Journal of Cleaner Production 148 (2017) 498–508

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Non-thermal plasma assisting the biofiltration of volatile organic compounds

Marco Schiavon [a,*], Milko Schiorlin [b], Vincenzo Torretta [c], Ronny Brandenburg [b], Marco Ragazzi [a]

[a] Department of Civil, Environmental and Mechanical Engineering, University of Trento, Via Mesiano 77, I-38123 Trento, Italy
[b] Leibniz Institute for Plasma Science and Technology (INP Greifswald), Felix-Hausdorff-Str. 2, D-17489 Greifswald, Germany
[c] Department of Theoretical and Applied Sciences, University of Insubria, Via G.B. Vico 46, I-21100 Varese, Italy

ARTICLE INFO

Article history:
Received 28 September 2016
Received in revised form
25 January 2017
Accepted 2 February 2017
Available online 3 February 2017

Keywords:
Dielectric barrier discharge
Biofilter
Air pollution control
Industrial wastewater
Loading rate
BTEX

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.

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

* Corresponding author.
E-mail addresses: marco.schiavon@unitn.it (M. Schiavon), milko.schiorlin@inp-greifswald.de (M. Schiorlin), vincenzo.torretta@uninsubria.it (V. Torretta), brandenburg@inp-greifswald.de (R. Brandenburg), marco.ragazzi@unitn.it (M. Ragazzi).

http://dx.doi.org/10.1016/j.jclepro.2017.02.008
0959-6526/

Nomenclature

NTP	non-thermal plasma
DBD	dielectric barrier discharge
RH	relative humidity [%]
ΔP	pressure drop [mmH_2O]
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.