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Comparative Analysis of AOPs and Biological Processes for the Control of VOCs Industrial Emissions

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Volatile Organic Compounds (VOCs) emissions from a wide range of industrial plants have become a major issue in the framework of atmospheric pollution, due to their negative effects on human and environmental health. VOC-laden emissions are also responsible for odour annoyance. To comply with the stringent regulations and to avoid complaints from the population living near these plants, the most suitable treatment technologies should be identified and implemented. Chemical-physical off-gas treatments such as adsorption and scrubbing, are proven and tested technologies; however, they only promote the transfer of the contaminants from the gaseous to solid or liquid phase, and further treatments are thus required. Biological processes and advanced oxidation processes (AOPs), instead, are able to support the degradation and mineralization of organic compounds, resulting in more effective solutions. This study presents and discusses a comparative analysis of the biological processes and AOPs for the removal of VOCs, focusing on assessing their potential application for industrial waste gas treatment. A numerical procedure, based on the quantification of a set of parameters classified into clusters, was proposed to evaluate the most suitable process for the treatment of the VOC-laden emissions in the different industrial sectors. The results, based on a semi-quantitative ranking of the different identified parameters, pointed out the weaknesses and strengths of the investigated processes. AOPs entailed high elimination capacities, but the emissions of hazardous by-products should be controlled and reduced. Biotechnologies have emerged as cost-effective and environmental friendly processes; however, the efficiencies of these processes are often limited by the presence of recalcitrant and toxic secondary metabolites.

1. Introduction

Nowadays, the severe effects of air pollution on environment and human health has been worldwide recognized since the rising concern about global warming and atmospheric pollutants toxicity (Boyjoo et al., 2017). Volatile organic compounds (VOCs) and odours are well-known pollutants emitted into the atmosphere mainly from industrial facilities, waste and wastewater treatment plants. The exposure to VOCs has been related both to acute symptoms such as nausea, headaches, loss of consciousness and to chronic effect associated to mutagenicity and carcinogenicity risks (Son, 2017). The formation of ozone and PAN (peroxy-acetyl nitrate) could be also triggered by the emission of VOCs (Parmar and Rao, 2008). Along with these effects, the correlated odour emissions may cause annoyance and discomfort to the exposed people (Naddeo et al., 2016). Cost-effective and environmental friendly treatments are thus required to adequately remove VOCs and odours from industrial waste gas stream. Chemical-physical treatments are among the most used technologies and consequently they are characterized by an established knowhow. These treatments, however, do not support the degradation of the gaseous compounds, but only the transfer of the contaminants from the gas to the solid or liquid phase(Boyjoo et al., 2017). Biological and oxidation processes, instead, are able to promote the partial or complete degradation of these organic compounds, resulting into their mineralization. Consequently, these processes do not require further treatment of the phases to which the contamination may be transferred. Biotechnologies, despite the fact that show an effective removal with economic and environmental processes, are often limited by the presence of recalcitrant and toxic secondary

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metabolites and the microbial activity may be inhibited by the oxygen limitation (Lebrero et al., 2016). AOPs support the degradation of a wide variety of VOCs also in presence of high Inlet Loads (ILs); however, the release of toxic by-products and high energy consumption represent the main drawbacks of this kind of processes (Akmirza et al., 2017). This study aims at define a methodology to address the choice of the most suitable treatment technologies for waste gas from industrial sources. The proposed methodology allows to highlight the strengths and weaknesses of the main processes used for VOCs and odours removal from gaseous stream. To overcome the main drawbacks, the combination of different technologies may be addressed analysing the possible synergy and mitigation effects among the processes analysed. The results, indeed, were discussed with regards to the performances of the processes towards different clusters of parameters.

2. Materials and methods

2.1 Methodology

With a view at selecting the most suitable waste gas treatment technology, it was proposed a methodology to combine the results of technical, environmental and economic evaluations (Soltani et al., 2016).

This method allowed to assign scores to different alternatives by using a pairwise comparison between different criteria (Hossaini et al., 2015; Kabir et al., 2014).

The method envisaged different steps of analysis: the first was to sketch up the decision making process organizing hierarchically different cluster of criteria; the second one was to assign a weight to each criterion and, within each one, a weight to each sub-criterion, through pair-wise comparison; the third stage was to rank the different alternatives according to the aggregate scores resulting from the mathematical process.

2.1.1 Step I

Four main criteria have been identified as efficacy, process charge, possibility of recovery, environmental impacts, as shown in Figure 1. The choice of these criteria was made on the behalf of the literature review. Literature review was performed on peer-reviewed journals and conference proceeding

The efficacy criteria was organized in four different sub-crieteria: removal efficiency; the range of inlet concentration the process is able to treat; the range of gas flowrate the process is able to treat; the typologies of VOCs the process is able to treat. The process charge criteria was organized in three different sub-crieteria: opereting costs; the necessity of a pre or post treatment, the necessity of using chemicals.

The third criterion was the possibility of recovery both energy and products.

The environmental impact criterion envisaged carbon footprint, the release of gaseous toxic by-products and the generation of secondary waste.

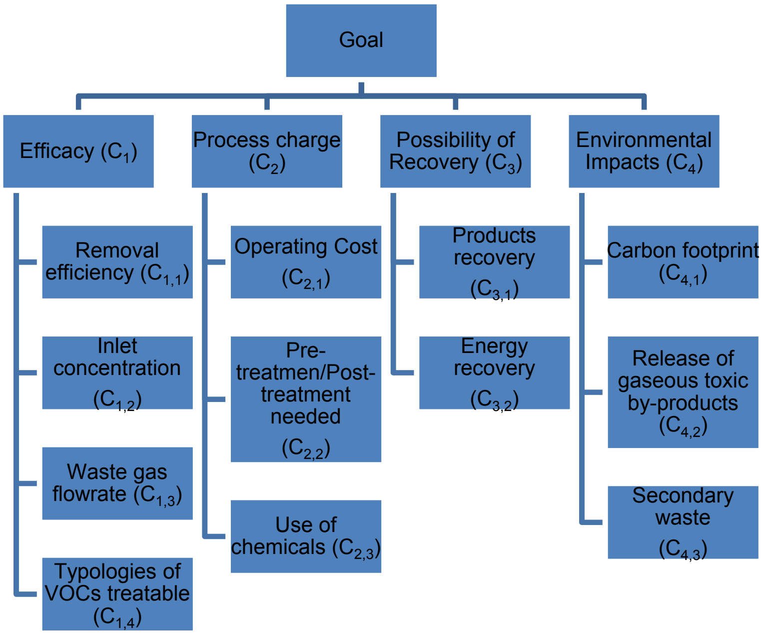

Figure 1 – Hierarchy of criteria

2.1.2 Step II

The assignment of the weights to each criterion and sub-criterion was carried out by the pairwise comparison. Five different matrices have been built, the first one to define the weights of each criterion and the others to assign the weights of each sub-criterion included in the same main criterion.

2.1.3 Step III

The score of each alternative was retrived according the following equations.

$$S_i(A_k) = \sum_{j=1}^{n} \omega_{i,j} \cdot s_{i,j} \tag{1}$$

Where:

- $\omega_{i,j}$ is the weight of the criteria $C_{i,j}$ obtained by the pairwise comparison of each sub-criterion referred to the criterion C_i;
- $s_{i,j}$ is the score of the alternative (A_k) towards the criterion $C_{i,j}$, obtained by the pair-comparison of each criteria referred to the criterion C_i;
- S_i is the score of the alternative (A_k) towards the criterion C_i.

$$S(A_k) = \sum_{j=1}^{n} \omega_i \cdot S_i \tag{2}$$

Where:

- ω_i is the weight of the criterion C_i.
- $S_{i,j}$ is the score of the alternative (A_k) towards the criterion C_i.
- S is the overall score of the alternative (A_k).

3. Results and discussion

3.1 Identification of the set of indicators and indexes

Based on the information retrieved from the scientific literature, there were selected the criteria and sub-criteria reported in the Figure 1 (Covarrubias-García et al., 2017; Khan and Kr. Ghoshal, 2000; Malakar et al., 2017). For each criterion, the corresponding indicator was converted as an index, following the normalization procedure. All the indicators were normalized according the method “high is better”, as reported in Table 1.

Table 1 – Indicators and indexes

Criterion	Indicator	U.M.	Index
$C_{1,1}$	Removal efficiency (RE)	%	RE/100
$C_{1,2}$	Maximum Inlet Concentration (IC)	$g\ m^{-3}$	IC/IC_{max}
$C_{1,3}$	Maximum Waste gas flow rate (Q)	$m^3\ h^{-1}$	Q/Q_{max}
$C_{1,4}$	Type of VOCs treatable	-	1/0 (all/selective)
$C_{2,1}$	Operating Cost (OC)	€ $m^{-3}\ h^{-1}$	$1 – (OC/OC_{max})$
$C_{2,2}$	Pre-treatment or post-treatment needed	-	0/1 (yes/no)
$C_{2,3}$	Use of chemicals	-	0/1 (yes/no)
$C_{3,1}$	Product recovery	-	1/0 (yes/no)
$C_{3,2}$	Energy recovery	-	1/0 (yes/no)
$C_{4,1}$	Carbon footprint	-	0/1 (high/low)
$C_{4,1}$	Release of by products	-	0/1 (yes/no)
$C_{4,1}$	Secondary waste	-	0/1 (yes/no)

The results of the pairwise comparisons of the sub-criteria belonging to the same criterion were reported in the Table 2.

The higher weights have been assigned to the efficacy and environmental impacts criteria. The possibility of recovering products was considered more important than the energy recover since in the framework of the waste management hierarchy the materials recovery is priority.

Table 2 – Weights of each criterion

Criterion	ω_i	**Sub-criterion**	$\omega_{i,j}$
1	0,35	**1.A**	0,40
		1.B	0,20
		1.C	0,20
		1.D	0,20
2	0,20	**2.A**	0,25
		2.B	0,50
		2.C	0,25
3	0,10	**3.A**	0,67
		3.B	0,33
4	0,35	**4.A**	0,25
		4.B	0,50
		4.C	0,25

3.2 Alternatives scores

The analysis of the scientific literature allowed to assign a value at each index corresponding to each sub-criterion (Covarrubias-García et al., 2017; Khan and Kr. Ghoshal, 2000; Malakar et al., 2017). The results are reported in the Table 3.

Table 3 – Score of the alternatives for each sub-criterion

Process	***Criterion 1***				***Criterion 2***			***Criterion 3***		***Criterion 4***		
	1.A	***1.B***	***1.C***	***1.D***	***2.A***	***2.B***	***2.C***	***3.A***	***3.B***	***4.A***	***4.B***	***4.C***
Absorption	0,90	0,02	0,60	1,00	0,14	0,00	0,00	1,00	0,00	1,00	1,00	0,00
Adsorption	0,90	0,00	0,50	0,00	0,74	0,00	0,00	1,00	0,00	1,00	1,00	0,00
Biofiltration	0,95	0,04	0,24	0,00	0,49	0,50	1,00	0,00	0,00	1,00	1,00	0,00
Condensation	0,85	0,08	0,20	1,00	0,14	1,00	0,00	1,00	0,00	0,00	1,00	0,00
Catalytic oxidation	0,98	0,04	1,00	1,00	0,36	1,00	1,00	0,00	1,00	0,00	0,00	1,00
Thermal oxidation	0,99	0,06	1,00	0,00	0,00	1,00	0,00	0,00	1,00	0,00	0,00	1,00
Plasma	0,90	1,00	1,00	1,00	0,07	1,00	1,00	0,00	0,00	0,00	0,00	1,00
Photocatalysis	1,00	0,80	1,00	1,00	0,07	1,00	0,00	0,00	0,00	0,00	0,00	1,00
UV ozone oxidation	1,00	0,80	1,00	1,00	0,07	1,00	1,00	0,00	0,00	0,00	0,00	1,00

In Table 4 are reported the results aggregated for criterion with a view at highlighting the weakness and strengths of the investigated processes.

Table 4 – Score of the alternatives for each criterion

Process	***Criteria***				***TOT***
	1	***2***	***3***	***4***	
Absorption	0,68	0,04	0,67	0,75	0,58
Adsorption	0,46	0,19	0,67	0,75	0,53
Biofiltration	0,44	0,62	0,00	0,75	0,54
Condensation	0,60	0,54	0,67	0,50	0,56
Catalytic oxidation	0,80	0,84	0,33	0,25	0,57
Thermal oxidation	0,61	0,50	0,33	0,25	0,43
Plasma	0,96	0,77	0,00	0,25	0,58
Photocatalysis	0,96	0,52	0,00	0,25	0,53
UV ozone oxidation	0,96	0,77	0,00	0,25	0,58

In the Figure 2 it is reported the distribution of the scores of each alternatives among the different criteria.
The results showed that the oxidation processes were characterized by the highest efficacies but resulted the most impactful options. Biofiltration allowed to achieve high RE: the efficiencies, however, may be reduced increasing the VOCs inlet concentrations. The highest overall scores were attributed to plasma, absorption and UV oxidation; nevertheless, all the investigated solutions revealed comparable results. Analysing the

score assigned to the indexes 1.B, 1.C it is possible to identify the processes able to treat high concentrations or gas flow rates. The outputs of the implementation of this methodology, thus, may be analysed to identify the adequacy of different treatment technologies to the particular waste gas industrial emission. When low inlet concentrations are expected, biofiltration could be considered the best options since these kind of processes resulted able to achieve high RE, besides low environmental and economic impacts (Muñoz et al., 2015). Conversely, when high performances are required plasma, photo-catalysis and UV oxidation may be considered more effective solutions. To reduce the emissions of by-products a combined process could be implemented, with a view at promoting an Advanced Oxidation pre-treatment (reducing the energy consumption of a single stage AOP) followed by a biological process. AOPs applied as pre-treatment at biological processes may improve VOCs bio-treatability and control the accumulation of biomass (Covarrubias-García et al., 2017; Oller et al., 2011). The combination of biological and advanced oxidation processes could be considered hence a sustainable platform to reduce the emission of undesirable by-products, besides treating high concentrations of VOCs.

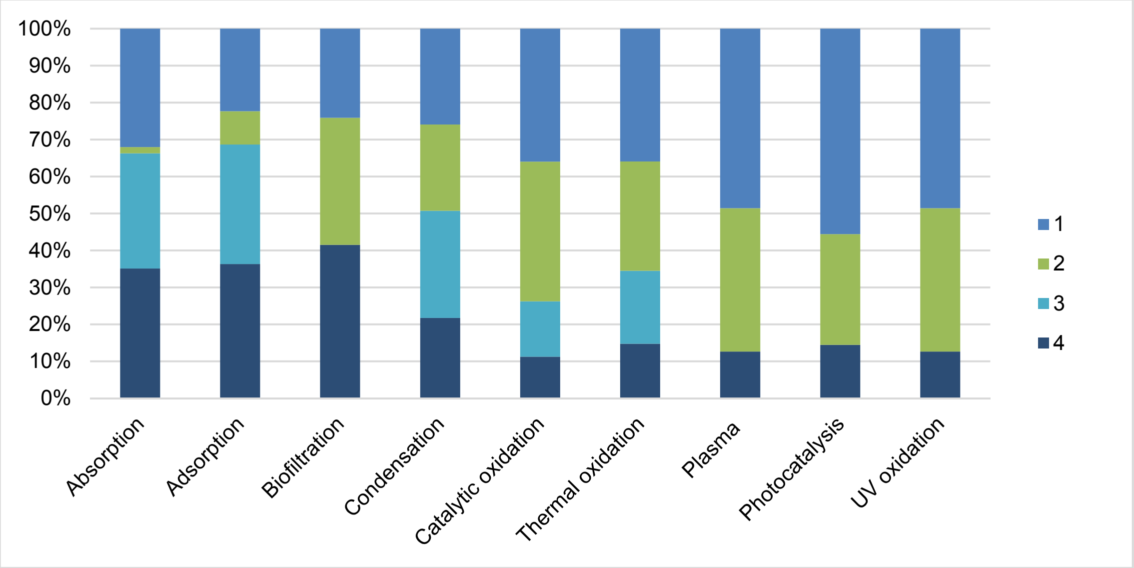

Figure 2 – Distribution of the scores of alternative related to the different criteria

4. Conclusions

The proposed methodology may provide a support within the making-decision process. The results highlighted the weak and strength points of the investigated processes. The overall scores of all the alternatives resulted comparable, but the performances regarding the single criteria may be applied as screening phase to verify the suitability of the selected process for the specific industrial waste gas stream. Furthermore, the synergic effects among different waste gas treatments could be identified analysing the scores of the different alternatives for the single criteria. The novelty of the proposed methodology was the hierarchic organization of the criteria within a multicriterial analysis. The validation of the achieved results with a sensitivity analysis should be performed involving multiple stakeholders.

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