

Abatement of odour emissions by advanced oxidation

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Abstract

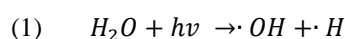
The growing expectations of the population in the urban areas with respect to air quality and the increasingly stringent regulations regarding air pollution have resulted in the need to minimize and conveniently treat the waste gas from different emission sources. The emissions from a large variety of plants, including waste and wastewater treatment plants, derive mainly from the degradation of organic matter. These emissions are composed of a complex of substances emitted at low concentrations from diffusive sources. These characteristics make complex their treatment on economically efficient conditions. The design and management of environmental engineering and industrial plants, therefore, require the implementation of focused processes for the control of the target compounds. The present study shows the applicability of an UV-Ozone lab-scale system for odours and VOCs removal. An artificial gaseous stream contaminated by toluene, at different incoming concentrations, was treated evaluating the abatement efficiencies in terms of odours and total VOCs as a function of power and contact time. The residue ozone concentrations was determined in order to optimize the set-up conditions. The results were discussed with the aim of evaluating the feasibility of the investigated solution for the advanced treatment of the waste gas from environmental facilities.

Keywords: VOCs, odours, AOPs, UV, Ozone

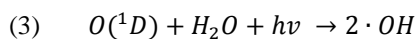
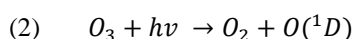
1. Introduction

The emission of Volatile Organic Compounds (VOCs) is of great concern in the management of a variety of facilities including wastewater treatment, composting, industrial and CAFO (Concentrated Animal Feeding Operations) plants, and landfill, due to their toxicity, odour pollution and contribution to photochemical oxidants (Navia and Muñoz, 2015; Wang *et al.*, 2013). Beside the effects on environment and human health, these emissions are related to odour annoyance among the population living surrounding the plants. The odour management is always more becoming a major issue for industrial operators (Belgiorno *et al.*, 2012). The urbanized areas have been expanding increasingly closer to industrial sites and, consequently, it results no longer effective to rely on buffer distances to avoid odour pollution (Hořub, 2014; Naddeo *et al.*, 2016a; Zarra *et al.*, 2008). Odours can substantially result in an environmental discomfort which may cause psychophysiological disorders, such as nausea,

headaches, insomnia, loss of appetite or respiratory problems, and to a general worsening of life quality (Lucernoni *et al.*, 2016; Naddeo *et al.*, 2016a; Zarra *et al.*, 2009). These aspects have led to the need of defining suitable tools to face the increasing number of administrative and legal complaints, merged in stricter regulations regarding emission and exposure levels (Estrada *et al.*, 2015; Naddeo *et al.*, 2013; Naddeo *et al.*, 2016b; Zarra *et al.*, 2012). The necessity to address compliance to regulations and good public image has forced the polluting plants to adopt effective off-gas abatement technologies (Lebrero *et al.*, 2011; Mudliar *et al.*, 2010). The most widespread technologies for odour abatement are biological and chemical-physical processes (Bindra *et al.*, 2015; Iranpour *et al.*, 2005). Biotechnologies represents an economic and environmental-friendly waste gas treatment solution. These technologies result also suitable for high concentrations of compounds containing sulphur, chlorine, and/or nitrogen, showing an high efficiency for biodegradable compounds. However, biomass builds up have to be disposed as waste and percolate water needs treatment; furthermore, poorly soluble components result difficult to abate and toxic compounds inhibit the process. Chemical-physical processes, instead, represent proven and tested technologies, resulting effective for large air volumes. These processes, however, promote the transfer of the contaminants from gaseous phase to liquid or solid phases, with the need of further treatments (Alfonsín *et al.*, 2015; Bindra *et al.*, 2015; Estrada *et al.*, 2015). To overcome the limitations of the conventional processes, the scientific literature has focused the attention on the Advanced Oxidation Processes (AOPs) as alternative technologies applicable to a wide variety of polluting compounds and at different range of concentrations (Idi *et al.*, 2015; Paz, 2010; Swetha *et al.*, 2017; Yao and Feilberg, 2015). Among the AOPs, the UV/O₃ process addresses the decomposition of gaseous VOCs providing direct photolysis by UV, direct oxidation by ozone molecules, and indirect oxidation by hydroxyl radicals. 185 and 254 nm dominant UV wavelengths are usually investigated to study the photochemical reactions of organic compounds in liquid and gas phases. The presence of water vapor allow the absorption at UV range of 100–200 nm. The dissociation of water vapor into hydrogen and hydroxyl radicals follows the equation (1) (Chou *et al.*, 2005).



Moreover, at wavelengths of 300 nm it is possible to detect also the conversion of ozone molecule into an oxygen molecule and an $O(^1D)$ atom and reacts with water vapor to form two hydroxyl radicals. These mechanisms are described by equation (2) and (3) (Chou *et al.*, 2005).



The hydroxyl radicals generated as showed in the equation 2 and 3 may, consequently, react with organic compounds, addressing their decomposition (Chou *et al.*, 2005). The present work illustrates the applicability of an UV-Ozone lab-scale system for odours abatement and VOCs removal from an artificial gaseous stream contaminated by toluene, selected as target VOC. The preliminary results of the study were discussed in terms of toluene and odours concentrations reduction, aiming at evaluating the performances of the investigated configurations as a function of the applied voltage and the incoming toluene concentrations. The main results highlight the suitability of the advanced ozonation UV-induced process for the treatment of off-gas from a great variety of odours emitting plants.

2. Materials and methods

2.1. Experimental set-up

The experiments were carried out in a lab-scale plant consisting in a steel photo-reactor composed of a central body (48.6 cm length x 33.7 cm height x 17.8 cm width) in which are located four UV lamps and two pyramidal-truncated hoods (25 cm height). The UV lamps are able to generate ozone. The scheme of the experimental system is shown in **Figure 1**. For the generation of the synthetic odorous waste stream, a metered stream of oil-free compressed air was passed through a Woulff-bottle pure toluene (Sigma Aldrich; CAS: 108-88-3) containing. This concentrated vapor was diluted to the expected concentration with oil-free water-saturated compressed air (Wang *et al.*, 2013). The waste gas stream was then fed to the reactor. In **Table 1** are reported the main operating parameters of the realized experimental set-up.

2.2. Ozone generation

The ozone generated by the UV lamps and the output residue ozone were measured by the Standard Method 2350E 106 (Ozone Demand/Requirement-Semi-Batch Method). In **Table 2** is reported the dependence of ozone generation rate on the applied voltage, obtained for an air flow rate equal to 13 lpm. The ozone generated resulted not linear dependent from the number of lamps on, expressed as applied voltage. This effect was probably related to the position of the lamps on and to the geometry of the reactor. The lamps which were not directly invested from the air flow contributed least to the ozone production. In the investigated conditions of air flow and humidity the maximum value of ozone produced was obtained with four lamps on and it was equal to 57.6 mg of ozone per minute.

2.3. Analytical methodology

Gas phase toluene concentration was measured using a Photoionization Detector (PID, Tiger, Ion Science) at point P1 and P2. Toluene removal efficiency (η) was calculated as follows:

$$(4) \quad \eta = \frac{C_{\text{toluene,in}} - C_{\text{toluene,out}}}{C_{\text{toluene,in}}} \cdot 100\%$$

In the same points, air samples were taken to carry out analysis by Dynamic Olfactometry (DO) and electronic nose (e.Nose seedOA) to determine the odours. Nalophan[®] sampling bags with 10 liters volume were used. DO was carried out according to EN 13725:2003 at the SEED (Sanitary Environmental Engineering Division) research center of University of Salerno, relying on a panel of four trained persons, based on the “yes/no” method (Zarra *et al.*, 2009). All analysis were conducted within 14 h after sampling, according to Zarra *et al.* (2012b) studies to reduce the variability of the mixture and increase the reliability. The results obtained by DO were used to train the e.Nose. The odour measurements performed with the multisensor array system seedOA (Sanitary Environmental Electronic Device for Odour Application) were carried out according to the procedure proposed by Giuliani *et al.*, (2012). The seedOA e.Nose consists in a set of 12 metal oxides non-specific gas sensors (MOS), 2 specific gas sensors and 2 internal conditions sensors (humidity and temperature), placed in a measurement chamber (CODE[®]), patented by the SEED research group of the University of Salerno, on two different levels (Viccione *et al.*, 2012). The working flow rate was settled to 300 ml/min. The hardware was controlled by a specific software, which allows the acquisition of the sensors signals. All the acquired data were processed by the the Partial Least Squares regression (PLS) statistical mathematical method to define the quantitative model.

3. Results and discussion

3.1. Toluene removal efficiencies

In **Figure 2** are reported the preliminary results in terms of toluene removal and reacted ozone percentages as function of the ozone dose. Increasing the applied voltage from 34 to 136 V, which resulted corresponding to an increasing of ozone rate from 45.6 mg/min to 57.6 mg/min, the removed toluene moved from the 76% to the 84%. In the same time, the reacted ozone decreased from 91% to the 56%. For the range of toluene concentration between 150 and 170 ppm, in the investigated operating conditions, the ozone did not constitute a limiting factor. For this reason, the efficiencies in terms of toluene removal resulted quite similar varying the applied power. In **Figure 3** are reported the results as a function of the incoming toluene concentration, for an applied voltage of 34 V (“A” lamp on). The results showed, even for an incoming concentration of 150 ppm, a removal of 78% of toluene, obtained turning on only the “A” lamp. The flow rate and, consequently, the residence time were maintained constant for the whole set of experiments.

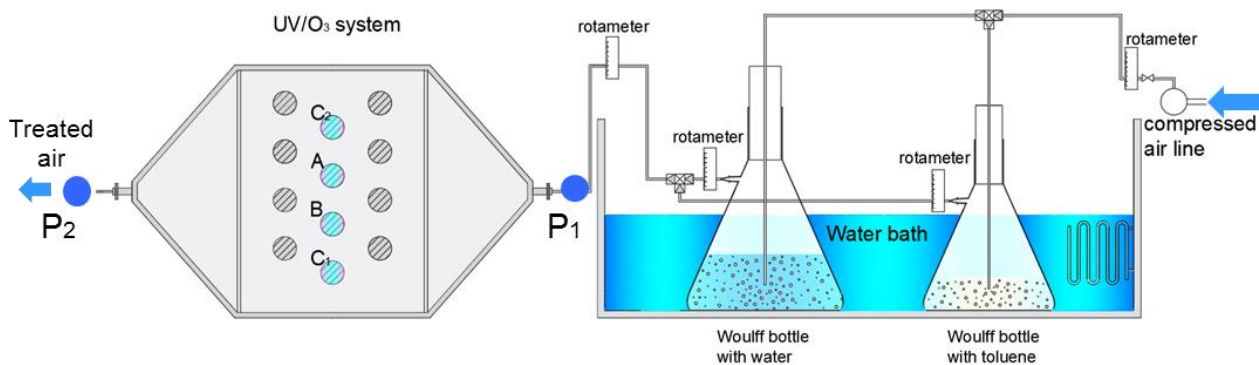


Figure 1. Experimental set-up system

Table 1. Operating parameters

Parameter	Value
Flow rate	13 lpm
Volume of reactor	0.0776 m ³
Overall Length of each lamp	287 mm
Lamp Wattage	14 W

Table 2. Ozone production rate

Number of lamps on	ID lamps on	Voltage [V]	Ozone rate [mg/min]
1	A	34	45.6
2	A,B	68	52.8
4	A,B,C ₁ ,C ₂	136	57.6

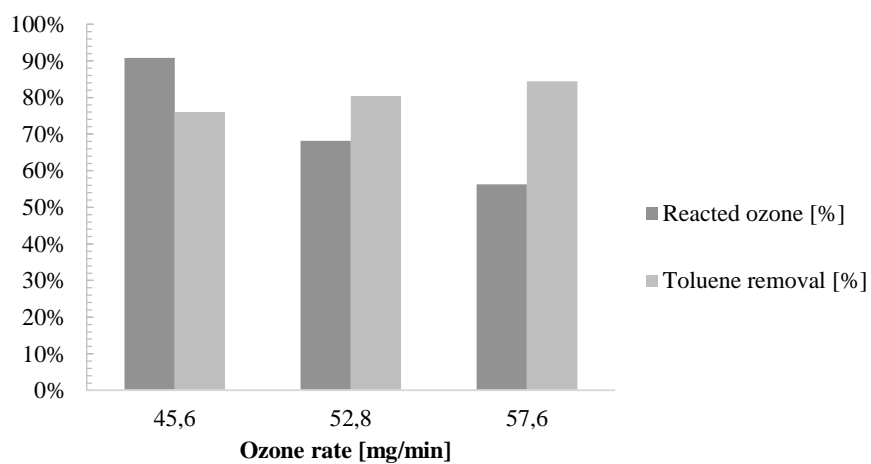


Figure 2. Toluene removal efficiencies and reacted ozone as a function of the ozone rate

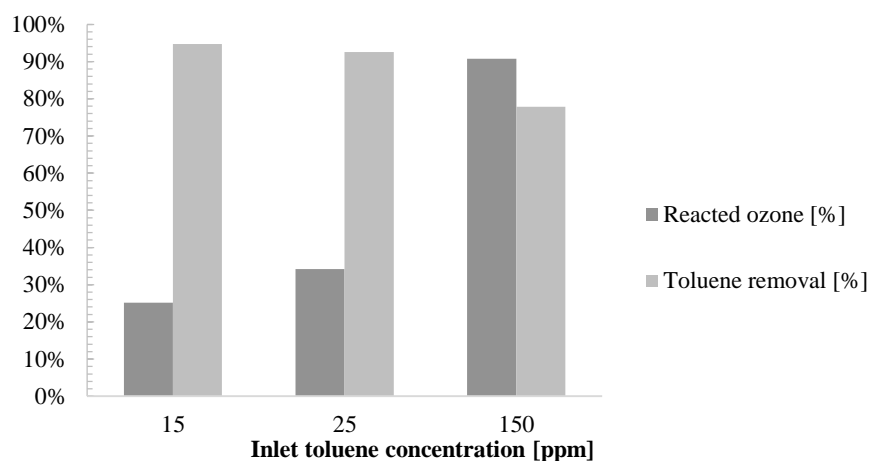


Figure 3. Toluene removal efficiencies and reacted ozone as a function of the inlet toluene concentration

3.2 Odour abatement

The preliminary results obtained in the above-mentioned operating conditions highlighted the removal of the odours for the investigated streams. The odour concentrations of the samples at P1 resulted between 20 and 30 ou_E/m³ for toluene concentrations lower than 25 ppm. For the inlet toluene concentrations between 150 and 170 ppm, the odour concentrations resulted equal to 140-160 ou_E/m³. The odour concentrations of all samples after the treatment, in each set of investigated conditions, resulted lower than the detection threshold. Indeed, these concentrations were corresponding to toluene concentrations lower than the odour threshold, equal to 50 mg of toluene per cubic meter, determined experimentally.

4. Conclusions

The preliminary results of the present work highlighted as the investigated process may be suitable with the aim at treating waste gas from environmental and industrial facilities in which are involved processes of organic degradation. Toluene removals up to 84% were obtained with regards to the contaminated stream at concentrations between 150 and 170 ppm, corresponding to an incoming load of 7,34 – 8,32 mg of toluene per second. In the investigating conditions, referring to inlet toluene concentrations in the range between 10-20 ppm of toluene, the results showed as the reactor may be considered over dimensioned; the ozone in the outlet stream, indeed, resulted over the 60% of the ozone produced. For incoming concentration equal to 150 ppm, also with the lowest ozone dose, a significant removal of toluene was obtained. Moreover, for the examined operating parameters, the odours in the streams outgoing the reactor resulted, with the instruments and methods used, not detectable. The odour threshold was experimentally determined for the real conditions of temperature and humidity, resulting equal to 50 mg of toluene per cubic meter of air. Further considerations should be addressed with regards to the control of the oxidant products. The combination with an additional treatment may be implemented, with a view at reducing the emissions of

oxidants and maximizing the removal of organic compounds

References

- Alfonsín, C., Lebrero, R., Estrada, J.M., Muñoz, R., Kraakman, N.J.R. (Bart), Feijoo, G., Moreira, M.T., 2015. Selection of odour removal technologies in wastewater treatment plants: A guideline based on Life Cycle Assessment. *J. Environ. Manage.* 149, 77–84. doi:10.1016/j.jenvman.2014.10.011
- Belgiorno V. Naddeo, V. and Zarra T. (2012). *Odour Impact Assessment Handbook*. John Wiley & Sons, Inc., 288 p., ISBN: 978111996928-0.
- Bindra, N., Dubey, B., Dutta, A., 2015. Technological and life cycle assessment of organics processing odour control technologies. *Sci. Total Environ.* 527–528, 401–412. doi:10.1016/j.scitotenv.2015.05.023
- Chou, M.-S., Huang, B.-J., Chang, H.-Y., 2005. Decomposition of Gas Phase 1,3-Butadiene by Ultraviolet/Ozone Process. *J. Air Waste Manag. Assoc.* 55, 919–929. doi:10.1080/10473289.2005.10464679
- Estrada, J.M., Kraakman, N.J.R., Lebrero, R., Muñoz, R., 2015. Integral approaches to wastewater treatment plant upgrading for odor prevention: Activated Sludge and Oxidized Ammonium Recycling. *Bioresour. Technol.* 196, 685–693. doi:10.1016/j.biortech.2015.08.044
- Giuliani, S., Zarra, T., Nicolas, J., Naddeo, V., Belgiorno, V., Romain, A.-C., 2012. An alternative approach of the e-nose training phase in odour impact assessment. *Chem. Eng. Trans.* 30, 139–144.
- Hořub, M., 2014. Plasma Supported Odour Removal from Waste Air in Water Treatment Plants: An Industrial Case Study. *Aerosol Air Qual. Res.* doi:10.4209/aaqr.2013.05.0171
- Idi, A., Md Nor, M.H., Abdul Wahab, M.F., Ibrahim, Z., 2015. Photosynthetic bacteria: an eco-friendly and cheap tool for bioremediation. *Rev. Environ. Sci. Biotechnol.* 14, 271–285. doi:10.1007/s11157-014-9355-1

- Iranpour, R., Cox, H.H.J., Deshusses, M.A., Schroeder, E.D., 2005. Literature review of air pollution control biofilters and biotrickling filters for odor and volatile organic compound removal. *Environ. Prog.* 24, 254–267. doi:10.1002/ep.10077
- Lebrero, R., Rodríguez, E., García-Encina, P.A., Muñoz, R., 2011. A comparative assessment of biofiltration and activated sludge diffusion for odour abatement. *J. Hazard. Mater.* 190, 622–630. doi:10.1016/j.jhazmat.2011.03.090
- Lucernoni, F., Tapparo, F., Capelli, L., Sironi, S., 2016. Evaluation of an Odour Emission Factor (OEF) to estimate odour emissions from landfill surfaces. *Atmos. Environ.* 144, 87–99. doi:10.1016/j.atmosenv.2016.08.064
- Mudliar, S., Giri, B., Padoley, K., Satpute, D., Dixit, R., Bhatt, P., Pandey, R., Juwarkar, A., Vaidya, A., 2010. Bioreactors for treatment of VOCs and odours – A review. *J. Environ. Manage.* 91, 1039–1054. doi:10.1016/j.jenvman.2010.01.006
- Naddeo, V., Belgiorno, V., Zarra, T. (Eds.), 2013. *Odour impact assessment handbook*. Wiley, A John Wiley & Sons, Ltd., Publications, Chichester, West Sussex, United Kingdom.
- Naddeo, V., Zarra, T., Olivaa, G., Chiavolab, A., Vivarellic, A., 2016a. Environmental Odour Impact Assessment of Landfill Expansion Scenarios: Case Study of Borgo Montello (Italy). *Chem. Eng.* 54.
- Naddeo, V., Zarra, T., Olivaa, G., Kubob, A., Ukidab, N., Higuchib, T., 2016b. Odour Measurement in Wastewater Treatment Plant by a New Prototype of e. Nose: Correlation and Comparison Study With Reference to both European and Japanese Approaches. *Chem. Eng.* 54.
- Navia, R., Muñoz, R., 2015. *Biotechnologies for gaseous emissions and by-products management in waste treatment facilities*. SAGE Publications.
- Paz, Y., 2010. Application of TiO₂ photocatalysis for air treatment: Patents' overview. *Appl. Catal. B Environ.* 99, 448–460. doi:10.1016/j.apcatb.2010.05.011
- Swetha, G., Gopi, T., Chandra Shekar, S., Ramakrishna, C., Saini, B., Rao, P.V.L., 2017. Combination of adsorption followed by ozone oxidation with pressure swing adsorption technology for the removal of VOCs from contaminated air streams. *Chem. Eng. Res. Des.* 117, 725–732. doi:10.1016/j.cherd.2016.11.036
- Viccione, G., Zarrab, T., Giulianib, S., Naddeob, V., Belgiornob, V., 2012. Performance study of e-nose measurement chamber for environmental odour monitoring. *Chem. Eng.* 30.
- Wang, Z., Xiu, G., Qiao, T., Zhao, K., Zhang, D., 2013. Coupling ozone and hollow fibers membrane bioreactor for enhanced treatment of gaseous xylene mixture. *Bioresour. Technol.* 130, 52–58. doi:10.1016/j.biortech.2012.11.106
- Yao, H., Feilberg, A., 2015. Characterisation of photocatalytic degradation of odorous compounds associated with livestock facilities by means of PTR-MS. *Chem. Eng. J.* 277, 341–351. doi:10.1016/j.cej.2015.04.094
- Zarra, T., Naddeo, V., Belgiorno, V., Reiser, M., Kranert, M., 2009. Instrumental characterization of odour: a combination of olfactory and analytical methods. *Water Sci. Technol. J. Int. Assoc. Water Pollut. Res.* 59, 1603–1609. doi:10.2166/wst.2009.125
- Zarra T., Giuliani S., Naddeo V., Belgiorno V. (2012), Control of odour emission in wastewater treatments plants by direct and undirected measurement of odour emission capacity, *Water Science and Technology*, 66 (8), 1627-1633.
- Zarra T., Reiser M., Naddeo V., Belgiorno V., Kranert V. (2012b). A comparative and critical evaluation of different sampling materials in the measurement of odour concentration by dynamic olfactometry. *Chemical Engineering Transactions*, vol. 30, p. 307-312, ISSN: 1974-979