phase separation was not optimal, an additional separation was performed by centrifugation (Sharpless Centrifuges, 16,000 rpm). The centrifuge was a three-phase clarifier with one outlet, where the centrifuged effluent was settled in a second settling tank (decanter #2). Finally, an additional buffer tank was positioned in order to carry out a final control of the quality of PDMS before its recirculation in the packed column.

2.2. Operating Procedure

The different phases of the experiment are summarized in Figure 2. Before the beginning of the trials, biomass acclimation was carried out for 28 days. Acclimation corresponds to the adaptation of the biological system to the mixture of targeted VOCs. A sample of mixed culture biomass from a wastewater treatment plant was used to inoculate the bioreactor. The initial dry matter concentration in the aqueous phase was 2 g L^{-1}. The regular addition of a liquid mixture of seven different VOCs (100 mL every 2–3 days) was carried

out in the aerated and stirred TPPB to stimulate the biomass growth. The liquid mixture, whose molecules and proportions were selected from the analysis of the composition of the real VOC flow emitted on the industrial site, had the following composition (% in volume): n-heptane (18%), ethyl acetate (23%), propan-2-ol (16%), methylisobutylketone (MIBK, 25%), toluene (8%), m-xylene (7%), 1,3,5-trimethylbenzene (1,3,5-TMB, 4%). To ensure a sufficient input of nutrients, a partial renewing of the aqueous phase was carried out once a week (6% of the total volume). The pH was maintained around 7 and adjusted with a sodium hydroxide solution (32% w/w).

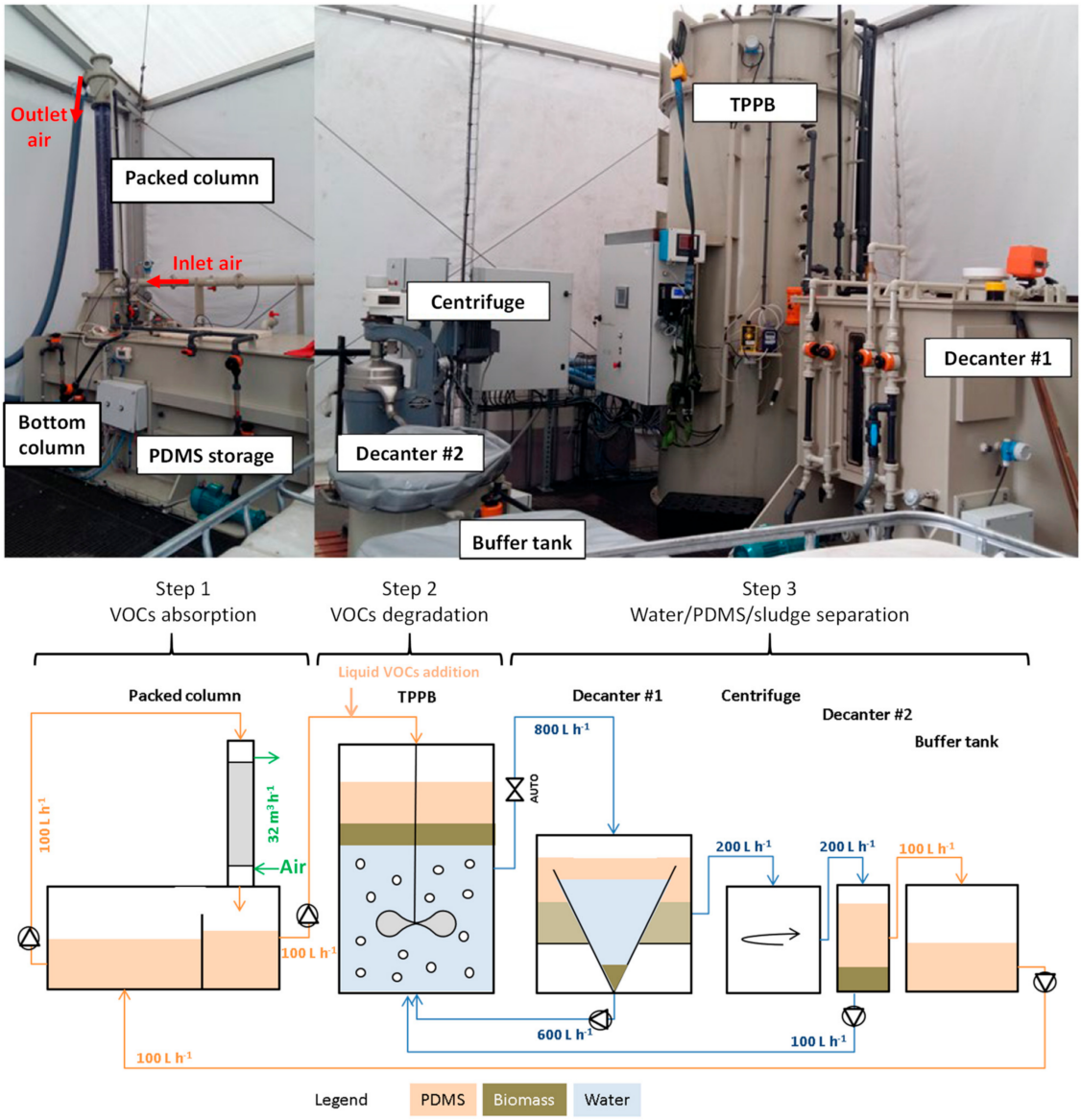

Figure 1. Photo and schematic overview of the large-scale installation combining (from left to right): VOC mass transfer between air and PDMS (PolyDiMethylSiloxane, i.e., silicone oil) in a packed absorption column, a biological regeneration of the PDMS in a two-phase partitioning bioreactor (TPPB), and a separation of phases including settling and centrifugation steps (green arrows: air flowing through the packed column; flow-rate: 32 m^3 h^{-1}).

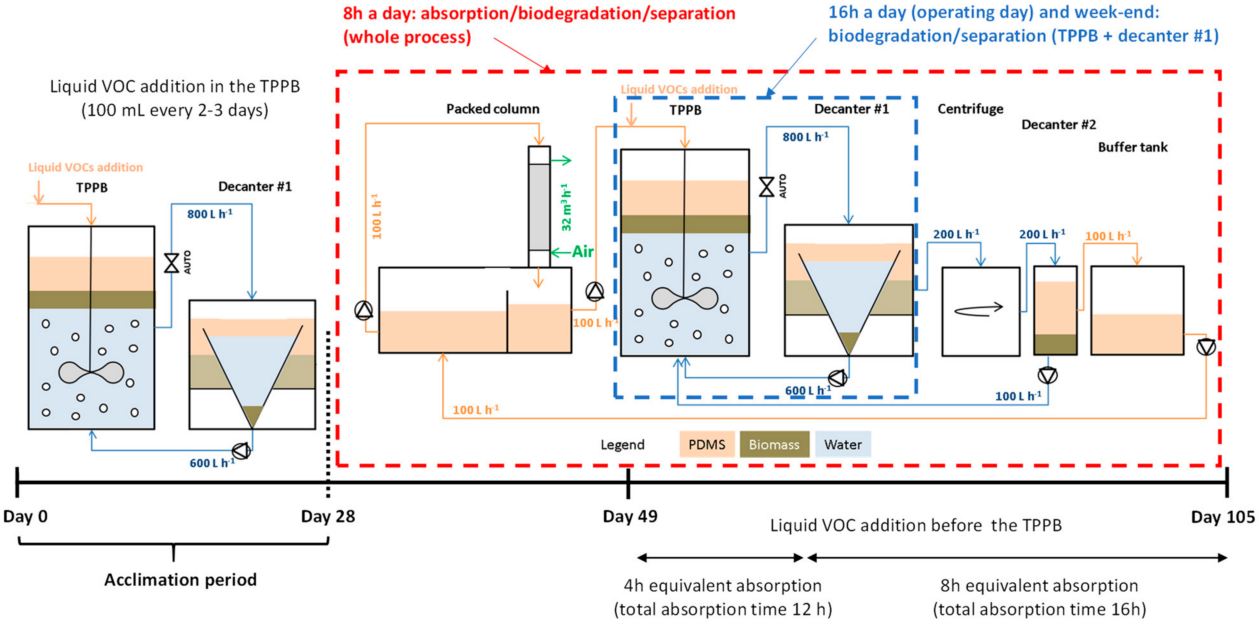

Figure 2. Summary of the different phases of the experiment and operating conditions.

After the acclimation period, and in order to respect the constraints imposed by the industrial site (e.g., trials were forbidden during the night), the absorption step worked only 8 h a day during working days. On weekends and during the night, only the TPPB and decanter #1 worked in order to recirculate the liquid in a closed loop between both apparatuses. This configuration allowed for homogenization and aeration of the biomass when absorption was not taking place, which therefore helped to achieve continuous degradation of VOCs and the regeneration of the PDMS in the TPPB. During working days, the gas flow rate was set at 32 m^3 h^{-1} (gas velocity U_G = 0.5 m s^{-1}) and the PDMS flow rate was 100 L h^{-1} (liquid-to-gas mass flow rate ratio L/G = 2.4). Because the total volume of PDMS in the pilot was 1.5 m^3, the total residence time of the PDMS in the installation was 15 h, with 5 h of contact with microorganisms (TPPB and decanter #1). Thus, 10 absorption/regeneration cycles of PDMS were performed during the operating period (total trial time: 158 h).

As the absorption step could only operate 8 h a day during working days, i.e., far from the real operating conditions of the industrial site (2 × 8 h per day), extra amounts of VOCs were added to the PDMS in a liquid form to artificially increase the amount of VOCs transferred from the air to PDMS during the absorption step. The objective was to reach a VOC load to be degraded by the biomass in the TPPB equivalent to the VOCs emitted during 12 h per day in a first approach (from day 49, Figure 2), then during 16 h per day. For this purpose, additions of a liquid mixture of seven target VOCs (i.e., the mixture used during the acclimation period), equivalent to a 4-h load of absorption of a real flow and then equivalent to 8 h running, were performed between the absorption column and the TPPB.

2.3. Measurements and Analyses

Pressure drop was monitored between the inlet and the outlet of the packed column (on the gas phase) using analogical pressure sensors (Cerabar S PMC71, Endress+Hauser, Reinach, Switzerland).

Total VOC concentration (expressed in mg m^{-3} of total carbon, i.e., mg_{TC} m^{-3}) was measured alternately at the inlet and the outlet of the packed column every 10 min by a Photo-Ionization Detector (PID, Pho-check Tiger, Ion Science Ltd., Fowlmere, UK) calibrated with isobutylene.

The VOC concentrations in PDMS were determined according to the following procedure. An amount of 0.5 mL of PDMS was sampled and introduced in a sealed 22 mL vial. The vial was then agitated in a rotational stirrer for 48 h at 25 °C in order to reach the equilibrium of VOCs between PDMS and the gaseous phase in the vial. Head-space was then analyzed by gas chromatography (GC-FID). The number of VOCs transferred from the industrial polluted air to the PDMS was more than 30 molecules. Because the mixture of transferred VOCs was very complex, the overall amount of desorbed VOCs was visually estimated by the size of the spectrum.

Concerning the aqueous phase analysis, Chemical Oxygen Demand (COD), nitrogen concentration, phosphorus concentration, and biomass concentration were determined. The chemical oxygen demand corresponds to the oxygen quantity necessary for the chemical degradation of carbon compounds. The analysis was monitored by a micro-method (C3/25, WTW®) in which oxidation is carried out with potassium dichromate $K_2Cr_2O_7$ and silver sulfate as a catalyst. Then, the remaining potassium dichromate was analyzed by spectrophotometry. Nitrogen concentration was monitored through nitrate concentrations measured by a micro-method (114764, WTW®). In a solution containing sulfuric and phosphoric acids, nitrates react with dimethyl-2,6-phenol (DMP) and nitro-4-dimethyl-2,6-phenol to generate a pink-colored solution analyzed by spectrophotometry. Phosphorus (173706, WTW®) was first totally mineralized in order to form orthophosphate ions, which then reacted with molybdate ions to form phosphomolybdic acid. This intermediate was finally reduced by ascorbic acid into phosphomolybdene blue, analyzed by spectrophotometry.

Biomass concentration in the TPPB was measured by centrifuging 60 mL of bioreactor content. The PDMS/aqueous phase interface was washed several times to extract the entirety of sludge contained in the initial sample. The sludge was then dried in an aluminum cup. Dry matter concentration was calculated, dividing the dried sludge by the sample volume. Difficulties in separation were often observed with sludge caught in the PDMS/aqueous phase interface.

2.4. Characterization of Microbial Communities

Biomass was sampled from the original sludge introduced in the pilot-scale TPPB (coming from the wastewater treatment plant) and from the TPPB after 3 months of process operation. Samples were centrifuged (4500 rpm, 10 min), and the pellet was stored at −20 °C. Genomic DNA extraction was performed with the Macherey–Nagel NucleoSpin® Soil kit from 250 mg of frozen pellet according to the manufacturer recommendations. Extracted DNA was eluted in a final water volume of 60 µL. The concentration and the quality of DNA were verified with a biophotometer (Eppendorf BioPhotometer® D30) and by electrophoresis on agarose gel (TAE 1X, 0.7% agarose w/v, 120 V, 40 min). Purified DNA was stored at −20 °C until high-throughput DNA sequencing.

High throughput DNA sequencing was performed at the INRAE PROSE sequencing facility (Antony, France) using Ion Torrent Personal Genome Machine methods and technologies (Life Technologies, Carlsbad, CA, USA), as described in detail in Fisgativa et al. [21]. Briefly, the V4-V5 hypervariable region of the 16S rRNA bacterial and archaeal genes was amplified using fusion primers derived from primers 515F (5′-CTGYCAGCMGCCGCGGTA-3′) and 928R (5′-CCCCGYCAATTCMTTTRAGT-3′). The resulting amplicons were sequenced using the Ion PGM Hi-Q View OT2 Kit and Ion PGM Hi-Q View Sequencing kit (Life Technologies). The 172,750 sequence reads (of approximately 420 base pairs) were analyzed using the Galaxy portal of the Migale bioinformatics platform of INRAE (Jouy-en-Josas, France) and the FROGS software pipeline ("Find Rapidly OTU with Galaxy Solution"), keeping the default settings [22]. The resulting 33,219 correct sequences, obtained from all samples, were clustered in Operational Taxonomic Units (OTUs) based on having more than 97% similarity within an OTU. Taxonomic affiliation of the OTUs was carried out, by both BLAST (NCBI, http://www.ncbi.nlm.nih.gov/BLAST, accessed on 1 March 2022) and Ribosomal Database Project II database (https://rdp.cme.msu.edu/, accessed on 1 March 2022) sequence alignment. OTU abundance analysis and diversity in-

dex of microbial communities were performed using a shiny web interface of the phyloseq package of the R software [23].

2.5. Biosurfactant

Foaming due to biosurfactant production is known to be a key issue in TPPB [15]. Biosurfactant contained in emulsion formed by sludge, aqueous phase, and PDMS was identified by FTIR (Fourier Transform InfraRed spectroscopy). Three spectra were acquired: (i) emulsion, (ii) water, and (iii) PDMS. By subtraction of water and PDMS spectra to the spectrum of the emulsion, biosurfactant could be identified by the characterization of non-designated bands. Additionally, biosurfactant production was evidenced from interfacial tension measurements between air and liquid phases (superficial tension) or between two liquid phases. Interfacial tension (N m^{-1}) was measured by a Krüss tensiometer with the Noüy ring method [24,25]. The calculation software allowed the assessment of the final average interfacial tension after several measurements.

3. Results and Discussion

3.1. Absorption

The purpose of the process was to efficiently remove VOCs from the industrial polluted air, while recycling the PDMS in the packed column after its biological regeneration in the TPPB. Thus, the efficiency of the VOC absorption step mainly depends on TPPB biological regeneration performances. Indeed, if the biodegradation of the absorbed VOCs is not effective, VOCs accumulate in the PDMS, leading to a decrease of the concentration gradient between PDMS and the gas phase in the absorption column, leading to a performance decay and an increase in the VOC concentration at the outlet of the column.

For convenience, the absorption performances monitored during the operating period are reduced to the duration of the 10 absorption/regeneration cycles of PDMS, corresponding to 158 h of operation (for clarity, downtimes are not shown). Results, expressed as total VOC concentration at the inlet and outlet of the packed column, are displayed in Figure 3A. The horizontal line represents the emission limit guide value of 110 mg_{TC} m^{-3}, in accordance with French regulation. First, the scattering of inlet VOC concentration in the polluted air around the average value of 149 mg_{TC} m^{-3} was very important because the concentrations varied between 5 and 788 mg_{TC} m^{-3} (data not shown) due to the variability of the activity of the industrial site. The disparity did not seem to influence the absorption efficiency, because outlet concentrations were always under the threshold regulatory value of 110 mg_{TC} m^{-3}. The mean value was approximately 24 mg_{TC} m^{-3}, with an average deviation of 12 mg_{TC} m^{-3}. Remarkably, the absorption performances of the process (absorption in the packed column and regeneration of PDMS in the TPPB and separation steps) was steady during the 10 successive absorption/regeneration cycles of PDMS. Thus, when the VOC load to be treated by the TPPB was gradually increased from the 8 h-air treatment to the 16 h-air treatment, no significant difference in the absorption efficiency could be noticed during pilot trials. This result demonstrates that the absorbed VOCs were efficiently removed for the real operating conditions of the industrial site (2 × 8 h per day).

The PDMS recirculation in the pilot between the separation step and the absorption column led to an apparent development of biomass on the packing elements. Indeed, on the one hand, attachment of some biomass was observed on the pieces of packing extracted from the column. On the other hand, the monitoring of the pressure drops between the top and the bottom of the packed column versus time showed a small increase, from 130 Pa at the beginning of the trial to 170 Pa at the end (Figure 3B). According to this figure, a periodic or cyclic change in the pressure drop can be observed: a decrease and then an arched pattern, indicated by the arrows on the figure. The lower values indicated by the arrows correspond to the reboot of the absorption step that was stopped every night or during the weekends (or for maintenance operation). When the absorption step restarted, the value of the pressure drop was lower than during functioning periods. It then increased to reach a maximum value and finally slightly decreased. This observation can

be explained by water settling in the tank used for feeding the packed column with PDMS. Indeed, during centrifugation, in order to separate the PDMS from water and biomass, a part of the water was brought with PDMS (0.5 to 2.6% in volume). During extended stop periods, this part of the water entirely settled at the bottom of the PDMS tank, near the aspiration point of the packed column feeding pump. Thus, the viscosity of the liquid flowing into the packed column decreased, leading to a lower pressure drop when restarting the installation. Then, when the water content in the flowing liquid phase decreased, the liquid viscosity increased again, leading to an increase in the pressure drop. Nevertheless, during the overall trial period, the monitored pressure drops were lower than the maximum value of 500 Pa recommended for the implementation of a packed column [26]. Moreover, the comparison between the curve's "pressure drop vs. gas velocities", carried out at the beginning and at the end of the trial (Figure 4) clearly confirmed that biomass development in the absorption column was very limited. However, at this stage of investigation, it is too early to affirm that there will be no clogging for long term operation.

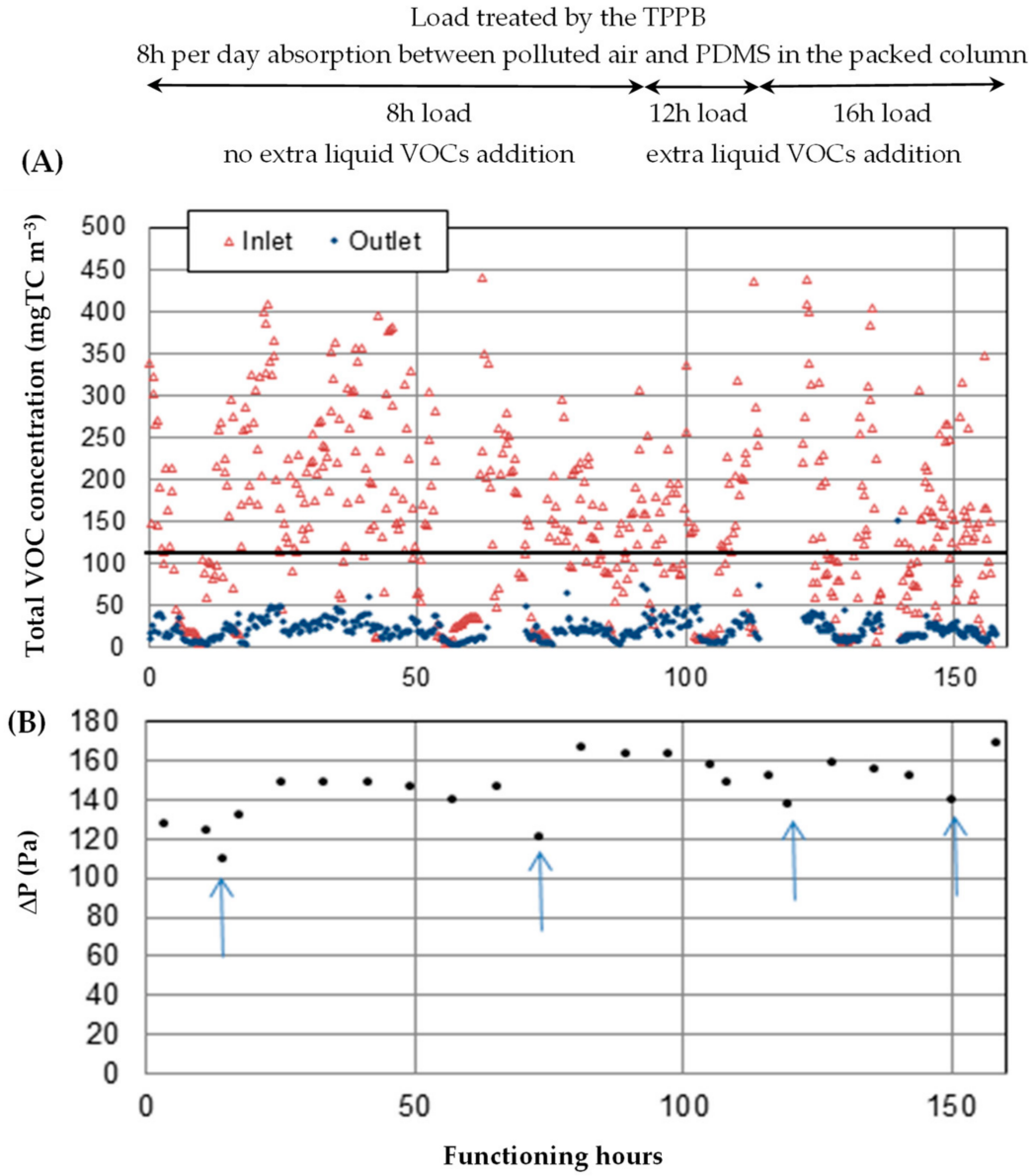

Figure 3. (**A**) Absorption performances during pilot operation (the value of 110 mg_{TC} m^{-3} represents the limit set by the French regulation) and (**B**) evolution of total pressure drop in the packed column.

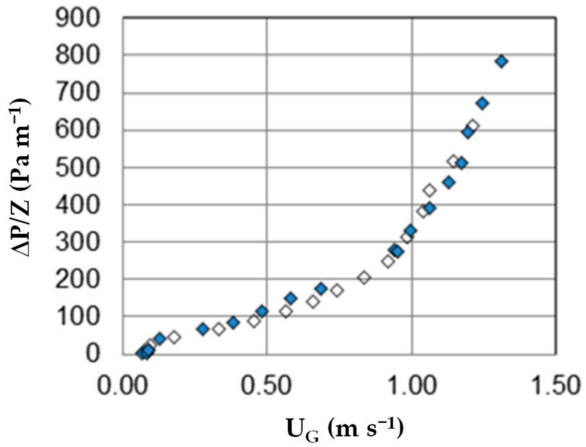

Figure 4. Influence of gas velocity on pressure drops per packing height unit at the beginning (empty diamond: clean column) and at the end of the trial (blue diamond: dirty column). Liquid flow rate = 100 L h^{-1}.

3.2. Biological Regeneration of the PDMS

Absorption efficiency results showed steady VOCs treatment performances during pilot trials; the correct PDMS regeneration by the TPPB had to be confirmed by the study of the aqueous phase content and the microbial communities' evolution.

3.2.1. Aqueous Phase Content

The aqueous phase of the TPPB contains nutrients necessary for the growth of microorganisms. It may also include VOCs or degradation by-products coming from VOC degradation. The only carbon sources brought to the TPPB are the VOCs absorbed in the PDMS or those added under the liquid form in order to increase the VOC load to be degraded. Some hydrophobic compounds are transferred from PDMS to microorganisms able to accumulate and grow at the PDMS/aqueous phase interface [15], while hydrophilic molecules migrate from PDMS to the aqueous phase. These mass transfers are governed by thermodynamic laws lying on partition coefficients. Carbon content monitoring was necessary to confirm VOC and by-product mineralization. The volumetric carbon load was calculated for each experimental period by measuring the Chemical Oxygen Demand (COD). Figure 5A shows that, during the acclimation period, COD values increased from 150 mg_{O2} L^{-1} to 400 mg_{O2} L^{-1} and then decreased to 100 mg_{O2} L^{-1}. After the acclimation period, the COD values remained constant, around 100 mg_{O2} L^{-1}, even during the period of liquid additions of VOCs. As a result, when volumetric VOC-load increased to reach a load equivalent to a VOC treatment of 16 h a day, the COD value did not shift, which is proof that a good mineralization occurred in the TPPB.

Nitrogen and phosphorus concentrations were also monitored to assess the "quality" of the culture medium. As reported in Figure 5B, nitrogen consumption was significant during the acclimation period. From day 40, the nitrogen amount in the bioreactor became negligible. Therefore, after 10 days of nitrogen starvation, urea was added in order to raise the nitrogen concentration to a correct value. Despite this addition, nitrogen concentration fell again. Consequently, nitrogen must be carefully controlled to guarantee a good working of the TPPB. As concerns phosphorus, after the acclimation period, the concentration remained constant, around the initial value, showing that phosphorus was present in large amounts, avoiding any significant variation of its concentration during the aerobic degradation process.

Dry matter concentration was also studied versus time. Figure 5C shows that the dry matter concentration increased during the acclimation period, as proposed previously as regards COD and nitrogen dynamics, and stabilized thereafter around 0.5 g L^{-1}. This value can seem low in comparison with those usually encountered in the activated sludge tanks of wastewater treatment plants (around 3 g L^{-1} [27]). However, one must keep

in mind the low availability of the carbon source (VOCs only) contrarily to traditional processes, because (i) most VOCs are poorly water soluble, and (ii) due to the process design, VOCs are solubilized in the PDMS, and consequently microorganisms have to migrate to the PDMS/aqueous phase interface to be provided with carbon. Moreover, as it will be developed later, the sludge contained in the TPPB and in decanter#1 formed a stable emulsion of PDMS and water, making the measurement of the dry matter concentration difficult.

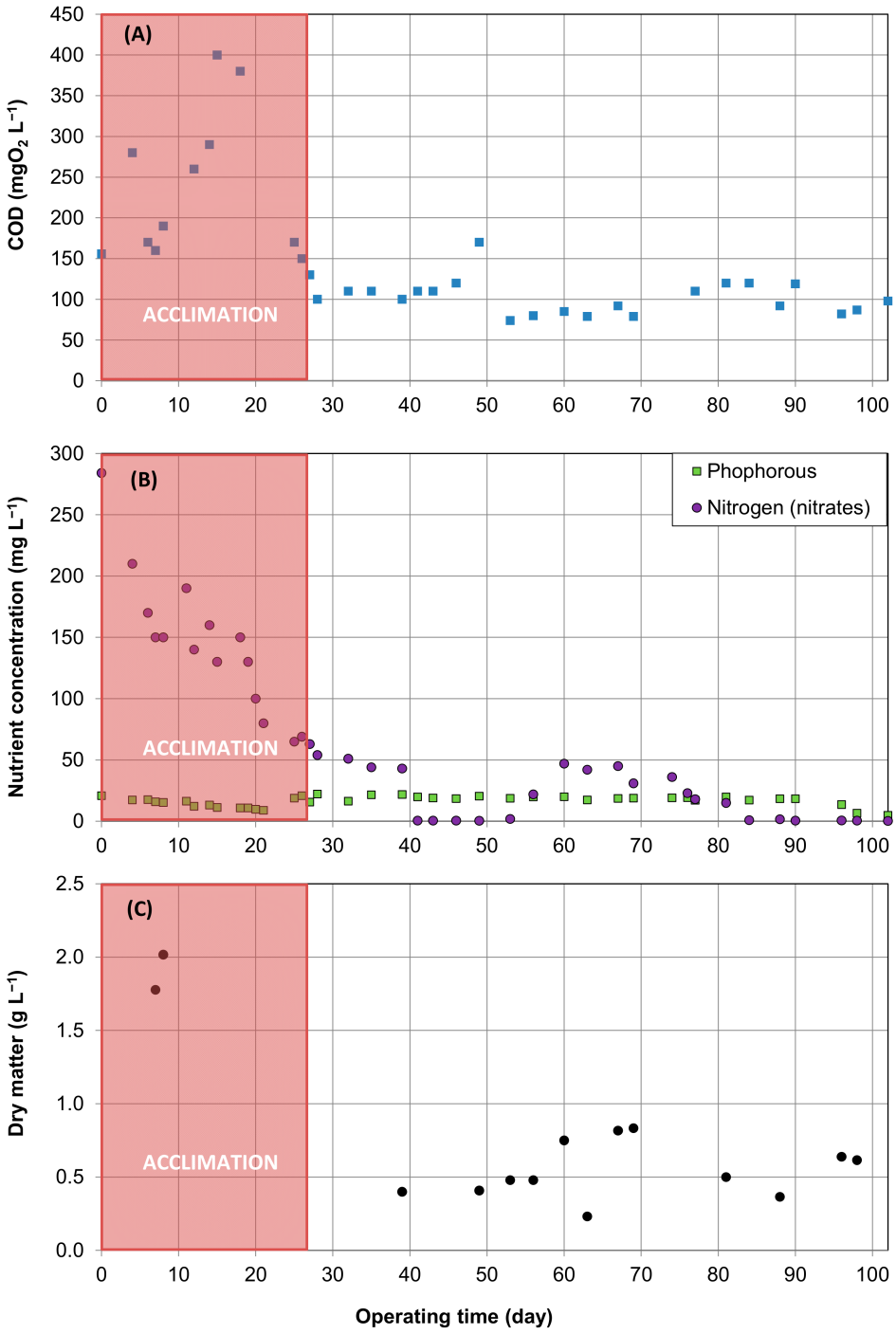

Figure 5. Change in operating parameters during acclimation and pilot operation: (**A**) chemical oxygen demand (COD); (**B**) nutrients concentrations (nitrogen and phosphorus) in the aqueous phase; (**C**) dry matter concentration.

Solvent bioavailability was also checked to ensure that the quality and the properties of PDMS did not change during operation. Biological Oxygen Demand (BOD) measurements were carried out on samples after 5 days, in the absence and the presence of PDMS. Values recorded were quite similar; the low biodegradability of PDMS already evidenced by Darracq et al. [12] from laboratory-scale experiments was therefore confirmed for this industrial application.

3.2.2. Microbial Community Dynamics

The study of microbial communities' composition provides relevant information on the biological degradation of VOCs. The community structure of initial and acclimated microorganisms in the TPPB-activated sludge was investigated by high-throughput DNA sequencing of 16S rDNA at the beginning and at the end of the trial. The sample "Initial" was from activated sludge used for pilot-scale inoculation (Table 2). "End(a)" and "End(b)" were from the same sample after 3 months operation of the process. The processing of sequence reads led to 8899 correct sequences for the sample "Initial" and 12,856 and 11,464 sequences for "End(a)" and "End(b)", respectively. The microbial communities' coverage of sequencing was very good, higher than 98% for all samples. The sample "Initial" showed a high microbial richness, with 529 operational taxonomic units (OTUs), typical of activated sludge. After the acclimation of microbial communities with VOCs and pilot operation, the number of OTUs decreased to 179 and 205 for "End(a)" and "End(b)", respectively (i.e., 66% and 61% decrease). The value of the Simpson index, corresponding to microbial species diversity, also decreased drastically from 0.98 to 0.83 and 0.87 for "End(a)" and "End(b)", respectively.

Table 2. Microbial diversity of studied samples.

Sample	Acclimation Duration	Final Sequence Number	Cover Rate	OTU Number (Richness)	Simpson Index Number
Initial	-	8899	0.98	529	0.98
End(a)	3 months	12,856	0.99	179	0.83
End(b)	3 months	11,464	0.99	205	0.87

Figure 6 presents the observed phyla in the studied samples. It shows the predominance of *Bacteroidetes* (55% of the total sequences), *Proteobacteria* (17%), *Chloroflexi* (9%), and *Actinobacteria* (4%) in activated sludge from the "initial" sludge in accordance with the literature [28]. After acclimation, the observed phyla are clearly different, with a strong predominance of *Proteobacteria* (74–76%) over *Bacteroidetes* (23–24%). The comparison of the sample microbial community structures by principal component analysis (data not shown) indicated that two microbial OTUs particularly distinguished the acclimated sludge from the initial one:

(1) *Alcaligenes faecalis* subsp. *Phenolicus*, which represented 0.17% of the total sequences of the "initial" sludge, was enriched up to 37% and 30% of the total sequences of the acclimated sludge ("End(a)" and "End(b)", respectively). It has to be noted that bacterial species belonging to the genus *Alcaligenes* have demonstrated versatile pollutant bioremediation ability, including phenols, polyaromatic hydrocarbon, and pesticides [29,30]. Because *Alcaligenes faecalis* subsp. *Phenolicus* is a denitrifying bacterium able to degrade phenol, it is possible that this bacterium is able to grow on the aromatic cycle molecules characterizing the composition of the real flow emitted on the industrial site, e.g., toluene, m-xylene, and 1,3,5-trimethylbenzene (1,3,5-TMB).

(2) *Thiopseudomonas denitrificans*, which was present at 0.04% in the "initial" sludge, made up to 12 and 15% of the total sequences after sludge acclimation ("End(a)" and "End(b)", respectively). *Thiopseudomonas denitrificans* is a denitrifying species able to oxidize sulfurs [31]. Its development was unexpected because the culture medium did not contain sulfur compounds. However, the presence of denitrifying bacteria such

as *Thiopseudomonas denitrificans* could explain the nitrogen consumption previously reported (Figure 5B). Moreover, this presence suggests that anaerobic zones certainly existed in the pilot, probably due to an inadequate sludge recirculation in the settling tank. As a result, investigation could be carried out to elucidate the enrichment of this microbial species in the reactor.

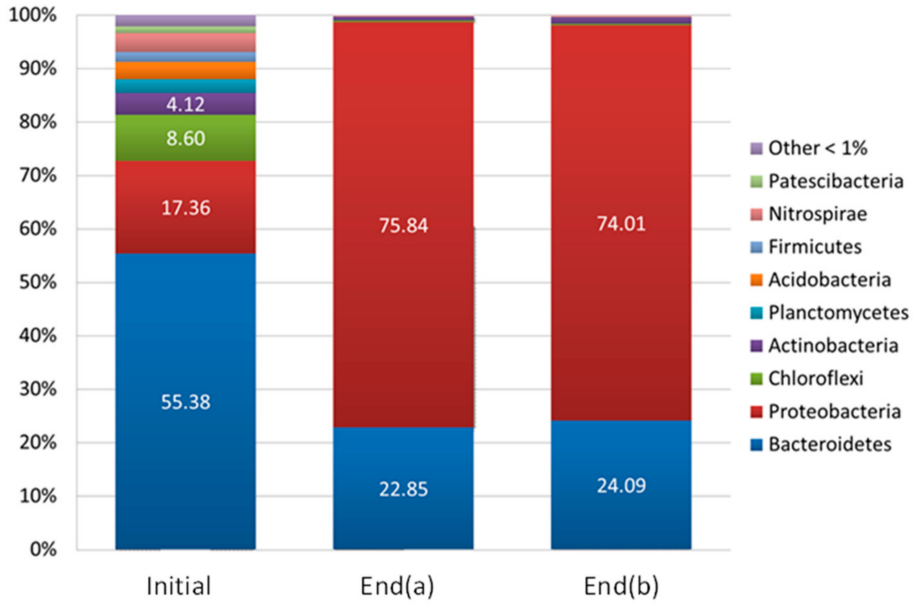

Figure 6. Phyla relative abundance repartition at the beginning (Initial) and at the end of the trial (End(a) and End(b)). Phyla present at less than 1% of the total sequences were summed in "Other < 1%".

3.3. Separation

As the trial progressed, the sludge contained in the TPPB and in decanter#1 formed a stable emulsion with the PDMS and water, making separation by decantation and centrifugation difficult. Moreover, the presence of air or an imbalance of the emulsion (too much water) in the centrifuge caused the formation of a foam, preventing recycling of the PDMS. Therefore, both these observations, which are usually reported as critical issues in the literature regarding TPPB studies carried out at laboratory-scale [15], provided evidence that biosurfactants have been produced by microorganisms. The presence of biosurfactants was confirmed from interfacial tension measurements between the air and liquid phases, water and PDMS, respectively. Thus, the interfacial tension between air and water decreased significantly after the operation of the pilot (from 71 to 45 mN m^{-1}), whereas the interfacial tension between air and PDMS did not change (20 mN m^{-1}). Additionally, the change in the surface tension between water and PDMS measured at the beginning and the end of the trial (from 36 to 27 mN m^{-1}, respectively) reinforces the production of biosurfactants. An attempt at biosurfactant identification was carried out by Fourier transform infrared analysis (FTIR) by subtracting the FTIR spectra of PDMS and water from the initial spectrum obtained from the PDMS/water emulsion (Figure 7). From spectra interpretation, it was assumed that biosurfactants produced by the microorganisms would be peptides with long hydrophobic alkyl chains, which agrees with the literature data. Indeed, biosurfactants can be mainly lipidic or peptidic [32–35], the peptidic biosurfactants usually being identified by typical absorption bands (1640 and 1518 cm^{-1} reflecting N-H, C=O, and C-N groups identifying amide functions, while 1368, 1450, and 2960 cm^{-1} reflect aliphatic chains -CH_3 and -CH_2-) [35].

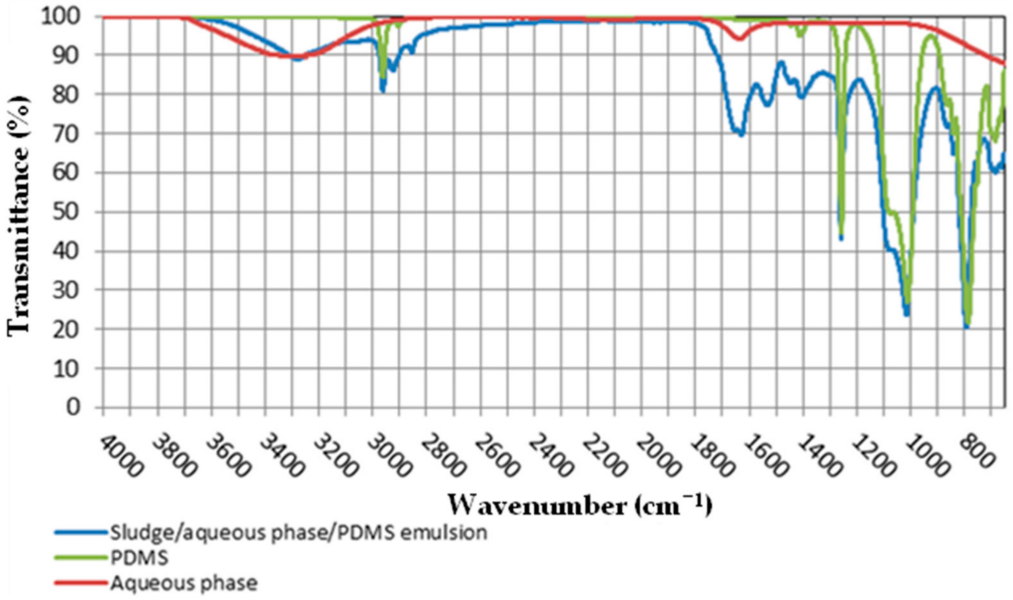

Figure 7. Fourier Transform Infrared (FTIR) of emulsion.

The formation of a foam preventing the recycling of the PDMS is therefore the main issue to solve in order to implement TPPB at an industrial scale. Although centrifugation was identified as the best technique for water/PDMS separation, a previous study evidenced that the addition of a non-biodegradable and non-toxic demulsifier could improve the phase separation [36]. Therefore, an attempt was carried out in a small emulsion sample in order to assess the influence of the addition of a commercial demulsifier (name of the demulsifier and data not shown for confidential reasons). Basically, the added compound destabilized the emulsion, which allowed the sludge to separate more efficiently from the liquid/liquid interface. Nonetheless, the effect of the demulsifier addition should be investigated regarding the process as a whole. Performance of separation as well as biodegradable, toxic, and economic aspects have to be considered.

3.4. Comparison to the Conventional Technologies

The performances of the pilot runs in terms of VOC absorption in the packed column and biological regeneration of the PDMS in the TPPB were very satisfactory. However, the separation of phases water/PDMS/sludge, critical for the recycling of the PDMS as well as sludge recirculation and possible clogging of the packed column, encountered difficulties due to the production of biosurfactants by the microorganisms, leading to the formation of a stable emulsion and foaming episodes. As the cost of the PDMS is probably the most important disadvantage for full-scale applications, an inefficient phase separation is detrimental for the development of the process in the future. Even if the cost of industrial-grade PDMS is significantly lower than the analytical grade, the price of one liter is nonetheless worth several euros [15], and consequently the operating costs would rapidly become prohibitive in the case of failure of the separation of the different phases (water, silicone oil, sludge). Compared to the conventional technologies available for air treatment (i.e., adsorption, chemical reaction absorption, photo-oxidation, cryogenic condensation, membrane separation, thermal oxidation, and catalytic oxidation, hybrid treatments combining the catalysis with other technologies [37,38]), thermal and catalytic oxidation, are the most appropriate technologies to efficiently treat large gaseous emissions containing a mixture of VOCs. However, these technologies are rather adapted to treat medium or high VOC concentrations (>5 g m^{-3}), whereas biological systems are more adapted to treat low VOC concentrations, such as those measured in the present study (i.e., <1 g m^{-3}; Figure 3). Moreover, for such low VOC concentrations, the cost of the natural gas, which represents a significant part of the total operating costs, although lower for

catalytic than for thermal oxidation, could be prohibitive [39]. Thus, the price of the PDMS and the price of the natural gas are the two operating costs that have to be preliminary considered to highlight the advantages of one technology over another (the initial capital costs being in the same order of magnitude; Table 3). Consequently, efforts must be made to improve the performance of the separation step in order to demonstrate that a process combining the absorption of VOCs in PDMS and a biological regeneration in a TPPB could compete the thermal and catalytic oxidation processes.

Table 3. Comparison between processes for VOCs removal.

Process	VOCs Concen-trations (g m^{-3})	Issues
Absorption in PDMS + TPPB	<1	PDMS cost PDMS/sludges separation step
Thermal oxidation	>5	Natural gas cost (T ≈ 850 °C) Impact of natural gas to climate change
Catalytic oxidation	>1	Natural gas cost (T from 200 to 400 °C) Catalyst cost Catalyst poisoning

4. Conclusions

For the first time, the treatment of a gaseous mixture of seven volatile organic compounds in air using a TPPB coupled with an absorption column and a separation system of phases was studied in real conditions on an industrial site. In this three-stages process, the absorption step and the biodegradation step were efficient, but the separation of the water/PDMS/sludge phases was the limiting step. The separation of phases, essential for recycling of the PDMS, was limited by biosurfactants produced by microorganisms, leading to the formation of a stable emulsion and foaming episodes. Moreover, the characterization of microbial communities allowed us to show a strong enrichment in *Alcaligenes faecalis* subsp. *Phenolicus* and in *Thiopseudomonas denitrificans*. The presence of denitrifying bacteria in the activated sludge samples suggested a denitrifying activity of the biomass during the operation, probably related to the formation of anoxic zones due to insufficient sludge recirculation in the settling tank. This finding, never before evidenced from laboratory-scale experiments, reinforces the need to study this three-stage process using a large pilot in real conditions. As a consequence, the separation of phases still has to be improved in order for TPPB to be considered as an efficient technique for the industrial treatment of hydrophobic VOCs. An efficient separation of the water/PDMS/sludge phases would benefit the sludge recirculation and limit the possible clogging of the packed column, and would especially reduce the consumption of PDMS. Without an efficient separation of phases, the process could not be competitive compared to thermal and catalytic oxidation processes for VOC treatment.

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