

Volatile organic compounds (VOCs) removal by combining bioscrubber and ozone pretreatment

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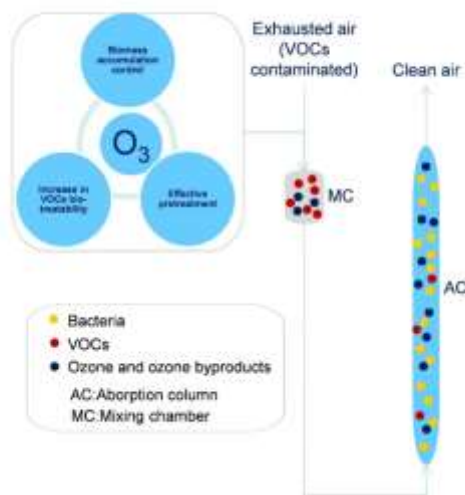
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Graphical abstract



Abstract

Volatile Organic Compounds (VOCs) are toxic for the environment and human health and their tendency to readily volatilize in the atmosphere can lead to problems connected to odours annoyance. Conventional VOCs gaseous emissions treatments entail the application of chemical-physical processes, only promoting the transfer of the contaminants from gas to liquid and/or solid phases. Advanced Oxidation Process (AOPs) and biological processes, conversely, support the oxidation of the organic pollutants, promoting their conversion into harmless and odourless compounds. The integration of both processes is suggested to increase treatability of VOC. The research presents the application of an innovative treatment system composed by an AOPs pretreatment coupled with a bio-scrubbing unit for the abatement of VOCs, with the aim to increase the removal efficiency. The evaluation of the performance of the proposed system is discussed with reference to the analysis carried out using toluene as model substance. Different operating conditions have been analyzed and investigated to optimize the removal efficiency.

The results show that the ozonation applied as pretreatment to the biological process may promote an increase of the pollutant biodegradability along with synergic effects due to the absorption of the ozone derived compounds into the culture growth, resulting in a significant enhancement of removal performances respect to the conventional biotechnologies. A toluene removal efficiency up to 95% were obtained under the investigated conditions.

1. Introduction

The increasing concerns about odours emissions from wastewater treatment plants, composting plants and landfill has driven to the needs of a sustainable process for their control (Ren *et al.*, 2019; Zarra *et al.*, 2012; Zarra *et al.*, 2016; Naddeo *et al.*, 2012; Belgiorno *et al.*, 2012). The raw gas emitted from the previously mentioned sources are mainly composed by GHGs, H₂S, NH₃ and Volatile Organic Compounds (VOCs) among the others (Zarra *et al.*, 2014; Zarra *et al.*, 2019). Toluene is a man-made aromatic hydrocarbon that is mainly used as solvent and industrial feedstock. Toluene is a VOC that has a narcotic and neurotoxic properties, which represent the main health hazards to humans (Berenjian *et al.*, 2012). World Health Organization has reported that long-term exposure to VOCs can causes leukemia (Hazrati *et al.*, 2016). Wherein, the 40% of toluene emissions came from the losses of refineries, 32% from automobile exhausts, 16% from solvents, 8% from petroleum loses to the sea, 2% from the loses from chemical industries and 8% from gasoline evaporation (IARC; Leusch and Bartkow, 2010).

Physical, chemicals and biological technologies has been applied for the removal of VOCs and are widely studied (Muñoz *et al.*, 2015). Thought, when physical and chemicals technologies are applied for the treatment of high flow rates and concentrations less than 100 ppm, the treatment process needs a huge amount of chemicals and more energy, resulting in a not economically viable process (Oliva *et al.*, 2019).

Ozone (O₃) is a very strong oxidant that extensively attracted interest for the degradation of organic pollutants. It has been used for the treatment of water

(Rosal *et al.*, 2008) and it is also used for the degradation of gaseous toluene (Oliva *et al.*, 2018). The degradation of organic substances using only O_3 is not possible (Rao and Chu, 2009) and therefore the ozone is used in the advanced oxidation process (AOPs) in combination with other oxidation techniques (Chang *et al.*, 2012; Kim, Yamashita, and Tanaka, 2009; Pengyi *et al.*, 2003; Rosal *et al.*, 2008). Pengyi *et al.* showed that in photocatalytic process the ozone addition greatly enhanced the decomposition of gaseous toluene (Pengyi *et al.*, 2003). The recent study conducted by Comia *et al.* involving ultrasonication with ozone addition showed low removal efficiency of toluene (Comia *et al.*, 2020).

On the other hand, biofiltration has been widely used as an efficient raw gas treatment technology thanks to the production of harmless by-products, less maintenance costs and operation under low temperature (25 °C) (Delhom nie *et al.*, 2002; Mudliar *et al.*, 2010). The VOCs can be a source of energy and carbon for microorganisms, which subsequently transformed it into CO_2 , water, and biomass (Anbalagan *et al.*, 2017; Oliva *et al.*, 2018). However, toluene is insoluble in water, hence the microbial removal of hydrophobic pollutant might be difficult (Miller *et al.*, 2019). The hydrophobicity of the pollutant in water affects its transport in the system which limits the microbial degradation (Haws *et al.*, 2006; Gospodarek *et al.*, 2019).

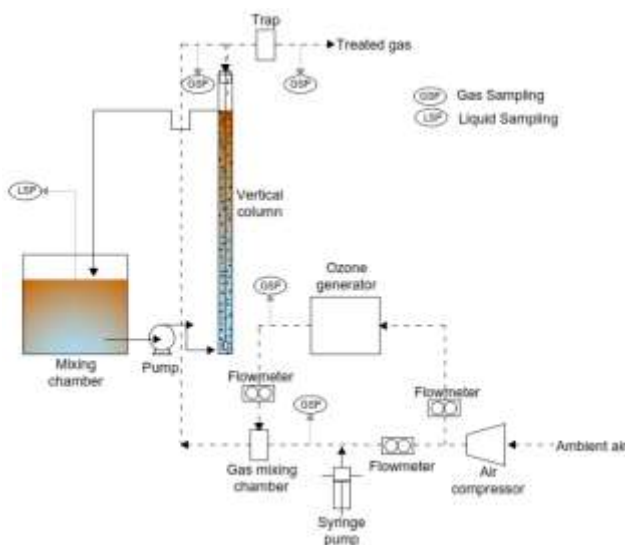


Figure 1. Experimental set-up

The research presents the application of an innovative treatment system composed by an integration of an adsorption and ozonation process, with the aim to treat raw gas contaminated with toluene. A vertical absorption column reactor inoculated with bacteria coming from activated sludge has been used and an ozone generator has been applied to promote a pretreatment. The synergistic approach of bioscrubber and ozonation on the elimination capacity, and removal efficiency, with respect to toluene load was analyzed. The total suspended solid (TSS) was used as a factor to evaluate the

biomass production control obtained by the ozonation pretreatment.

2. Material and methods

2.1. Experimental set-up

The experimental setup showed in Figure 1 consisted of a vertical absorption column (VAC), a liquid mixing chamber, gas mixing chamber and O_3 generator. The VAC was made of a PVC cylinder with 130 cm height and 6 cm diameter, and filled with 3.3 L of inoculum with activated sludge sampled from a municipal wastewater treatment plant. The O_3 generator was made of a metallic cylinder equipped with UV lamp. The O_3 enriched air was generated from the oxygen coming from the pressurized ambient air using an air compressor. Liquid toluene was directly injected to the system using a syringe pump (NO300, New Era Pump System) and mixed with O_3 in a gas mixing chamber. The gas produced after ozonation was diffused into the bioscrubber utilizing a metallic diffuser (Knaur Mobile Phase Filter, SS, 2 μm , 1/8" pipe OD). Four gas sampling ports (GSPs) were located in different point of the set-up as shows in Figure 1 for monitor the toluene and ozone concentrations in the system. Two GSPs were located before the gas mixing chamber to measure the toluene inlet concentration, and after the ozone generator to measure the ozone produced. The others two GSPs were placed before and after the bioscrubber to measure the toluene concentration before and after the absorption process. The volume of the liquid mixing chamber was around 18 L. A manometers were also implemented to measure the pressure in the system.

2.2. Inoculation of microorganisms

The inoculation of microorganisms was prepared with 0.50 L of activated sludge, centrifuged for 10 mins at 600 rpm, suspended to 0.25 L mineral salt medium (MSM). The initial pH value and TSS were set to 7.0 and 7 g L^{-1} , respectively (Oliva *et al.*, 2018).

2.3. Chemicals

The MSM was composed of: Na_2HPO_4 (2.44 g L^{-1}); KH_2PO_4 (1.52 g L^{-1}); NH_4SO_4 (1.00 g L^{-1}); $MgSO_4 \cdot 7H_2O$ (0.20 g L^{-1}) and $CaCl_2 \cdot 2H_2O$ (0.08 g L^{-1}); 10 mL L^{-1} of SL-4; and 100 mL of SL-6. The stock solution SL-4 contained EDTA (0.50 g L^{-1}), and $FeSO_4 \cdot 7H_2O$ (0.20 g L^{-1}). The SL-6 stock solution composed of: $ZnSO_4 \cdot 7H_2O$ (0.10 g L^{-1}); $MnCl_2 \cdot 4H_2O$ (0.03 g L^{-1}); H_3BO_3 (0.30 g L^{-1}); $CoCl_2$ (0.20 g L^{-1}); $CuCl_2 \cdot 2H_2O$ (0.01 g L^{-1}); $NiCl_2 \cdot 6H_2O$ (0.02 g L^{-1}); $Na_2MoO_4 \cdot 2H_2O$ (0.03 g L^{-1}). The 99.9% of toluene used in this study obtained from Sigma-Aldrich Corporation (Darmstadt, Germany) was employed in this work. Potassium iodide (KI), sulfuric acid (H_2SO_4) and sodium thiosulfate ($Na_2S_2O_3$) have been used for the estimation of the ozone dose.

2.4. Operating conditions

The experiments were conducted at a temperature between 25 and 30 °C and the gas flow rate was adjusted at 1.6 $L \text{ min}^{-1}$, corresponding to an empty bed retention time (EBRT) of 2 min.

Four different operating conditions have been investigated (Table 1). The bio-scrubber was operated continuously for 92 days. The first 30 days were run for the stabilization of the system. In the next 62 days, the

inlet toluene concentrations were gradually increased from 150 to 300 mg m⁻³ and the toluene inlet load were varied from 4.5 to 9 g m⁻³ h⁻¹. Subsequently, the ozone loading rate was increased from 50 to 100 g m⁻³ h⁻¹.

Table 1. Operating parameters

Operating parameters	Stage (days)			
	I (30–44)	II (45–60)	III (61–78)	IV (79–92)
EBRT (min)	2			
Q _{liq} (L min ⁻¹)	0.8			
Q _{gas} (L min ⁻¹)	1.6			
L/G	0.5			
IL _{tol} (g m ⁻³ h ⁻¹)	4.5	4.5	9	9
C _{toluene,in} (mg m ⁻³)	150	150	300	300
LR _{O₃} (g m ⁻³ h ⁻¹)	~50	-	-	~100

2.5. Toluene removal performance parameters

The evaluation of the performances of the combined process has been made by calculating the removal efficiency (RE%) and the elimination capacity (EC) (Muñoz *et al.*, 2015).

Removal efficiency (RE, %):

$$RE(\%) = \frac{C_{in} - C_{out}}{C_{in}} \cdot 100$$

Elimination capacity (EC, mg m⁻³ h⁻¹):

$$EC = \frac{Q(C_{in} - C_{out})}{V}$$

Where C_{in} is the inlet concentration of toluene (mg m⁻³), C_{out} is the outlet concentration of toluene (mg m⁻³), Q is the gas flow rate (m³ h⁻¹) and V is the volume of the bio-scrubber (m³).

3. Results and discussion

Figure 2 reports the results in terms of elimination capacity (EC) and removal efficiency (RE) as function of the inlet load of toluene (IL) during the whole operation period.

Table 2. Total suspended solid under the four different conditions investigated

Stages	TSS [mg L ⁻¹]	LR _{O₃} [g m ⁻³ h ⁻¹]
I	91	50
II	126	-
III	114	-
IV	60	100

When the ozone was applied as a pretreatment with an ozone loading rate respectively of 50 and 100 g m⁻³ h⁻¹, in the first and fourth stage, the removal efficiency of toluene changed from the 88 % to 92 %. Moreover, during the two stages with the ozonation, as reported in Table 2, a lower biomass was detected. A 50 % reduction in biomass was obtained compared to the process without ozone.

During steady-state operation, for IL up to 10.6 ± 1.9 g m⁻³ h⁻¹ a 78 ± 2 % removal of toluene was achieved without ozonation. At the ozone loading rate of

920 g m⁻³ h⁻¹ was obtained a removal efficiency of 95 %, corresponding to an EC of 13.81 ± 2.0 g m⁻³ h⁻¹.

4. Conclusion

A bio-scrubber coupled with ozonation was investigated under different toluene loading rates. The research shows the compatibility of ozonation process and its efficacy as a pretreatment system in order to enhance the absorption and the biodegradability rate of toluene.

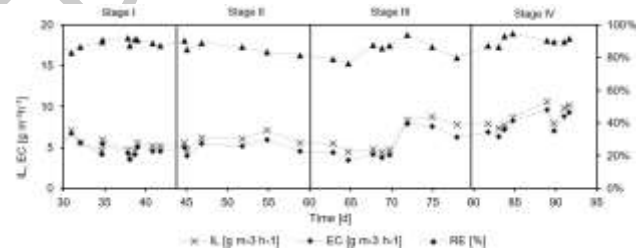


Figure 2. Toluene removal as a function of time

Results highlighted a good synergism between the two processes, emphasizing that ozone pretreatment may promote not only the increase in pollutants biodegradability, preventing inhibiting conditions for the activity of microorganisms even at high concentration of toluene, but also the accumulation of excess biomass. Intact, a removal efficiency of 95 %, corresponding to an EC of 13.81 ± 2.0 g m⁻³ h⁻¹ was achieved and a 50% of biomass reduction was reached in the fourth stage.

Further studies are required in order to evaluate the availability of the investigated system for the treatment of a mixture of different organic and inorganic compounds.

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