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Biological potentiality to remove organic solvents from exhausted air emissions

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Abstract— **The performance of an industrial prototype of a biological system was investigated during more than two years, for the treatment of exhaust gas from air emission of wooden painting activities. Two different type of VOCs mixture were treated at different weather conditions. Removal efficiencies were sufficiently high to maintain the outlet emissions within the legal thresholds. Particularly low costs for management were experienced, confirming the biofiltration a sustainable technology.**

Keywords—biofiltration; painting; solvent; microorganisms, environment

I. INTRODUCTION

The biodegradation of those compounds better defined as *solvents* is well known and reported in the open literature. The most documented applications are performed at lab scale, or in small pilot plants, and good performance of biological processes in removing solvents from contaminated air streams is reported. Only a few applications are described at industrial level, and biological processes are usually not involved [1, 2]. This may depend upon the biodegradation rate which is not as quick as the applications requires, or difficulties can be encountered when complex mixtures of solvents are involved. Of course, if the biological process suffers technical limits, the factory management may opt for physical or chemical technologies as an alternative [3]. Biological processes may have success in those fields where physical or chemical treatments have low economic sustainability. In fact, in most cases the biological technology involves low capital and management costs, especially when compared to alternative techniques.

From our experience with an industrial pilot plant, biological technologies for the removal of solvents from contaminated emissions are favorable when they are considered as a part of a strategy for the reduction of emissions in the whole factory. In order to comply with laws and directives stating limits for the emission of VOCs, industry has to target a number of different categories of VOC sources. Improving the painting process, increasing the dry residue in the paint, using water based paints are the first steps that should accompany the biological technologies in order to achieve the goals of the solvent management plan. In this context, two most important purposes have been pursued: the respect of rules and the economical sustainability of the biological process.

The effectiveness of biodegradation is someway proportional to the volume of the filter, thus it can be hard to respect the emission limits imposed by the Directive 2004/42/CE in the case there is not enough free room in the factory to allocate the plant. However the biofilter can be seen as a fundamental step in the management plan for the reduction of VOC emissions. From this point of view, reaching the maximum effectiveness is not the only goal, because other aspects like stability, ease of management and durability of performance have great importance.

II. WOOD INDUSTRIAL DISTRICT

Our project was started many years ago and several difficulties have been overcome during the scaling up. This initiative was born from a pool of entrepreneurs of the Friuli Venezia Giulia Region that were well aware of the regional and national VOC emission levels. For some of them, post combustion plants could have been the solution, because the VOC concentration in their off gas would be high enough to make this technology affordable. At the same time, there was interest to find a solution for small companies, where the combustion technology is not economically feasible. For such reasons, in the past some small companies tried to investigate the reduction of emissions by applying biological processes, as a possible technology to apply in the regional and national wood sectors.

In this general context, several steps were programmed to scale up our previous lab experiments [4].

The solvent management plan of three out of six companies was investigated with the purpose of a thorough knowledge of their solvent mass balance, and to check the possible similarity among the painting processes, in order to extend the results obtained from the first prototype of the biofilter [5].

In the factories under investigation, painting is performed through spraying techniques involving an anthropomorphic robotic sprayer and surface painting. Painted wood is then moved to a withering area.

The typical compositions of paints consist of a mixture of solvents, including hydrophobic aromatics (e.g. toluene and xylenes), acetates, aldehydes and ketones, alcohols and other hydrophilic compounds. The emissions from the withering zone were chosen to feed the biological treatment plant. The steady and moderately high concentration of these VOCs emissions are helpful for the research activity in the first start up period.

Withering processes typically result in air emissions characterized by relatively low concentration of solvents and high air flow rates, thus making extremely expensive the treatment of such emissions by thermal or physical-chemical processes (Figure 1).

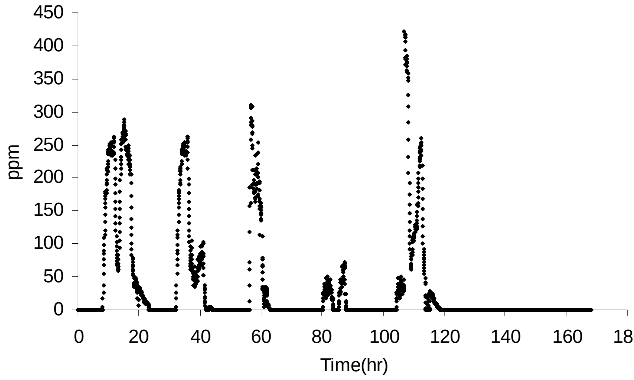

Fig. 1. Weekly VOCs concentration of withering zone emissions

III. BIOLOGICAL TREATMENTS

Vapor-phase biotreatments have been classified as Best Available Technologies for the abatement of VOC in air from various chemical industries by the European IPPC Bureau [6]. When recovery is not feasible, waste gas end-of-pipe treatment should give preference to low energy techniques.

Among abatement techniques for VOC compounds, three principal technologies are available: biofiltration, bioscrubbing, biotrickling.

Biofiltration has large applications treating odours. The waste gas stream is passed through a bed of organic material or some inert material such as clay, charcoal or polyurethane, where it is biologically oxidised by naturally occurring micro-organisms into carbon dioxide, water and biomass. Generally, the plants are organized as open biofilters, but enclosed biofilters may optimize the control of the process. The effectiveness of biofiltration is related to the chemical constituents and concentration, to the residence time, to the biofilter medium and its humidity and pH.

Bioscrubbing combines wet gas scrubbing (absorption) and biodegradation. The scrubbing water contains a microbe community suitable to oxidise the noxious gas components. The microbes are suspended in water. The conditions to use bioscrubbers depend upon contaminant properties. The process should be able to wash out contaminants and the washed-out constituents must be biodegradable under aerobic conditions.

Biotrickling works with similar conditions to bioscrubbing where an aqueous phase is continuously circulated through a bed of inert material. In contrast to bioscrubbing, the microbes are fixed on supporting elements. The surface properties should be such that the biofilm adheres firmly. The pollutants in the waste gas and the oxygen are absorbed by the water phase and transported to the biofilm, where the biological transformation takes place. Performance of reactors depends essentially on the mass transfer, and the prevention of clogging and exceeding salt formation is crucial.

IV. THE APPLICATION INVESTIGATED

A. *The plant*

For our investigations a combined process including all the three technologies was chosen, with the aim of energy saving and reduction of water and sludge disposal.

The prototype was built to control a fraction of the withering emissions from the factory. It has a working volume of 25 m^3 and a max capacity to treat 16000 m^3/h of exhausted air. A system of pipes and valves on vent holes was designed to allow for a possible reduction of the VOCs' concentration at the inlet of the prototype through dilution with clean air. Air flow rate was imposed by regulation of the velocity of the air extractor [7].

B. *Chemical parameters measurement*

CEE CEN 264 n.326 and UNI EN 13526 standards to determine TOC, VOC and CH_4 in emissions were applied to monitor continuously the biofilter performance. By means of alternate (3 min^{-1}) online sampling between inlet and outlet air flows, air samples were continuously withdrawn (0.6 l/min) by a F.I.D. analyzer (SIEMENS mod. FIDAMAT 6). In discontinuous mode, coconut charcoal tubes (Anasorb CSC, SKC Inc.) were positioned on the outlet pump flow for 30 min to confirm VOC concentrations by gas-chromatographic (GC) analysis [8].

C. *Microbial parameters measurement*

Detection and enumeration of microbial parameters were made by selective and not selective media utilizing decimal dilutions method of the specimen.

Plate-Count-Agar, was used for standard plate count of heterotrophic bacteria at 30°C [9].

Malt Extract Agar is a medium for the detection, isolation and enumeration of yeasts and moulds. Bacteria may be suppressed by the addition of 200 µg /ml tetracycline. Incubation was at 30°C [10].

VOC degraders strains were carried out by suspending solid or sludge samples collected from prototype in 50 mM phosphate buffer at pH 7.0. The suspension was then shaken (600 rpm) for 30 min. After dilutions, aliquots of these suspensions were plated on a solid minimal salt basal medium MSB (15 g l-1 Noble Agar, Difco, Detroit, MC, USA), transferred in an atmosphere saturated with the same VOC and incubated at 30°C [11].

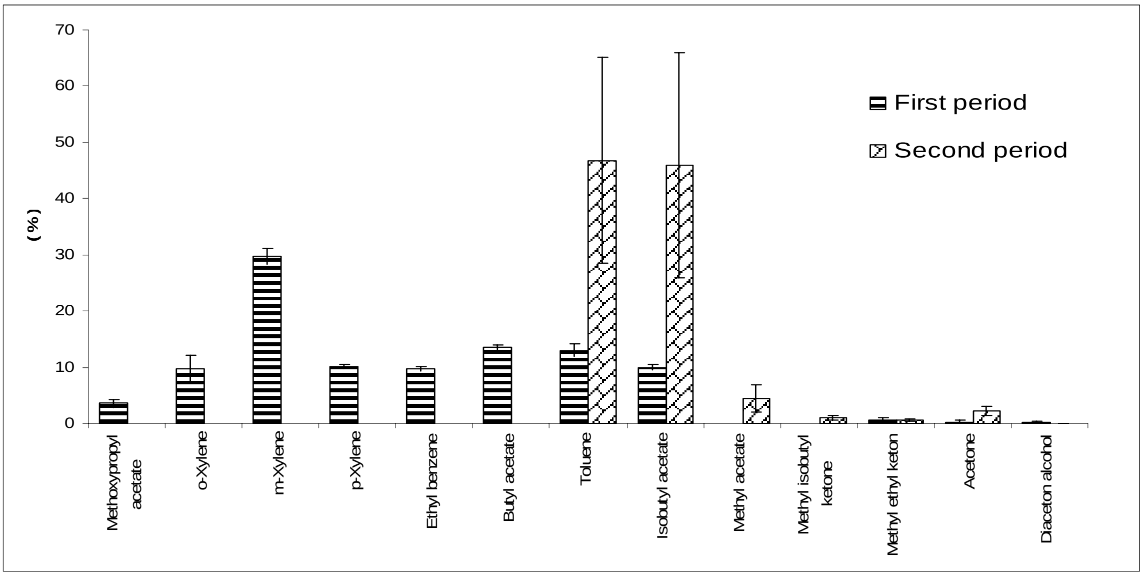

Fig. 2. VOC speciation of emissions in the first period (cold season) and in the second one (warm season)

MacConkey agar was used for the isolation of gram-negative enteric bacteria and the differentiation of lactose fermenting from lactose non-fermenting gram-negative bacteria. Incubation were at 37 °C and 42 °C [12].

Mannitol Salt Agar is a selective and differential medium for the detection and enumeration of staphylococci, incubation was at 37 °C [9].

V. RESULTS

The system start up was in July 2009. During the first period, fluid dynamic parameters have been optimized. Preliminary operation in the absence of any matrix was performed to check the absence of dilution due to clean air infiltration, and to optimize the equilibrium flow conditions between the biological system, the blower and the line connections to the drying room.

Considering that it would not have been possible to have a parallel control during the operation, undesired dilution phenomena were excluded, verifying the overlap of inlet and outlet VOC traces when the apparatus was empty of any filling material [13].

The start phase continued during the next four months, after loading a quantity of matrix, consisting of a mixture of inorganic and organic composted materials. The experiments were performed especially devoted to the evaluation of pressure drop in the material. As a starting parameter, a flow rate of 6000 m^3/h was chosen for all tests discussed here. In this phase reduced contact times (3-5 s) were maintained in order to evaluate the moisture content and pressure drop [13].

In the second period, a further quantity of prepared substrate was loaded into the biofilter, to reach the total working volume. The resulting empty bed residence time generally was of 30 s, but ranged between 10 and 70 s.

Organic loads of VOCs during the observed period were between 10 and 110 g C $m^{-3}h^{-1}$.

The temperature of both the material and the air was continuously recorded at various points, showing good control also in the occurrence of harsh weather conditions.

The operation of the biological system was extended over two periods, characterized by two different compositions of the emissions due to different varnish used for painting. The VOC speciation is reported in Fig. 2, where amounts are expressed in terms of average % value and standard deviation. The first period corresponds to the colder environmental conditions (matrix temperature range from 5 to 20 °C, average value 11.4 °C), whereas in the second period the matrix temperature is in the range from 15 to 25 °C (average value 19.1 °C).

A thorough control of emissions from plants and their reduction by filtration requires a continuous or very frequent measurement of VOC concentration. Various methods for VOC detection can be applied, with different ability to deal with quick variations in composition and concentration which can be encountered and actually lead to a misleading interpretation of the results. For the purpose of comparing some of such methods, for about two years the behavior of a pilot plant has been monitored by on line FID and by discontinuous sampling with sorbent tubes.

As mentioned above, fluctuations in the composition of the mixture often encountered in plants showed to influence the response factors of the instruments adopted to control VOC emission [8]. For this reason, the results from some analysis of samples taken discontinuously with sorbent tubes were compared with on line measurements by FID and PID taken during the sampling time (Fig. 3).

The comparison of concentrations at the inlet and outlet of the prototype allows for the evaluation of the removal efficiency as reported in Fig. 4, as a function of time and of the kind of sampling (continuous/discontinuous). In Fig. 5 the average values of the removal efficiency evaluated from continuous sampling are reported as a function of the inlet concentration. Standard deviations are also reported and the number of samples *n* is given [14],

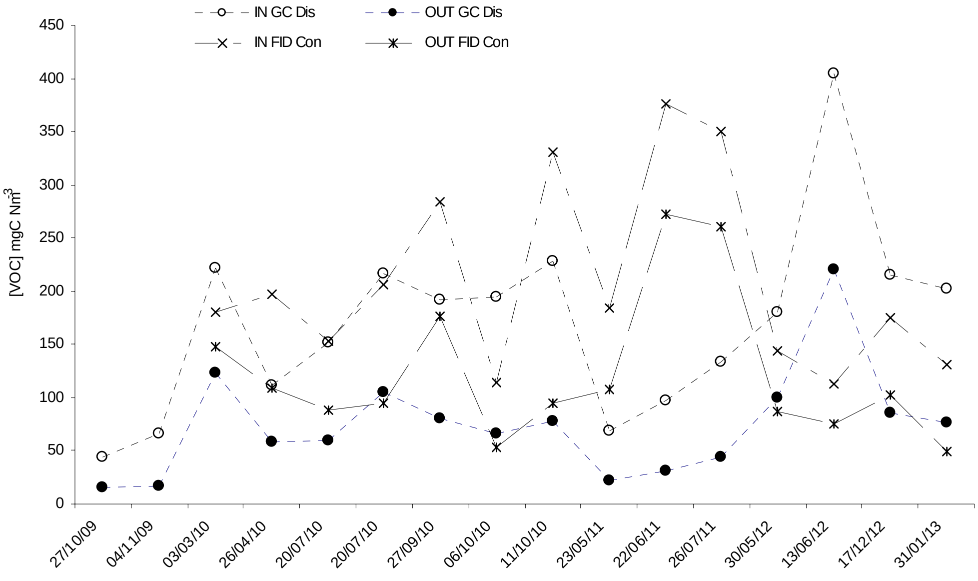

Fig. 3. VOCs concentration in discontinuos mode - GC Dis (IN and OUT) and continuous mode - FID Con (IN and OUT)

A correct management of the retention time and of the organic load at the inlet of the prototype was helpful to guarantee the respect of a threshold value.

The VOCs reduction was estimated on the basis of both the continuous and discontinuous VOCs measurements. Within each period, the reduction was found to be dependent on both the organic load and inlet VOCs concentration, but not on the septum temperature (range between 7°C and 25°C).

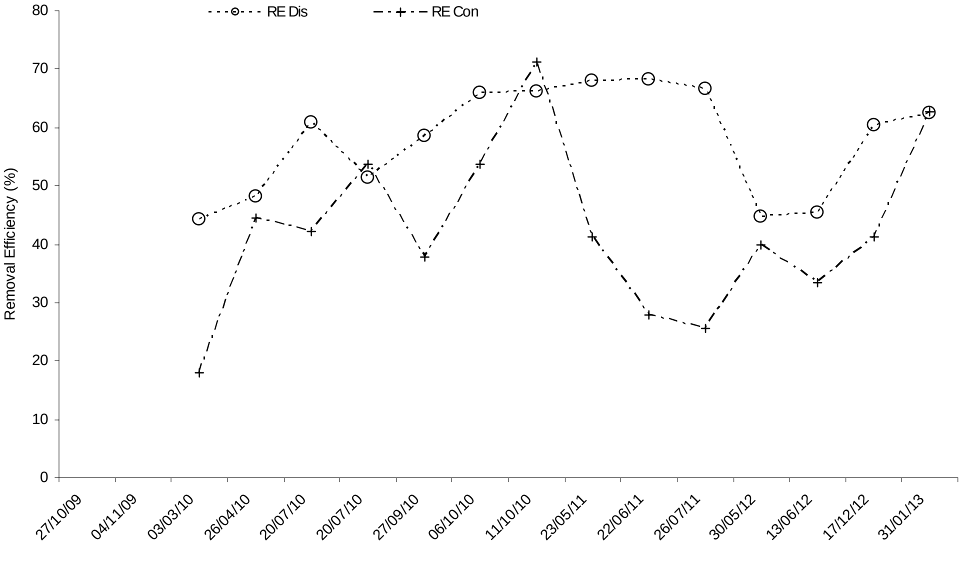

Fig. 4. Removal efficiency (%) at different interval times

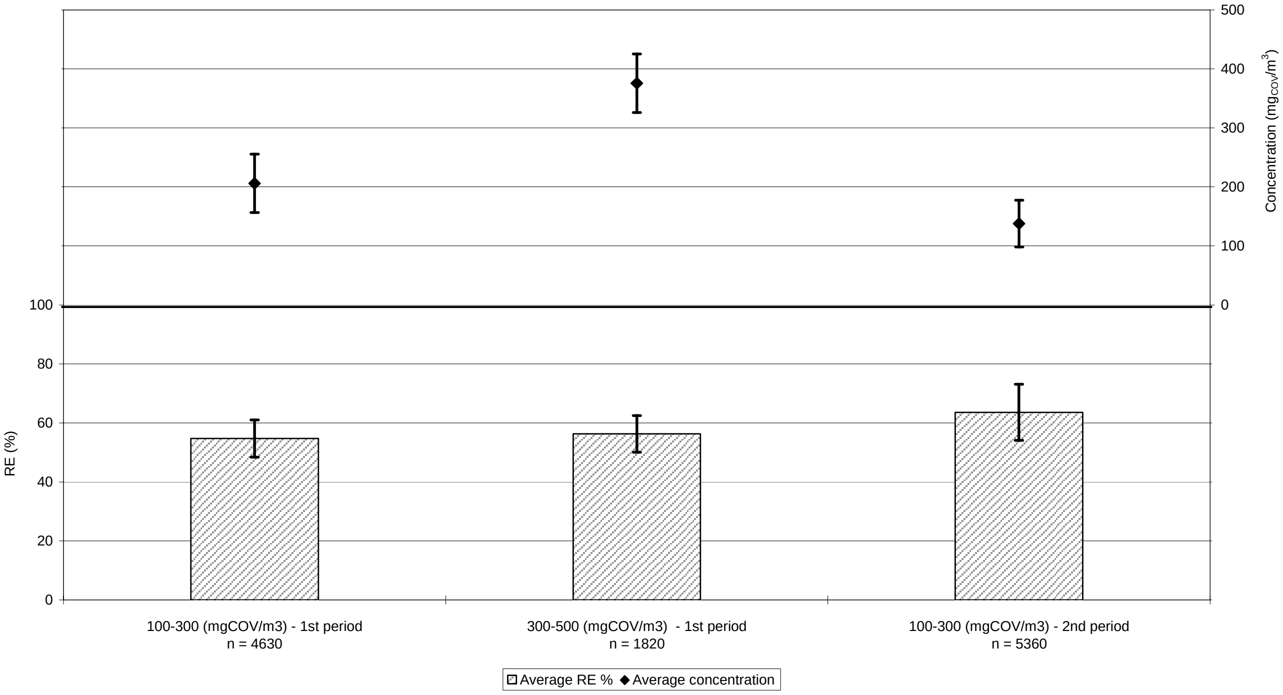

Fig. 5. Average removal efficiency (%) and inlet concentration at various concentration ranges and periods. Standard deviations are evaluated, being *n* the number of samples

VI. MICROBIAL ENUMERATION OF DIFFERENT FUNCTIONAL GROUPS

The research studied the main microbial populations involved in contaminated air treatment at different time intervals. In this case, a group of organisms that demonstrates the efficacy of a process was chosen as indicator.

The number of bacteria (ufc gr^{-1} d.w.) varied by type microbial indicators ranging from $1,96*10^9$ to $3,30*10^6$ heterotrophic bacteria, $2,4*10^7$ to $2*10^5$ yeast and moulds, $1,06*10^7$ to $8*10^3$ gram negative bacteria, $1,59*10^7$ to $2,34*10^4$ staphilococci bacteria, whereas degraders ranging from $2,27*10^9$ to $1,90*10^4$AB$^+$,$4,31*10^8$ to $1,69*10^3$ AC$^+$, $3,85*10^8$ to $1,13*10^4$ AE$^+$, $2,27*10^9$ to $5,72*10^4$ EPA$^+$, $7,48*10^8$ to $2,60*10^3$ MEK$^+$, $1,59*10^8$ to $4,19*10^5$ MIBK$^+$, $9,07*10^8$ to $1,75*10^3$ NAFT$^+$, $6,80*10^8$ to $2,60*10^4$ TOL$^+$, $1,61*10^9$ to $3,12*10^4$ XYL$^+$.

The behavior of microbial populations in the matrix of the prototype (growth, survival, or death) was determined by the properties of matrix and the operational conditions (e.g., temperature, relative humidity, and atmosphere). As a general consideration, it was possible to observe a constant microbial presence in all different sampling periods. This quantitative study showed a reduced effects in microbial populations and no correlation was found with variations of the main parameters (e.g. temperature). Other techniques should be implemented to follow the complex dynamics with microbial community allowing to understand the microbial ecology of the matrix.

VII. CONCLUSIONS

During two years of uninterrupted working period, the prototype gave the performance expected. Adopting an oligotrophic management it was also possible to maintain low operating costs. The removal efficiency of complex mixture of VOCs was considered good, with respect to the retention time adopted. The results of this work allow to set up some design rules for other VOCs abatement systems, with particular regard to their effectiveness, which is crucial when the area available for the plant is limited and the plant itself is considered as a part of an integrated solvent reduction management plan.

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