



Removal of odorous sulphur compounds from industrial gases by biotrickling filters

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Vincenzo Torretta¹; Marco Schiavon²; Enrico Anselmo Papa¹, Paolo Caruson³; Andrea G. Capodaglio^{4*}

¹Università degli Studi dell'Insubria, Varese, Italy
Department of Biotechnologies and Life Sciences

²Università degli Studi di Trento, Trento, Italy
Department of Civil, Environmental and Mechanical Engineering

³Air Clean Srl, Rho, Milano, Italy

⁴Università degli Studi di Pavia, Pavia, Italy
Department of Civil Engineering and Architecture

*Corresponding author: e-mail: capo@unipv.it,
vincenzo.torretta@uninsubria.it, marco.schiavon@unitn.it,
enricoanselmo.papa@uninsubria.it, paolo.caruson@aircleansrl.com

ABSTRACT

A pilot plant for the treatment of Sulphur-based odorous gases was installed in a line of a phosphoric acid plant located in Skhira, Tunisia. The air pollution control system train consisted of a first stage, including a chemical scrubber operating with an alkaline solution containing caustic soda, followed by a two-stage biotrickling filter (BTF) filled with *Mytilus edulis* shells. This study evaluated the performance of the dual-stage BTF in removing hydrogen sulphide (H₂S), sulphur dioxide (SO₂) and dimethyl sulphide (DMS) from the phosphoric acid reactor's exhaust air current. Concentrations of H₂S, SO₂ and DMS at the inlet of the two-stage BTF were 10-30 ppm, < 1-20 ppm and 16-30 ppm, respectively. All of the respective concentrations at the outlet of the biological step were < 1 ppm, except for the H₂S in the outlet during the first day of operation (10 ppm). Removal efficiencies were generally higher than 95% for all compounds, and remained high even with an increase of the off-gas flow rate. Mass-removal capacity was at least 2.0 g m⁻³ h⁻¹, 0.5 g m⁻³ h⁻¹ and 6.2 g m⁻³ h⁻¹, for H₂S, SO₂ and DMS, respectively. The removal efficiencies of the process were satisfactory, especially considering the already low inlet concentrations, due to the high quality of the raw phosphate used.

Keywords: hydrogen sulphide, odor abatement, phosphoric acid production.

Remoção de odores de compostos sulfurados de gases industriais por filtros biotrickling

RESUMO

Uma estação piloto para o tratamento de gases odoríferos à base de enxofre foi instalado em uma linha de uma fábrica de ácido fosfórico localizada em Skhira (Tunísia). A estação piloto é constituída por um primeiro estágio que inclui um scrubber químico que usa uma

solução alcalina à base de soda cáustica. O scrubber é seguido por um filtro biotrickling (BTF) de duplo estágio, preenchido com conchas *Mytilus edulis*. O objetivo deste trabalho é avaliar o desempenho do BTF na remoção do ácido sulfídrico (H_2S), dióxido de enxofre (SO_2) e sulfureto de dimetilo (DMS) contidos no efluente do reator de ácido fosfórico. As concentrações de H_2S , DMS e SO_2 na entrada do BTF de duplo estágio foram 10-30 ppm, < 1-20 ppm e 16-30 ppm, respectivamente. Todas as respectivas concentrações na saída do tratamento biológico foram < 1 ppm, com a exceção da concentração de H_2S durante o primeiro dia de funcionamento (10 ppm). As eficiências da remoção foram geralmente > 95% para todos os compostos e resultaram altas também após o aumento do fluxo do efluente gasoso. As capacidades de eliminação de H_2S , SO_2 e DMS foram > 2,0 $\text{g m}^{-3} \text{h}^{-1}$, 0,5 $\text{g m}^{-3} \text{h}^{-1}$ e 6,2 $\text{g m}^{-3} \text{h}^{-1}$, respectivamente. Apesar das baixas concentrações de entrada, principalmente devidas à alta qualidade do fosfato bruto, a instalação piloto mostrou resultados satisfatórios, tendo em vista o seu redimensionamento e a sua aplicação a uma escala maior.

Palavras-chave: abatimento de odores, ácido sulfídrico, produção de ácido fosfórico.

1. INTRODUCTION

Exposure to odorants is more a nuisance than an hazard to human health. However, prolonged exposure to odorants may cause adverse reactions ranging from emotional stress, such as anxiety, headache, or depression, to physical symptoms, such as eye irritation, respiratory problems, nausea or vomiting (Capodaglio et al., 2002; Shareefdeen and Singh, 2004). For these reasons, industrial activities that emit odorous compounds need appropriate removal systems in order to limit their presence in exhaust gases.

Control of pollution in large air flows with low concentrations of pollutants (generally < 100 ppm) is generally not economically viable when removal technologies require large amounts of fuel (electric energy), or when chemicals and adsorbents are adopted, due to the low achievable efficiencies (Hunter and Oyama, 2014). For this reason, the application of biologically-based technologies, which turn out to be more cost-effective than conventional ones (e.g., activated carbon adsorption, thermal or catalytic oxidation, absorption, selective catalytic or non-catalytic reduction), is becoming a popular alternative for industrial air pollution control.

Among biological technologies, biotrickling filters (BTFs) have recently gained increased attention due to their comparatively low cost and energy efficiency. In particular, BTFs have proven very effective in the treatment of industrial air streams (Rada et al., 2014), and have shown several advantages compared to the more common biofilters. These advantages are their limited size, longer life, lower pressure drop with subsequent lower power consumption, easy control of temperature, pH, salt concentration and metabolite accumulation, wide range of treatable pollutants, greater stability of operation and better atmospheric dilution of the plume (Xue et al., 2013). BTFs have been widely tested and applied in the treatment of exhaust air pollutants from pharmaceutical (Chen et al., 2006), paint (Mathur and Majumder, 2008), refinery (Viotti et al., 2015) and livestock industries (van Groenestijn and Kraakman, 2005), as well as wastewater (Lebrero et al., 2014) and solid waste treatment facilities (Gutierrez et al., 2014). BTFs are reactors partly filled with inert materials, such as lava rock, shells, and plastic spheres or rings, which serve as a physical support for the growth of biomass. Water is sprayed at the top of the reactor, creating a liquid biofilm on the filler for the absorption of pollutants, providing the microorganisms with the required nutrients and removing excess sludge or decomposition products from the reactor by scouring. The water is collected at the bottom of the reactor and recirculated back. Therefore, both pollutant absorption into the biofilm and biodegradation occur in BTFs.

A pilot treatment line for the removal of odorous sulphur gases, including hydrogen sulphide (H_2S), sulphur dioxide (SO_2) and dimethyl sulphide (DMS), was established at a phosphoric acid production facility in Skhira, Tunisia. Phosphoric acid is primarily used in fertilizer production and, secondarily, in the production of synthetic detergents, animal feed and pesticides. In this application, phosphoric acid is obtained by a wet process, consisting of the attack of ground phosphate rocks with sulphuric acid, the filtration of phosphoric acid from calcium sulphate (a byproduct of the chemical reaction), and the concentration of the phosphoric acid to the desired level. The chemical reaction leads to the formation of carbon monoxide, nitrogen oxides, SO_2 , hydrogen fluoride, ammonia, H_2S and DMS gases.

The adopted air pollution control system was designed to remove sulphur pollutants by means of a scrubber followed by a dual-stage BTF, and was operated for two months on site. This paper evaluates the performance of the dual-stage BTF in degrading the H_2S , SO_2 and DMS contained in the phosphoric acid reactor's off-gas. The paper presents the biological processes used in the test, the operating and testing procedures, and the results achieved in the abatement of these compounds.

2. MATERIALS AND METHODS

The treatment system studied is shown in Figure 1 and consists of:

- a chemical scrubber, operating with an alkaline solution for SO_2 reduction and H_2S partial abatement;
- a dual-stage BTF, downstream of the chemical scrubber, for the removal of the remaining sulphur odorous compounds;
- water recirculation pumps;
- an off-gas centrifugal pump;
- a control cabinet.

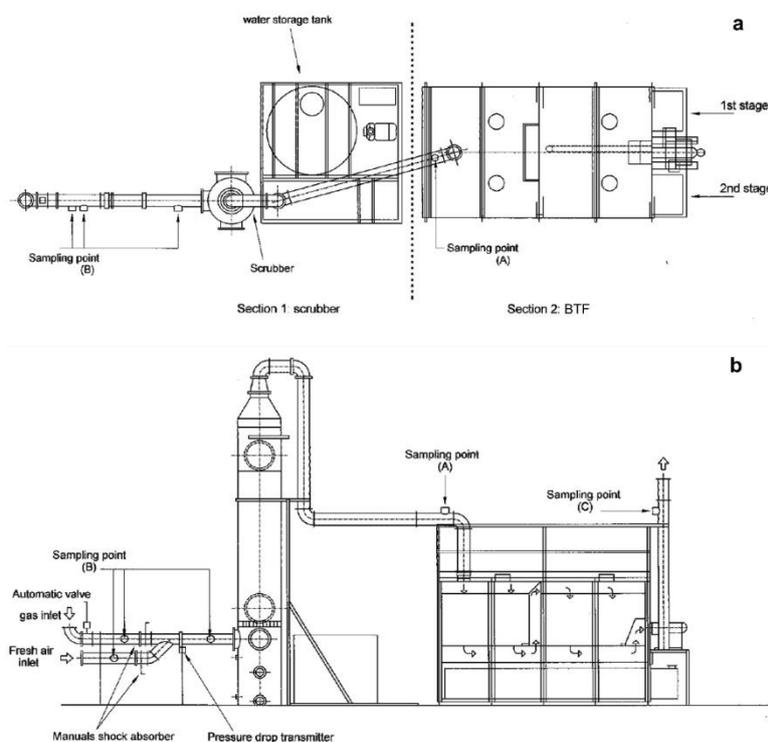


Figure 1. Exhaust air plant views: *a)* horizontal and *b)* vertical, with indication of sampling points.

The exhaust air under treatment is drawn by a centrifugal blower, located downstream of the entire system. The blower operates with a power of 3 kW, allowing a maximum flow rate of $1800 \text{ Nm}^3 \text{ h}^{-1}$. Air passes first through the scrubber, and reaches the BTF unit at a temperature lower than 45°C , a relative humidity around 80-100% and solid particle content lower than 20 mg m^{-3} . Throughout the whole experimental period, both the scrubber and the dual-stage BTF were operated continuously (24/7).

2.1. Scrubber operation

The scrubber used in this system consists of a vertical polypropylene cylinder with internal diameter of 0.8 m and height of 6.3 m. The scrubber operates with alkaline washing of caustic soda (NaOH solution $< 30\% \text{ v/v}$).

The main role of the chemical scrubber is to absorb the soluble pollutants in the exhaust gas stream into water, resulting in attenuation of the H_2S and SO_2 peak concentrations. In addition, due to its buffering capacity, the alkaline NaOH washing solution allows for the control of the pH of the gas prior to the biological treatment. The scrubber also serves as a backup system to control gas temperature and to protect the biological stage.

The washing solution is introduced from the top of the scrubber through spray nozzles, flowing by gravity through the absorption column to the bottom, where it is collected in a reservoir (diameter of 1.55 m and height of 0.33 m). The reservoir is equipped with a tap for NaOH addition, and another for water replenishment, ensuring a constant level and concentration of the washing solution in the tank. The washing solution is recirculated to the top of the scrubber with a pump, while the exhaust gas flows counter-currently from the bottom to the top of the absorption column, which contains plastic fillers with large specific surface area to improve the contact between the gas and liquid phases, thus enhancing chemical exchange. This, combined with a high ratio between liquid and gas flows, results in a high elimination capacity of the incoming pollutants. Finally, a high-efficiency droplet separator ensures good aerosol retention before transition to the biological stage.

2.2. Dual-stage BTF operation

The unit consists of a dual-stage biological filter and could be considered a biological washing tower. The incoming air from the chemical scrubber is passed vertically through an area filled with calcareous sea shells, continuously humidified by the water recirculated within the system via a centrifugal pump.

The filling material is a bed of natural shells belonging to blue mussels of the *Mytilus edulis* species, pre-treated prior to installation by an exclusive process (Monashell[®], patented). The filter bed has different functions, such as supporting the growth of the microorganisms that biologically oxidize DMS, H_2S and sulphuric acid; supplying additional nutrients to the biomass; humidity retention; forming a surface where pollutants can be absorbed; and stabilizing the pH. The latter is made possible through chemical reactions between the filter bed itself and the sulfates in the air stream. The *Mytilus edulis* shells are rich in calcium carbonate, present high affinity with weak acids, and provide a high buffering power to the system. The choice of this filling material offers several economical and process-related advantages: from an economic perspective, it is a recovered waste material and is thus available at low cost (compared to the costs required for its disposal); from the biological perspective, it facilitates absorption, since many odorous compounds are not easily soluble in the natural state. An additional advantage is low operating costs; for example, less water is necessary for pH restoration than in a bioscrubber, since pH is controlled by the filter bed itself.

The dual-stage unit consists of a modular bioreactor with a volume of 17 m^3 , where the filling material occupies a volume of 8 m^3 , placed within a container with a flat roof, all

supported by a concrete platform. The recirculation of the washing solution is supported by two pumps, each with a power of 1.1 kW, and connected with two nozzles working at the pressure of 0.8 Bar, with total flowrate of about 20 L min⁻¹. The treated emissions are released to the atmosphere through a stack (diameter of 0.2 m), providing a maximum outlet velocity of 16 m s⁻¹.

In the first stage, the recirculated water sprayed on the top of the filter bed flows through the filling material and exits through a PVC pipe, collecting the water to repeat the cycle. The first-stage effluent air is sent to the second BTF stage, characterized by separate circulation water and spray systems, where the cycle is repeated. The water levels in the storage tanks of both stages are controlled with level sensors.

In order to keep the solution clean and avoid a pH decrease of the recirculation water in the second stage, part of the washing solution is periodically wasted through a time-controlled (4 s h⁻¹) solenoid valve. An equal amount of water from the first stage is automatically transferred to the second stage, and fresh make-up water is drawn into the first stage tank from the supply network.

The BTF was initially seeded with a bacterial inoculum of *Thiosphaera pantotropha*, a selected bacterial culture capable of assimilating reduced-sulphur compounds.

2.3. Test Procedure

The pilot system was operated continuously for about 10 weeks. During this period, chemical, physical and microbiological analyses were carried out on the off-gas, in addition to microbiological analyses on the cell count of the mesophilic bacteria, both in the water solution and in the filtering material.

Off-gas analyses included temperature and H₂S, DMS, SO₂ concentrations; the latter were measured at the sampling points located upstream of the dual-stage BTF (A) and at the outlet (C). These are compounds of interest due to their abundance in the exhausts and to the low odor threshold values, equal to 0.00041 ppm, 0.0030 ppm and 0.87 ppm, respectively (Nagata, 2003). Tests were performed by varying the gas flow rate between 1200 and 1500 Nm³ h⁻¹, corresponding to an empty bed residence time (EBRT) between 16 and 24 s. In addition, the off-gas temperature was monitored at A, C and at a sampling point located upstream of the scrubber (B). The pressure drop between B and A and between A and C was measured also. Dräger tubes (Drägerwerk AG & Co. KGaA, Germany) were used for the analysis of H₂S, DMS and SO₂ concentrations. Analyses of recirculation water of both stages concerned pH, sulphate (SO₄²⁻) concentration, and temperature. SO₄²⁻ is an oxidation product of H₂S, SO₂ and mercaptans in the circulation water (Zhang et al., 2015); its concentration was measured with colorimetric strips (Merck KGaA, Germany). The presence of SO₄²⁻ in the BTF recirculation water is an indicator of biodegradation effectiveness.

During the ordinary running period, air concentrations of H₂S, SO₂ and DMS, and pH, SO₄²⁻ content and the temperature of the BTF recirculation water were sampled at least once per week.

3. RESULTS AND DISCUSSION

The combined scrubber-BTF system was initially tested at different airflow rates, with a maximum of 1800 Nm³ h⁻¹, as reported in Table 1. The purpose of this initial test was the quantification of the pressure drop at increasing flow rates. The total pressure drop, measured between the sampling points B and C, ranged from 70 to 245 mm H₂O when the air flow rate increased from 1200 to 1800 Nm³ h⁻¹. This airflow increase induced an increase in the pressure drop over the BTF that was anyway limited to between 10 and 45 mmH₂O.

In addition to the removal of the initial pollutants, a positive effect deriving from the scrubber unit operation is the reduction of the off-gas temperature from 44.0-53.6 °C in B to 32.0-36.7 °C in A (Table 1), favoring the growth of the biofilm.

After inoculation, the dual-stage BTF was started up. During the tests, thanks to the replenishing scheme of the recirculation water, its pH never fell below 6.5, from a maximum of 7.5 (Table 2).

Table 1. Velocity, temperature and pressure drop of the exhaust gas measured at sampling points A, B and C with different gas flow rates.

Gas flow rate [Nm ³ h ⁻¹]	Velocity [m s ⁻¹]			Temperature [°C]			Pressure drop [mmH ₂ O] scrubber biofilter	
	Sampling point			Sampling point			Sampling points	
	B	A	C	B	A	C	B-A	A-C
1200	11.4	10.7	10.6	53.6	35.6	32.0	60	10
1490	12.9	12.6	13.2	51.5	36.7	32.1	62	20
1470	15.0	12.1	13.0	50.3	35.0	31.3	90	30
1540	16.0	15.5	13.6	46.0	34.3	31.6	160	35
1810	16.5	16.2	16.0	47.0	33.2	32.2	196	45
1800	15.0	15.3	15.9	44.0	32.0	31.7	200	45

Three days after the BTF start-up, the biological bed was fully active; however, an acclimation period of about four weeks was necessary to reach full efficiency (Table 3). The concentrations of H₂S, DMS and SO₂ at the inlet of the dual-stage BTF (sampling point A) were in the ranges between 10 and 30 ppm, 16 and 30 ppm, < 1 and 20 ppm, respectively. The respective concentrations at the outlet of the biological step (sampling point C) were all < 1 ppm, except for the H₂S concentration during the very first day of operation (10 ppm). Removal efficiencies were generally higher than 95% for all compounds. Elimination rates were, at minimum, 2.0 g m⁻³ h⁻¹, 0.5 g m⁻³ h⁻¹ and 6.2 g m⁻³ h⁻¹, for H₂S, SO₂ and DMS, respectively. The analytical methodology used did not allow for the determination of concentrations < 1 ppm; therefore, the effective elimination rates may be higher than those here reported.

The removal efficiencies of the incoming pollutants were high even when higher off-gas flow rates were used. Concentration of SO₄²⁻ in the BTF recirculation water ranged between 20 and 90 ppm, indicating the presence of microbial activity degrading sulphur compounds (Table 2).

Other BTF pilot- and laboratory-scale applications for the removal of sulphur compounds reported in the literature generally referred to higher inlet concentrations: Chen et al. (2006) worked with H₂S inlet concentrations about 10 times higher than those reported in this paper, obtaining removal efficiencies > 90% at an EBRT of 9 s. Removal efficiencies > 95%, and elimination rates of about 50 g m⁻³ h⁻¹ were obtained by a BTF operating with an EBRT of 29 s, and inlet concentrations 10 times higher than those observed here (Montebello et al., 2013). Biodegradation of SO₂ was documented in a recent publication (Zhang et al., 2015) where a biofilter, operating with EBRT of 18 s degraded SO₂ in an air stream at 100-200 ppm, showing a removal efficiency > 93% and a maximum elimination rate of 50.67 g m⁻³ h⁻¹. DMS removal was the object of a study on a BTF application operating with EBRT of 120 s, which achieved a removal efficiency > 90% and a maximum elimination rate of 7.2 g m⁻³ h⁻¹, from an initial concentration of 117 ppm (Sercu et al., 2005).

Table 2. Chemical and physical characteristics of the recirculation water.

Day	1		2		3		8		13		21		27		36		48	
Gas flow rate [Nm ³ h ⁻¹]	1200		1200		1200		1200		1200		1470		1470		1480		1500	
BTF stage	1 st	2 nd																
pH [-]	7.3	7.3	7.2	7.3	7.3	7.2	7.4	7.5	7.3	7.4	7.2	7.0	7.0	6.5	6.8	6.6	7.0	6.6
SO ₄ ²⁻ [ppm]	-	-	-	-	-	-	60	60	20	20	60	30	30	90	30	30	-	-
Temperature [°C]	28.5	27.7	37.0	38.0	31.0	31.8	34.0	34.0	36.0	34.00	34.0	35.0	33.00	36.0	32.0	33.0	34.0	42.0

Table 3. Pollutant concentrations measured at sampling points A, B and C during the operational period of exhaust-treatment plant.

Day	1		2		3		8		13		21		27		36		48	
Gas flow rate [Nm ³ h ⁻¹]	1200		1200		1200		1200		1200		1470		1470		1480		1500	
Concentration at sampling points	A	C	A	C	A	C	A	C	A	C	A	C	A	C	A	C	A	C
H ₂ S [ppm]	30	10	20	< 1	20	< 1	13	< 1	10	< 1	15	< 1	10	< 1	13	< 1	10	< 1
SO ₂ [ppm]	20	1	20	< 1	20	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	2	< 1	-	-
DMS [ppm]	-	-	-	-	-	-	16	< 1	20	< 1	-	-	-	-	-	-	-	-

4. CONCLUSIONS

The performance of a pilot air pollution control system, consisting of a chemical scrubber followed by a dual-stage BTF, was evaluated on the off-gas line of a phosphoric acid production plant in Skhira, Tunisia. Analyses were performed of the off-gas sulphur compounds, specifically, of H₂S, SO₂ and DMS concentrations upstream and downstream of the BTF.

Based on the results obtained during the unit operation, the dual-stage BTF resulted in the very satisfactory abatement of sulphur compounds, reaching removal efficiencies generally > 95%, although inlet concentrations were already relatively low, compared to the values reported in similar studies. These were due to the high quality of the phosphate introduced into the phosphoric acid production reactor in the Skhira plant.

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