Non-thermal plasma assisting the biofiltration of volatile organic compounds

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ABSTRACT

Unsteady loading rates can affect the proper operation of a biofilter. In addition, biofiltration is known to be less effective when dealing with poorly soluble substances, like some volatile organic compounds (VOCs). A non-thermal plasma (NTP) produced with a dielectric barrier discharge (DBD) was studied as an option to pre-treat an air stream contaminated by a mixture of VOCs. Therefore, the plasma reactor was operated upstream of a laboratory-scale biofilter. Air admixed with toluene, n-heptane, p-xylene, ethylbenzene and benzene with average concentrations of 95.6, 49.4, 60.8, 47.3 and 36.6 ppm, respectively, was used as a model polluted gas, as these contaminants represent the air stripped by an oil-refinery wastewater treatment plant. Peaks of loading rates at the inlet of the biofilter were simulated by the increase of the flow rates of VOCs. The operation of NTP, with specific energy densities between 92 J L^{-1} and 256 J L^{-1} allowed reducing the VOC concentrations down to the level of optimal biofilter operation. In addition, non-water soluble VOCs were converted to more soluble compounds by the plasma treatment. In this first attempt to investigate the synergies between NTP and biofiltration, NTP reveals as a promising option to pre-treat effluents upstream of biofilters for optimized operation.

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1. Introduction

Volatile organic compounds (VOCs) are air pollutants that originates both from natural sources (*e.g.*, forest fires, deciduous trees) and from several types of anthropogenic activities, such as transportation, usage and production of solvents, oil refineries, chemical industry, agriculture, gas leakage from waste landfills and waste treatments (Derwent, 1995). A 56% decrease in VOC emissions have been observed in Europe between 1990 and 2010 (European Environmental Agency, 2012), due to improved air pollution control technologies and energy efficiency in the transportation sector, which were also driven by more restrictive emission standards. The contribution from other sectors remained substantially stable during this period. The joint contributions of

VOCs from industrial processes and the waste sector accounted for 8% of the total VOC emissions in 2010 (European Environmental Agency, 2012). Industrial sites are generally equipped with wastewater treatment plants (WWTPs) to recycle process water or wastewater and/or purify it before its release into the environment (Deshmukh et al., 2015). Industrial WWTPs are known sources of fugitive emissions of VOCs (Cunningham, 1995). Oil-refinery WWTPs, in particular, are important contributors of aromatics and, more specifically, benzene, toluene, ethylbenzene and xylene, also referred to as BTEX (Wei et al., 2014). Due to their volatilization, VOCs are released from wastewater and are dispersed within the atmosphere (Fatone et al., 2011). Here VOCs produce adverse effects to the environment, since they are promoters of tropospheric ozone (O_3) and contribute to the formation of radicals and aerosols (Schiavon et al., 2016). At a local scale, VOCs can have adverse effects on humans by inhalation, both in terms of nuisance (due to their odor impact) and, especially, in terms of risks for health (Peishi et al., 2004; Civan et al., 2015; Ni et al., 2015). Indeed, some VOCs are carcinogens for humans. Thus, long-term exposure to VOCs in ambient air may induce the risk of cancer both in

Nomenclature

NTP	non-thermal plasma
DBD	dielectric barrier discharge
RH	relative humidity [%]
ΔP	pressure drop [mmH$_2$O]
EBRT	empty bed residence time [s]
SL	surface loading rate [m^3 m^{-2} h^{-1}]
ML	mass loading rate [g m^{-3} h^{-1}]
RE	removal efficiency [%]
EC	elimination capacity [g m^{-3} h^{-1}]
SED	specific energy density [J L^{-1}]
EY	energy yield [g (kWh)$^{-1}$]
P	discharge power [W]
C_{in}	inlet concentration [ppm]
M	molar mass [g mol^{-1}]
V_m	molar volume [L mol^{-1}]
EC_{max}	maximum EC [g m^{-3} h^{-1}]
EY_{max}	maximum EY [g (kWh)$^{-1}$]
RE_{NTP}	RE of the NTP unit [%]
$RE_{NTP,max}$	maximum RE_{NTP} [%]

workers and in the populations settled in the vicinity of VOC emission sources.

To reduce VOC releases from industrial WWTPs, the air of the different compartments is aspirated and treated before being released to the atmosphere. The traditional technologies for the removal of VOCs from air streams are based on physical-chemical methods, such as activated carbon adsorption, thermal or catalytic incineration and chemical scrubbing (Tan, 2014; Schnelle et al., 2016). However, such methods revealed to be unsuitable for the treatment of large air flows at relatively low concentration of contaminants (<100 ppm), due to their impacts in terms of material and chemicals required, energy consumption, generation of waste products and related costs (Fridman, 2008). The current solution to this issue is represented by biological technologies for air pollution control. During the last decades, VOC removal and odor control at the outlet of mechanical-biological treatments of waste or wastewater treatments have been successfully achieved through biofiltration (Cabrera et al., 2011). In the so-called biofilters, the air flows through a filtering bed. The pollutant molecules transfer into a thin biofilm that develops on the surface of the packing material. Microorganisms, such as bacteria and fungi, are immobilized in the biofilm. They capture and biologically degrade the pollutant molecules. Biofilters still represent the most convenient method to treat the stripped air from WWTPs (Dorado et al., 2015). However, biological technologies are susceptible to unsteady conditions of flow rate and pollutant concentration (Elías et al., 2010), negatively influencing the adaptation time of the microorganisms (Ragazzi et al., 2014). Peaks of concentrations may also cause shock to the microorganisms responsible of biodegradation and this can affect the proper operation of the biofilter. In addition, the biodegradation of hydrophobic compounds is problematic, because of the limited diffusion of pollutants from the gaseous phase to the biofilm.

Activated carbon adsorption has been traditionally adopted as an equalization system to ensure constant mass loading rate to biofilters. However, adsorption requires periodical replacement or regeneration of the activated carbon. Therefore, a double activated carbon bed should be used to ensure loading rate equalization during maintenance period of one bed, and this implies larger space availability. In addition, adsorption cannot help

biodegradation, since the contaminants are not converted into more soluble compounds. Flow equalization may also be achieved with absorption columns. However, a waste flow is formed, with additional costs for disposal.

A possible solution to these typical drawbacks of biological technologies for air pollution control consists in pre-treating the gaseous effluent with a dual purpose: removing part of the inlet mass load (in the case of peaks of concentrations and/or airflow rate) and increasing the solubility of the mixture of incoming pollutants. A technology based on the generation of non-thermal plasma (NTP) may help to achieve both these targets, as demonstrated in recent laboratory experiments: Brandenburg et al. (2014) achieved satisfying results in the removal of hydrocarbons from air and in the formation of water-soluble byproducts like formic acid after application of NTPs; Schiavon et al. (2015), converted three VOCs in air to carbon monoxide (CO), carbon dioxide (CO$_2$) and minor organic byproducts that were more water-soluble than the VOCs in the starting mixture.

In a recent work (Stasiulaitiene et al., 2016), through a comparative life-cycle assessment, the authors concluded that NTP merits gaining consideration against traditional methods for air pollution control, especially for its considerable lower impacts on health and environment. NTP for air pollution control and, especially, VOC and odor removal has been the object of laboratory-scale studies as well as in industrial installations. Several studies were carried out on the application of NTP to remove single VOCs from air: Ye et al. (2008) adopted a dielectric barrier discharge (DBD) to remove benzene from air, both a laboratory scale and at pilot scale; Schiorlin et al. (2009) applied different kinds of corona discharges to abate toluene in air, providing possible mechanisms of oxidation; Ragazzi et al. (2014) removed methyl ethyl ketone from dry synthetic air by applying a DBD in a closed hydraulic circuit; Schmidt et al. (2015) adopted a DBD reactor to remove toluene both from dry and wet synthetic air.

Less frequently, studies on VOC removal with NTPs were carried out on mixtures of compounds: Kim et al. (2007) applied a plasma-driven catalysis (PDC) system, both as a flow-type reactor and as a closed circuit, to remove a mixture of benzene and toluene from air; Subrahmanyam et al. (2007) worked on a PDC system based on a DBD to remove toluene, isopropanol and trichloroethylene from air by testing different catalysts; Schiavon et al. (2015) applied a DBD to remove two mixtures of VOCs: ethanol and ethyl acetate, in a first experiment, and toluene, benzene and *n*-octane in another experiment.

Only recently, fewer studies have investigated the combination of NTPs with biological technologies for air pollution control. Wei et al. (2013) applied a biotrickling filter to remove the residual dimethyl sulfide and the byproducts formed after applying a NTP to a mixture of dimethyl sulfide and compressed air; Hołub et al. (2014) applied a NTP to ambient air, in order to generate O$_3$, which was only used to treat part of the flow coming from the stripping air of a WWTP and, in an alternative configuration, the effluent from a biofilter.

An investigation of the effects of an NTP pre-treatment on the biodegradation of VOCs is still lacking. This paper focuses on a laboratory-scale study that aims at investigating possible synergistic effects of NTP treatment and biofiltration in removing or converting a mixture of VOCs from air. Therefore, a mixture of five VOCs was chosen to represent the stripping air of an industrial WWTP. After completion of the startup phase of a laboratory-scale biofilter, a DBD reactor was installed prior to the biofilter. It was studied whether the NTP treatment is able to manage peaks of the inlet mass loading of pollutants, which often occur in real cases.

2. Material and methods

2.1. Selection of the VOC mixture

Five VOCs in total were chosen with the intention to represent a typical effluent stripped from the wastewater of a petrochemical industry rather than to study the specifics of plasma chemistry. Toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene were the most abundant VOCs measured in the emissions from an existing industrial wastewater treatment plant located in Sicily (Italy). In addition to the previously mentioned impacts of VOCs released into the atmosphere, benzene and ethylbenzene are particularly important also from a toxicological point of view, since they are carcinogenic compounds. The International Agency for Research on Cancer (IARC) classifies benzene as a demonstrated carcinogen for humans (Group 1) and ethylbenzene as a possible carcinogen to humans (Group 2B) (IARC, 2016). Thus, assuring a proper operation of a biofilter subject to unsteady flow conditions reveals essential to limit human exposure by inhalation and the consequent cancer risk in the population settled in the vicinity of an industrial wastewater treatment plant.

All the substances were purchased as liquids from Sigma Aldrich Co. (USA). Toluene and benzene have a purity ≥99.9%, while the purity of the other three compounds is ≥ 99.0%.

2.2. Experimental setup

The experimental setup consists in four main parts:

- five bubblers for the generation of vapor-phase VOCs and one bubbler containing demineralized water for defined humidification of the air flow;
- the NTP unit, energized with a programmable AC source (61604, Chroma, USA) and a high-voltage transformer. The electrical operational parameters were recorded using a digital oscilloscope (DPO4104, Tektronix, USA) connected to a high-voltage probe (P6015A, Tektronix, USA) and a 100 nF capacitor for voltage and charge measurements;
- the biofilter, manufactured by AirClean Srl (Italy);
- the analytical setup, composed of a Fourier-Transform-Infrared (FTIR) spectrometer (Antaris IGS Analyzer, Thermo Scientific, USA), a gas-chromatograph (GC) (7890B, Agilent Technologies, USA) coupled with a single quadrupole mass spectrometer detector (MS) (5977A MSD, Agilent Technologies, USA) and a Micro-GC (3000 Micro GC, Inficon, Germany).

A scheme of the experimental setup is presented in Fig. 1.

The five bubblers containing VOCs were fed with nitrogen (N_2) and each flow rate was adjusted till obtaining the desired inlet concentrations of VOCs. Two flows of compressed air were used to generate the main air flow: the first one was mixed with the five N_2 flows containing VOCs and its airflow rate was kept at 62–71 L h^{-1}; the second flow was made passing through the bubbler containing demineralized water and its flow rate was kept at 79–88 L h^{-1}; the two flows were adjusted in order to generate a total air flow rate of 150 L h^{-1} with a relative humidity (RH) of about 50%. Each single air flow was adjusted day by day, due to the outdoor temperature variation, slightly influencing the temperature of the incoming compressed air. The choice of working with a humid flow rate is motivated by the conditions in real applications. Dry flow conditions are unlikely to occur when stripping air from wastewater. On the other hand, working with RH > 50% would not allow correctly quantifying the discharge power of the NTP unit. The relative humidity and the temperature of the inlet airflow were measured by means of a portable thermo-hygrometer (HP-22A, Rotronic,

Switzerland). The pressure drop (ΔP) between the inlet and the outlet of the biofilter was kept under observation by two digital manometers (454 Data logger, Testo, Germany).

2.3. The biofilter

The laboratory-scale biofilter consists of a cylinder made of transparent polyvinyl chloride (PVC), with internal diameter of 0.08 m and height of 0.80 m. The biofilter was filled with a specialized patented peat (Mónafil®, Bord Na Móna PLC, Ireland), till reaching a total filling height of 0.50 m. The incoming air flow enters the biofilter from the bottom, passes through the bed material and leaves the biofilter at the top outlet. The filling material is supported by a grid, placed at 0.10 m from the bottom of the biofilter, favoring the contact between air and peat. The concepts of empty bed residence time (EBRT, *i.e.*, the empty bed biofilter volume divided by the airflow rate), surface loading rate (SL, *i.e.*, the airflow rate normalized to the area of the transversal section of the bed) and mass loading rate (ML, *i.e.*, the mass flow rate per unit volume of the biofilter bed) turns useful to contextualize the experiments and facilitate future comparisons with other studies on laboratory-scale biofilters. At the flow rate investigated in this study (150 L h^{-1}), EBRT and SL are 60 s and 29.8 m^3 m^{-2} h^{-1}, respectively. The performance of a biofilter is usually evaluated by means of the concepts of removal efficiency (RE) and elimination capacity (EC, *i.e.*, difference between incoming and outgoing mass flows).

Before inserting the filling material into the biofilter, the peat was mixed with a small amount of lyophilized microbial inoculum (Air Clean Srl, Italy). The inoculum consists of a mixture of aerobic bacteria, cultivated after extraction from the filling material of a former biofilter degrading VOCs and odorants.

2.4. The DBD

The NTP unit is composed of a single-stack DBD reactor (Müller and Zahn, 2007). The high-voltage and the ground electrodes are both made of a stainless-steel mesh, while the dielectric consists of a layer of mica with a thickness of 0.5 mm. The reactor is enclosed in a volume of 250 mL, providing a residence time of 6 s at the flow rate investigated in this study. Along with RE, the concepts of specific energy density (SED) and energy yield (EY) are used to assess the performance of NTP in removing air pollutants. SED and EY are defined as follows:

$$SED = \frac{P}{Q} \tag{1}$$

$$EY = \frac{C_{in} \cdot RE \cdot M}{SED \cdot V_m} \tag{2}$$

where P is the discharge power (W), calculated through integration of the area of the voltage-charge plots measured by electrical measurements and computed by the oscilloscope. Q is the airflow rate (L h^{-1}), C_{in} is the inlet concentration (ppm), M is the molar mass of the compound (g mol^{-1}), V_m is the molar volume, which at standard conditions (293 K and 101,325 Pa) is 24.04 L mol^{-1}. SED and EY are expressed as J L^{-1} and g (kWh)$^{-1}$, respectively.

2.5. Analytical setup

The experimental setup was built in order to allow a complete characterization of the VOC/air mixture prior to the NTP unit (sampling point A), between the NTP unit and the biofilter (sampling point B) and downstream of the biofilter (sampling point C)
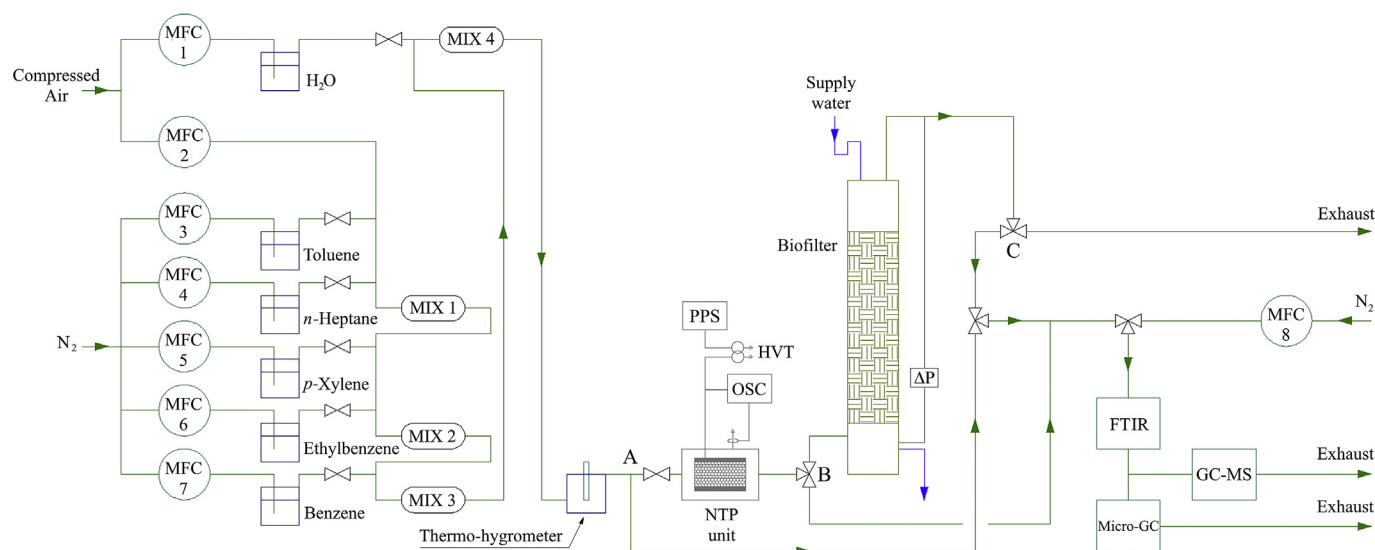
Figure 1. Configuration of the experimental setup (MFC: mass flow controller; MIX: mixing chamber; OSC: oscilloscope; HVT: high-voltage transformer; PPS: programmable power source).

(Fig. 1). Through proper regulation of the valves composing the system, the flow of interest passes through the FTIR first, subsequently flows to the GC-MS and the Micro-GC, and is finally sent out to an exhaust aspiration system. The FTIR was used to quantify CO, CO_2 and the O_3 generated by the DBD; the Micro-GC was used to quantify each of the five VOCs; the byproducts of the DBD treatment were identified with the GC-MS. The Micro-GC was calibrated with cylinder gases containing dry synthetic air (20% O_2 and 80% N_2) and the five components of the VOC mixture under investigation, at reference concentrations. The mixture was purchased from Air Liquide (France). The FTIR, previously calibrated for CO and CO_2, was also calibrated for O_3, through an ozonizer and subsequent comparison between the areas of the O_3 peaks measured on the FTIR and the O_3 concentrations measured by an O_3 monitor (Ozomat MP, Anseros, Germany). The pH of the filling material and of the water collected at the bottom of the biofilter was measured by means of the Litmus test. Microbiological analyses were also carried out on samples of filling material, in order to assess the vitality and the type of the microorganisms involved in VOC biodegradation.

2.6. Biofilter startup

To allow for a proper growth of the bacteria initially present in the inoculum, biofilters require a startup phase of several weeks. During this phase, ML is gradually increased till reaching stable removal performance. In this study, the initial VOC concentrations were increased at the design air flow rate (150 L h^{-1}). The biofilter was initially fed with only toluene, starting from a concentration of about 30 ppm. The biofilter was daily monitored and, every time the biofilter reached a RE > 90%, the initial concentration was subsequently increased till reaching a target concentration. Afterwards, a new compound was added to the mixture and the same procedure was followed with the remaining VOCs. During the startup phase, the air temperature remained comprised between 24.0 and 25.6 °C.

At the end of the startup phase, the average concentrations of the single VOCs at the inlet of the biofilter resulted as 95.6 ppm of toluene, 49.4 ppm of *n*-heptane, 60.8 ppm of *p*-xylene, 47.3 ppm of ethylbenzene and 36.6 ppm of benzene.

A proper humidification of the filtering medium was assured by

the partially humidified air flow and by regular addition of 100 mL of water every 72 h. After completion of the startup phase, this interval was increased to 96 h. Except from water, no nutrient solution was added to the biofilter during the whole period.

2.7. Experimental procedure

After the completion of the startup phase, the airflow rate was kept constant at 150 L h^{-1} and the inlet VOC concentrations were kept as close as possible to the reference average concentrations reported above.

To test the application of NTP on emission peaks of VOCs and, meanwhile, not to stress the microorganisms in the biofilter, the following test procedure was implemented. The rates of the N_2 gas flows feeding the bubblers were increased by 25%; the VOC concentrations in the air flow consequently increased; the NTP was switched on and the energy provided to the discharge was gradually increased to the energy necessary to obtain again the initial total concentration of the five starting VOCs (about 290 ppm) at the inlet of the biofilter. This way, the DBD can be studied as a pretreatment module to reduce peaks of concentrations and to level the concentrations in the flow exiting the DBD to the values the biofilter was acclimated at. Keeping the concentrations constant at the inlet of the biofilter would preserve microorganisms from shock, would allow a proper operation of the biofilter and would not negatively affect its RE. Meanwhile, the efficiency and the energy consumption of the DBD can be tested.

After carrying out these tests, the same procedure was repeated with increasing the rates of the N_2 flows feeding the bubblers containing VOCs by 50% and 100%. All the errors were determined by the error propagation formula, considering the instrumental and calibration errors.

3. Results and discussion

3.1. Biofilter startup

Four days after the startup of the biofilter, the RE of toluene became close to 90%, so that its concentration at the inlet of the biofilter was increased to about 70 ppm. After 9 d of operation, the biofilter was capable to degrade toluene at its target concentration

(95.6 ppm) with a 99% RE. Afterwards, *n*-heptane was inserted into the mixture at an initial concentration of 25 ppm. 25 d later, a 99% RE was obtained and, then, its inlet concentration was increased to the reference average value (49.4 ppm). *p*-Xylene, ethylbenzene and benzene were added to the system one by one, after that REs >99% had been reached with regards to every new VOC introduced. The acclimation period of the microorganisms to these three VOCs was particularly short: indeed, after a total time of 30 d of operation, the biofilter became fully operative and the RE was >99% for all the VOCs in the mixture, with the only exception of *n*-heptane. The inlet VOC concentrations and their RE values during the startup phase of the biofilter are reported in Fig. 2. Microbiological analyses on samples of peat revealed that the microorganisms present in the filling material belonged to the *Pseudomonas* and *Bacillus* strains. The cell count at the end of the startup phase resulted in 3.95×10^5 CFU g^{-1} of dry material. During the whole period of operation of the biofilter, the maximal ΔP between B and C resulted in 40 mmH$_2$O.

3.2. Application of NTP

After increasing the N$_2$ flow rates of every VOC line by 25%, 50%

and 100%, the inlet VOC concentrations changed to the values reported in Table 1. The SED provided to the DBD reactor was gradually increased from 46 J L^{-1} to 128 J L^{-1}, from 49 J L^{-1} to 165 J L^{-1} and from 92 J L^{-1} to 256 J L^{-1}, in the case of a 25%, 50% and 100% increase of N$_2$ flow rates, respectively. With every increase in the power provided to the DBD, the VOC concentrations were continuously monitored both at the sampling point B and at the sampling point C, in order to assess both the performance of the only NTP treatment and of the NTP-biofilter combined system. The VOC concentrations at the outlet of the NTP unit (B), at the different SED values investigated, are reported in Fig. 3. Hereinafter, for an easier view of the graphs, the errors associated with the SED (estimated as equal to 10% of the value) are not shown.

As expected, the VOC concentrations decrease with the increase of SED due to the conversion of the initial compounds by plasma chemical reactions. However, a threshold SED of 70–125 J L^{-1} can be observed before a significant removal can be obtained. This can be explained by the presence of humidity in the airflow, *i.e.*, a part of the energy provided to the DBD is dissipated through excitation of the vibrational levels and polarization of water molecules instead of formation of reactive species for VOC conversion.

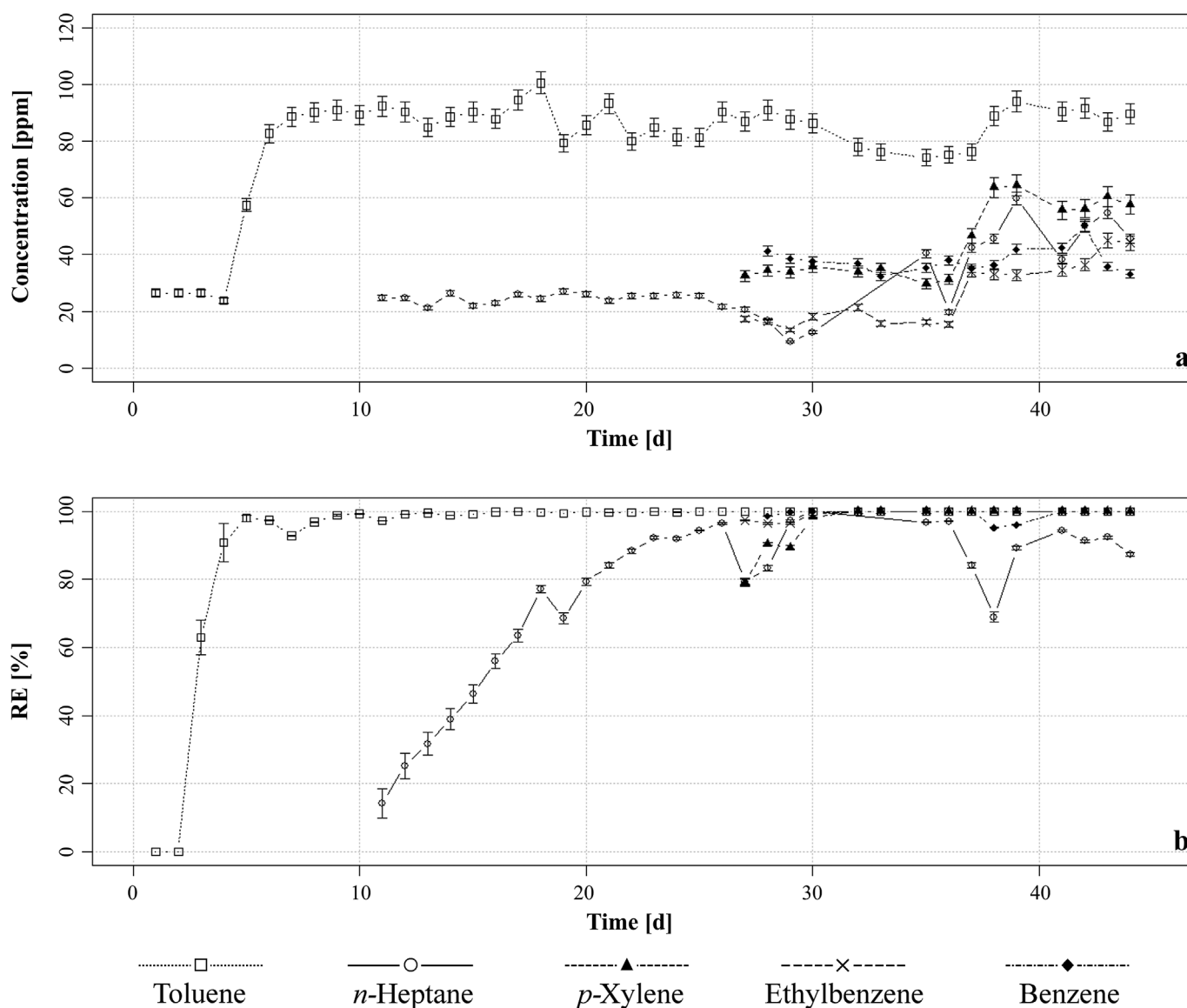The VOC showing the smallest degradation of all VOCs is

Figure 2. Trends *a*) of the VOC concentrations at the inlet of the biofilter and *b*) of the respective RE values during the startup phase of the biofilter.

Table 1
VOC concentrations (expressed as ppm) measured at the sampling point A, before and after each increase in the VOC flow rates.

		Toluene	*n*-Heptane	*p*-Xylene	Ethylbenzene	Benzene
25% increase	Before	101.0 ± 3.9	52.5 ± 1.9	68.3 ± 3.9	47.9 ± 2.7	39.4 ± 1.7
	After	125.7 ± 4.8	63.9 ± 2.3	85.1 ± 4.9	62.1 ± 3.6	47.3 ± 2.0
50% increase	Before	94.4 ± 3.6	48.3 ± 1.8	58.7 ± 3.4	46.1 ± 2.6	36.9 ± 1.6
	After	140.3 ± 5.4	71.0 ± 2.6	88.1 ± 5.0	73.4 ± 4.2	53.3 ± 2.3
100% increase	Before	91.3 ± 3.5	47.5 ± 1.7	55.4 ± 3.2	47.9 ± 2.7	33.6 ± 1.5
	After	182.3 ± 7.0	98.3 ± 3.6	126.5 ± 7.2	96.5 ± 5.5	70.3 ± 3.0

benzene, which seems to be even reformed at a SED comprised between 95 J L^{-1} (in the case of a 25% increase of the N$_2$ flow rates feeding the bubblers containing the initial VOCs) and 125 J L^{-1} (in the case of a 100% increase). This is consistent with the results of a former experiment (Schiavon et al., 2015) on toluene, benzene and *n*-octane, in which the reformation of benzene was ascribed to toluene degradation operated by NTP. The formation of benzene was also reported by Huang et al. (2011) after treatment of gaseous toluene in humid air with a PDC system. At the maximal SED values investigated, the concentrations of every VOC at the inlet of the biofilter (B) are close to the inlet concentrations achieved at the end of the startup phase, thus before any tests with plasma.

Trace concentrations of benzaldehyde, acetophenone, styrene and formic acid were detected in the effluent from the DBD reactor, as the main organic byproducts of the NTP degradation of the VOCs initially present in the mixture. At increasing SED, the formation of such byproducts is more and more reduced. All the byproducts formed are more water-soluble than the initial VOCs. These results are in line with a previous study, in which a mixture of benzene, toluene and *n*-octane was converted to CO$_2$, CO and to more water-soluble trace VOCs like benzaldehyde, phenol, benzyl alcohol, benzyloxy-benzene, cresols and isomers of octanedione (Schiavon et al., 2015). In addition, at the outlet of the NTP unit, the carcinogenic potential of the mixture is reduced, since it is related only to residual benzene and ethylbenzene, and to traces of styrene (generated by the application of NTP), classified in the Group 2B by the IARC (IARC, 2016) and not classified as a carcinogen by the United States Environmental Protection Agency (USEPA, 2016). The remaining organic byproducts (benzaldehyde, acetophenone and formic acid) are not carcinogenic to humans. USEPA provides a "no observed adverse effect level" (NOAEL) of 10,000 ppm for acetophenone and only an oral reference dose value for benzaldehyde (USEPA, 2017). No NOAEL or reference concentration value is available for formic acid. NTP generated a maximal O$_3$ concentration of 250 ppm, which is considered tolerable by microbial populations, as reported by Wang et al. (2013), who injected O$_3$ in a membrane bioreactor at a concentration of about 280 ppm with no observed adverse effects on the microbial populations. The maximal CO$_2$ concentrations generated by NTP were achieved at the maximal SED applied, and varied between 333 and 840 ppm in the case of a 25% and a 100% increase in the VOC flow rates, respectively. The DBD also generated maximal CO concentrations of 227 and 504 ppm, after increasing the VOC flow rates by 25% and 100%, respectively.
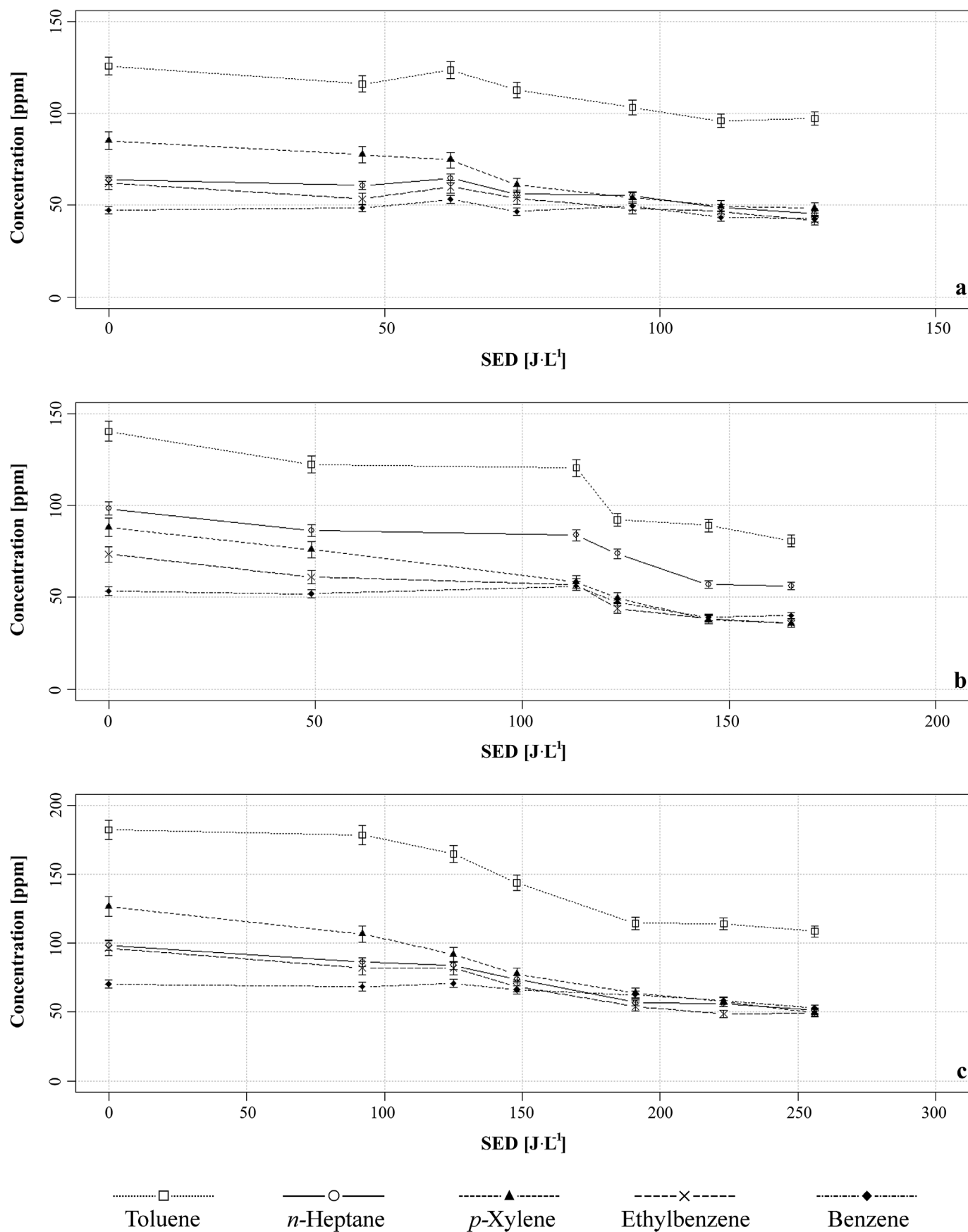
The overall RE values of the five initial VOCs after the combined NTP-biofilter treatments (sampling point C) at increased VOC concentrations are presented in Fig. 4 as a function of the SED. At the maximal SED values (128, 165 and 256 J L^{-1}, in the case of a 25%, 50% and 100% increase in the N$_2$ flow rates, respectively), the RE values of the initial VOCs were >93%, with the only exception of *n*-heptane, whose maximal RE varied in the range 81–91%, the lowest value being referred to the case with a 100% increase in the VOC flow rates. Such value is in good agreement with the RE of *n*-

heptane obtained only with the biofilter and before increasing the initial VOC concentrations. To confirm that the biofilter alone would have not been able to ensure satisfying RE values after increasing the ML of the five VOCs, the RE of the biofilter was investigated after switching off the DBD (*i.e.*, SED = 0 J L^{-1}), at the end of the test with N$_2$ flow rates increased by 100%, before lowering the VOC concentrations to the initial values. Under these conditions, the RE values of toluene, *n*-heptane, *p*-xylene, ethylbenzene and benzene were significantly reduced, namely at 60%, 23%, 87%, 76% and 28%, respectively.

The CO concentration at the outlet of the biofilter was up to 10% lower than its concentration after the NTP unit. This suggests that part of CO, toxic to several bacterial strains, may have been metabolized by the microorganisms, with possible poisoning. The cell count at the end of all the tests with NTP resulted in 2.95×10^5 CFU g^{-1} of dry material, *i.e.*, 25% lower than the value measured at the end of the startup phase of the biofilter. At the present state, CO production represents an important drawback of the application of NTPs as a pre-treatment of biofiltration. Such limitation requires further research in view of upscaling this technology to pilot and real scales. As a solution to this possible criticality, CO could be treated in a first biofilter stage inoculated with CO-degrading populations under aerobic conditions, *e.g.*, the *Pseudomonas carboxydovorans* (Meyer and Schlegel, 1978). However, such decrease in the cell count might also be attributed to two additional causes: the temporary unavoidable stress to bacteria during the transient phase between the concentration increases and the adjustment of the NTP unit to reach optimal removal conditions; the absence of micronutrients supplied to the microorganisms.

The maximal EC (EC$_{max}$) of the five initial VOCs during each of the three tests are reported in Table 2 together with the respective SED and ML values. Since the tests were carried out by gradually increasing the SED with the aim of achieving satisfying overall RE, EC$_{max}$ increases with increasing the ML. In the case of toluene and benzene, after a 25% and 50% increase in the N$_2$ flow rates, EC$_{max}$ was achieved with the biofilter alone, which assured almost complete removal of these compounds. The highest EC$_{max}$ values were achieved by toluene (24.40, 37.75 and 49.02 g m^{-3} h^{-1} after increasing the N$_2$ flow rates by 25%, 50% and 100%, respectively), which is the most concentrated VOC in the mixture. The lowest EC$_{max}$ values were achieved by benzene (9.05, 10.37 and 13.72 g m^{-3} h^{-1} after increasing the N$_2$ flow rates by 25%, 50% and 100%, respectively), which is the least concentrated VOC. Although the ML values of the remaining VOCs are similar, EC$_{max}$ increases when moving from *n*-heptane to ethylbenzene and, finally, to *p*-xylene.

Table 3 presents the maximal EY (EY$_{max}$) obtained for each VOC after the NTP treatment, the respective SED, the corresponding overall RE of the NTP-biofilter combined treatment, the respective RE of the NTP treatment alone (RE$_{NTP}$) and the maximal RE of the NTP treatment alone (RE$_{NTP,max}$) achieved within the range of SED investigated in each test with increased initial concentrations. From

Figure 3. VOC concentrations measured at point B as a function of the SED during the tests with a *a*) 25%, *b*) 50% and *c*) 100% increase in the N$_2$ flow rates feeding the bubblers containing the VOCs.
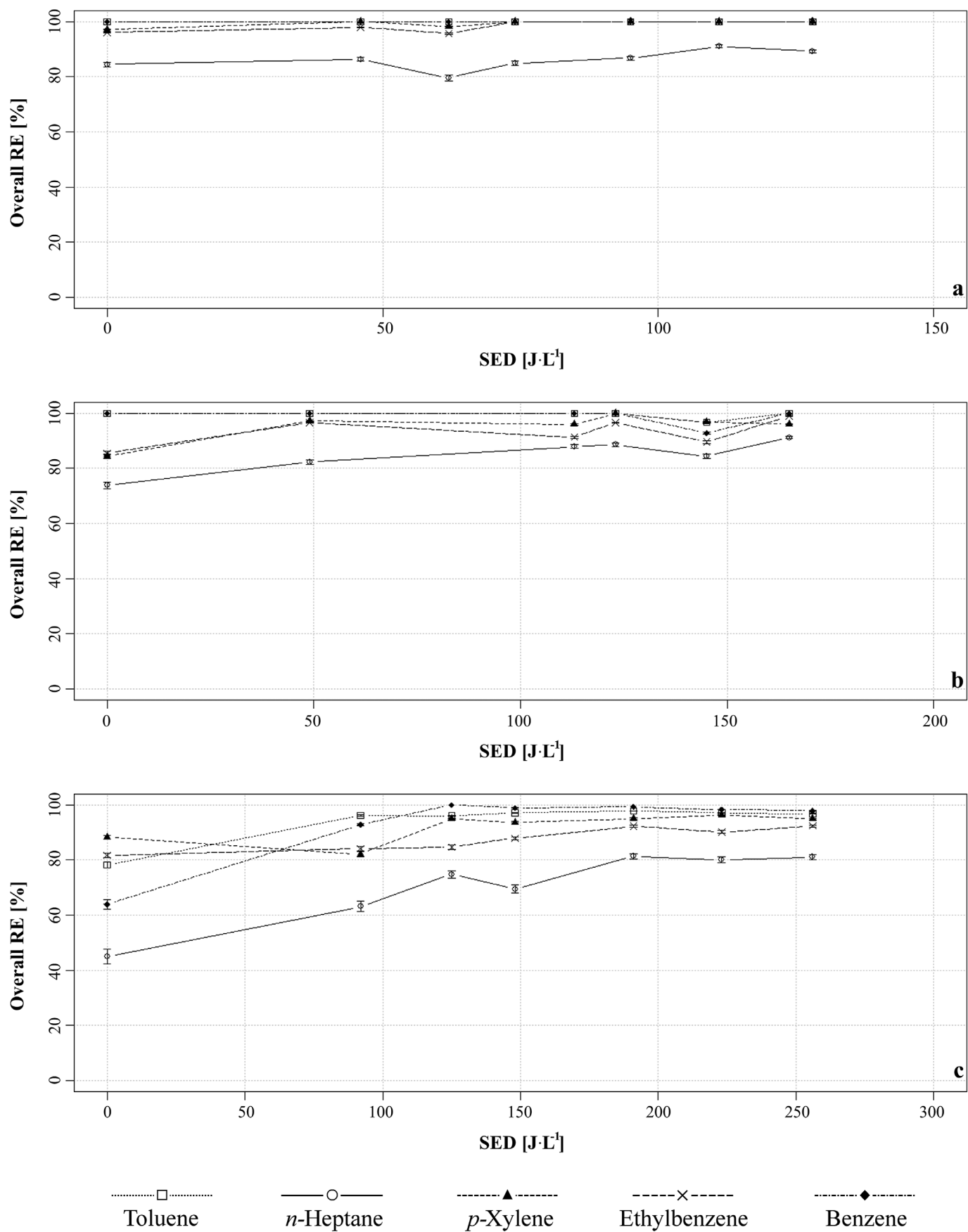
Figure 4. Overall RE values of the five reference VOCs after the combined NTP-biofilter treatment with a *a*) 25%, *b*) 50% and *c*) 100% increase in the initial VOC concentrations.

Table 2
EC_{max} of the biofilter and respective ML and SED values of the five reference VOCs achieved during the three tests with a 25%, 50% and 100% increase in the VOC flow rates (ML and EC_{max} are expressed as g m^{-3} h^{-1}, SED is expressed as J L^{-1}).

		25% increase	50% increase	100% increase
Toluene	EC_{max}	28.40 ± 1.09	31.69 ± 1.22	40.27 ± 1.55
	ML	28.40 ± 1.09	31.69 ± 1.22	41.18 ± 1.58
	SED	0 ± 0	0 ± 0	191 ± 10
n-Heptane	EC_{max}	14.30 ± 0.54	15.90 ± 0.59	16.95 ± 0.74
	ML	15.70 ± 0.58	17.43 ± 0.64	24.15 ± 0.89
	SED	111 ± 6	165 ± 8	191 ± 10
p-Xylene	EC_{max}	22.16 ± 1.27	22.93 ± 1.31	31.69 ± 1.82
	ML	22.16 ± 1.27	22.93 ± 1.31	32.91 ± 1.88
	SED	46 ± 2	123 ± 8	223 ± 11
Ethylbenzene	EC_{max}	16.16 ± 0.92	18.89 ± 1.08	23.21 ± 1.34
	ML	16.16 ± 0.92	19.09 ± 1.09	25.12 ± 1.44
	SED	74 ± 4	165 ± 8	191 ± 10
Benzene	EC_{max}	9.05 ± 0.39	10.20 ± 0.44	13.46 ± 0.58
	ML	9.05 ± 0.39	10.20 ± 0.44	13.46 ± 0.58
	SED	0 ± 0	0 ± 0	125 ± 6

Table 3
EY_{max} and respective SED, overall RE, RE_{NTP} and $RE_{NTP,max}$ of the five reference VOCs obtained during the three tests with increased initial concentrations (EY_{max} is expressed as g kWh^{-1}, SED in J L^{-1} and RE values as a percentage).

		25% increase	50% increase	100% increase
Toluene	EY_{max}	3.63 ± 0.87	5.29 ± 0.92	4.82 ± 0.78
	SED	111 ± 6	123 ± 6	191 ± 10
	overall RE	100.0 ± 0.0	100.0 ± 0.0	97.8 ± 0.1
	RE_{NTP}	23.7 ± 3.8	34.3 ± 3.3	37.3 ± 3.1
	$RE_{NTP,max}$	23.7 ± 3.8	42.4 ± 2.9	40.5 ± 3.0
n-Heptane	EY_{max}	2.13 ± 0.43	3.17 ± 0.44	3.20 ± 0.47
	SED	128 ± 6	145 ± 7	191 ± 10
	overall RE	89.2 ± 0.5	84.4 ± 0.8	81.4 ± 0.9
	RE_{NTP}	28.9 ± 3.6	44.0 ± 2.8	42.2 ± 2.9
	$RE_{NTP,max}$	28.9 ± 3.6	45.5 ± 2.7	48.0 ± 2.6
p-Xylene	EY_{max}	5.09 ± 1.14	5.39 ± 0.73	5.15 ± 1.09
	SED	74 ± 4	145 ± 7	148 ± 7
	overall RE	100.0 ± 0.0	96.7 ± 0.2	93.7 ± 0.5
	RE_{NTP}	28.4 ± 3.6	57.0 ± 2.2	38.6 ± 4.4
	$RE_{NTP,max}$	43.1 ± 2.8	59.4 ± 2.0	60.7 ± 2.8
Ethylbenzene	EY_{max}	2.95 ± 1.19	3.95 ± 1.36	3.49 ± 0.56
	SED	46 ± 2	49 ± 2	191 ± 10
	overall RE	97.9 ± 0.1	96.6 ± 0.2	92.3 ± 0.4
	RE_{NTP}	14.0 ± 4.3	16.9 ± 4.2	44.1 ± 2.8
	$RE_{NTP,max}$	32.9 ± 3.4	51.5 ± 2.4	49.5 ± 2.5
Benzene	EY_{max}	0.41 ± 0.26	1.12 ± 0.25	0.78 ± 0.18
	SED	111 ± 6	145 ± 7	256 ± 13
	overall RE	100.0 ± 0.0	92.8 ± 0.4	97.9 ± 0.1
	RE_{NTP}	8.2 ± 4.6	26.6 ± 3.7	24.6 ± 3.8
	$RE_{NTP,max}$	9.6 ± 4.5	26.6 ± 3.7	24.6 ± 3.8

the point of view of energy consumption, the most difficult compound to be degraded by NTP is benzene, whose degradation requires more energy than the other VOCs in the mixture. In analogy with EC_{max} (Table 2), benzene is followed by *n*-heptane, ethylbenzene, *p*-xylene and toluene, which gradually allow for higher EY.

In general, the more the initial compounds are concentrated (*e.g.*, after a 100% increase in the N_2 flow rates), the higher EY_{max} is. In fact, at higher initial concentrations, the probability of reaction between O_3 and radicals with the initial compounds increases. Two exceptions are only for toluene and benzene, whose EY_{max} after a 50% increase of the N_2 flow rates is 5.29 and 1.12 g kWh^{-1}, respectively, while the respective EY_{max} reduces to 4.82 and 0.78 g kWh^{-1} after a 100% increases of the N_2 flow rates. The overall RE corresponding to EY_{max} is always >92%, with the exception of *n*-heptane, whose overall RE is equal to 89%, 84% and 81% when increasing the VOC flow rates by 25%, 50% and 100%, respectively.

NTP upscaling may be achieved by placing multiple stack reactors in parallel one to another. Number and size of the stack reactors and their distance would depend on the characteristics of the effluent (airflow rate and VOC concentration). It is expected that the results of a full-scale application will be similar to those obtained at laboratory-scale, especially concerning byproduct formation, if the inlet VOC mixture was the same. Energy consumption will be higher, but the use of NTP would be limited to the abatement of peaks of concentrations that would destabilize the biomass in a biofilter. Furthermore, NTPs would be a more flexible solution compared to traditional buffer systems, since plasma can be activated and deactivated at every moment, with a consequent energy and material saving.

4. Conclusions

This study presented a first investigation on the synergistic effects between NTP and biofiltration for VOC removal. As a result of the tests carried out, NTP reveals as a promising technology to pre-

treat a VOC-containing effluent during increases in the ML that compromise the proper operation of a biofilter. Satisfying overall RE values were obtained with relatively low energy consumption, since the maximal SED used was 256 J L^{-1}. Although performance parameters like EC$_{max}$ and EY$_{max}$ are partially influenced by the initial VOC concentrations, a ranking of the VOCs most difficult to be abated by NTP and by the combined NTP-biofilter system can be anyway drawn up. Benzene resulted as the most energy-demanding and, in general, less degradable VOC, followed by n-heptane, ethylbenzene, p-xylene and toluene. NTP helps to keep the concentrations constant at the inlet of the biofilter (in spite of the increases in the concentrations induced on purpose), which can be done on demand as the NTP needs no acclimation and is directly controlled by its electrical operation parameters such as high voltage amplitude and frequency. Furthermore, it demonstrates to be capable of generating byproducts that are more soluble in water than the initial VOCs and this could further help the biodegradation. Finally, the byproducts formed during these tests are less toxic than the initial VOCs. However, a 25% decrease in the microbial cell number was observed during the tests, probably because of poisoning effects of the CO generated by the DBD, as well as absence of nutrients for microorganisms and the stress to the microbial populations provoked during the attempts to adjust the energy provided to the DBD till reaching satisfying RE. CO generation represents the main limitation of an NTP-biofiltration combined system at the present state.

In view of future applications, appropriate solutions including the primary removal of the CO generated by plasma, the supply of nutrients and the optimization of the adjustment of the NTP settings should be pursued. In addition, further steps should include an understanding of the mechanisms leading to the formation of the byproducts detected: the relatively high number of initial VOCs (motivated by the intention to get as close as possible to real-world conditions) complicates the identification of pathways of byproduct formation, which falls out of the topic of this study (centered on innovative technologies for air cleaning purposes) and would deserve a dedicated investigation in the field of plasma chemistry.

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