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PRELIMINARY TRIAL APPLICATION OF BIOLOGICAL DESULFONATION IN ANAEROBIC DIGESTORS FROM PIG FARMS

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Abstract

This paper describes preliminary tests carried out in treatment plants serving two different pig farms in Northern Italy, in order to assess the feasibility of implementing biological sulphur removal from biogas produced by anaerobic digestion processes. This normally consists of mixture of CH_4, CO_2, and other gases; in the presence of sulphur, H_2S is also formed, which must be removed prior to the gas use in thermal engines, to avoid corrosion phenomena. Sulphur removal in the plants considered is currently achieved by means of chemical filtration, however this adds costs to the process and generates a waste to be disposed of. As a process alternative, biological sulphur removal by means of *Thiobacillus sp.* bacteria can also be obtained. The process, however, requires specific conditions in the gas stream in order to achieve high process efficiency. Biological desulfonation was applied on a trial basis in two biogas production plants, with different layouts, and encouraging results. These confirms the validity of the process, although the maximum foreseen removal efficiencies were not achieved due to structural drawbacks of the tested facilities, that will have to be revamped in order to apply this process with full satisfaction and effectiveness.

Key words: anaerobic digestion, biogas, desulfonation, *Thiobacillus*

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1. Introduction

Pig farming, in Italy, is concentrated in the Po Valley area and, specifically, in the Regions of Lombardy and Emilia Romagna, where the 60% of the whole national sector is located (ENEL, 1996; Regione Emilia-Romagna, 1993). Even with some differences, based on different setup of facilities, swine farming produces mainly liquid wastes (2-3% SS) due of the great volumes of water (13-18 L/d·100 kg live weight) used in the conduction of this activity (ENEL, 1996). For this reason, unlike cow farming that produces mostly "palable" manure, which can thus be treated in place as a solid, pig farming requires specific processes, suitable to the liquid nature of the waste. Most swine farms in Italy are integrated in a larger rural economic setting, in which reuse and recovery of renewable resources are highly valued and encouraged by specific incentives from central and local governments. With these premises, it makes sense to choose a treatment alternative that requires as little energetic input as possible, and from which a renewable source of energy can be recovered: hence the widespread use of anaerobic digestion processes.

In the technical literature, methane productivity resulted in anaerobic digestion of pig and cow manure is theoretically determined as 516 and 530 L/kg VS respectively, while in practice their actual ultimate productivity lies somewhere between 275 and 356 L/kg VS in uninhibited conditions (Moller et al., 2003; Torretta et al., 2013). Ammonia inhibition can lower these yields by 50% or more (Hansen et al., 1998). Methane produced can thus be used to feed turbines and co-

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generators to produce heat and electricity that can be either used locally or, in case of the latter, sold to the national electrical energy grid at competitive rates (Rada et al., 2013).

The process of biogas production is well known in all its three main phases: *hydrolysis*, *acidification* and *methanogenesis*. In this third phase, when the production of methane takes place, other components of biogas are also formed (CO_2, N_2, H_2 and H_2S) and are therefore present in the final mixture. The variability of biogas composition is a direct consequence of the original substrate composition, and of the process variability that may occur during the digestion process as a result of changes in feed and environmental conditions. While biogas composition *per se* doesn't represent a major problem for its energetic use, the presence of water and sulphur compounds in the mixture requires the introduction of additional treatments (e.g. water condensation and sulphur removal) prior to its use. On the average, sulphur in biogas is less than 1% by volume (approx. less than 10 ppt), however, concentrations higher than 1,500-2,000 ppm already represent a serious obstacle for energetic use: with the combustion process sulphur (generally present as H_2S) oxidizes to SO_2 and SO_3 that, combining with water (steam) becomes sulphuric acid (H_2SO_4) and may induce serious corrosion problems to engines and turbines.

Currently, most commercial technologies for the removal of H_2S are chemically-based and relatively expensive to operate (Cha et al., 1999; Gabriel and Deshusses, 2003; Monteith et al., 2005) thereby reducing the financial benefits associated with potential revenues from the energy produced in a cogeneration plant. In our case studies' plants, iron oxide removal is currently adopted with good results, however, the disposal of the spent iron wool is becoming increasingly costly. For this reason, biological treatment for hydrogen sulphide removal has been considered as a possible alternative to the current processes (Oyarzún et al., 2003; Sercu et al., 2005) and has been implemented on a trial basis, in two biogas-producing facilities, located in Northern Italy, in the Provinces of Cremona and Bergamo, that are in need of structural expansion and technological updates. The aim of this work was to assess the potential to run a biological desulfonation process in full-scale anaerobic pig manure digesters, to the determine the correct ratio of air, verify the suitability of the environmental parameters necessary to start and maintain the biological removal reaction, while assessing the specific upgrading needs of the two plants considered in view of the possible introduction of this process.

2. Methods

The biological process implies the use of specific bacteria for the sulphur removal, *Thiobacillus*, a well known facultative species (Shrihari et al., 1993). *Thiobacillus* is an acidophilic species, widely diffused in the environment, particularly in presence of sulphur compounds; although it can use iron as electron receptor in anaerobic conditions, its ideal reaction is aerobic:

$$H_2S + OH^- \rightarrow HS^- + H_2O \tag{1}$$

$$HS^- + 0.5O_2 \rightarrow OH^- + S^0 \tag{2}$$

$$H_2S + 0.5O_2 \rightarrow S^0 + H_2O \tag{3}$$

In order to achieve microbiological oxidation of sulphur it is essential to add fairly precise stoichiometric amounts of oxygen to the biogas. Depending on the concentration of H_2S in the biogas, and on its overall composition, these correspond to approx. 2 to 6% of air in the gas. The simplest method is to add oxygen, or ambient air, directly into the digester, or in the gas holder. *Thiobacilli* are a ubiquitous specie, and thus do not usually require inoculation. They proliferate on the surface of the digestate, which provides a micro-aerophilic surface and the necessary nutrients, forming visible yellow clusters of sulphur. Depending on environmental parameters (temperature, reaction time, amount and mixing of the added air), hydrogen sulphide concentrations can be quickly reduced by 95 %, to less than 50 ppm in optimal conditions, as reported in the literature (Kijlstra et al., 2001). The optimal pH interval for *Thiobacillus* to operate is between 1.3 and 4.5, with an operative temperature range between 10 and 37 °C, although the optimal range for maximum efficiency is mesophilic, with interval between 30-35 °C.

In Plant 1, the digester receives biological sludge from the farm/dairy factory wastewater treatment plant. The plug-flow reactor is designed to operate at mesophilic conditions, achieved by sludge heating and external insulation. Biogas is collected in the gasholder dome which maintains the gas at the required operating pressure (200 mm air column); after this it is collected, desulfurized (iron oxide process), and send to a co-generator that provides 90 kW (electric), sufficient to meet the plant's needs, and about 175 kW (thermal) as hot water (at 70°C) that is used for digester heating and other general uses within the farm.

In Plant 2, the anaerobic digester is fed with separated (primary) sludge, while the clarified wastewater is conveyed and treated at a public WWTP. The digester, an up-flow type reactor, is operated in mesothermal conditions, to guarantee sewage stabilization with a hydraulic retention time of twenty days. A gasholder dome provides gas capture and operating pressure control. The gas is subsequently filtered and treated for the removal of water content, so to be used in co-generation in a gas-fed engine with a maximum output of about 80 kW. The mean biogas composition of both facilities, in the period preceding the tests are reported in Table 1.

Table 1. Biogas mean composition

CH_4	66-73%
CO_2	30-31%
N_2	2-5%
O_2	0.3%
H_2	1-2%
H_2S	0.18-0.5%

Initially, produced biogas was sampled at both locations, in order to evaluate O_2, CH_4, H_2S contents; external air and sewage temperature were also monitored, with sampling frequencies varying during the study. As both plants were not originally fitted with biogas meters, produced volumes were inferred by the count of the co-generation engines' running hours (at known, and constant, consumption) as these were registered by a connected computer. With these biogas production (daily) estimates, it was possible to define the correct amount of air to insufflate into the digesters by time-controlled, constant-flow pumps ($Q_{max} = 60$ m^3/h). All subsequent tests, at both plants, were run by adding increasing volumes of air into the digesters, and by sampling of CH_4, O_2 and H_2S to check concentrations variability.

On the basis of examined literature data, the initial target amount of digesters' air-to-biogas ratio necessary to achieve an effective biological sulphur removal, to be experimentally confirmed, was estimated to be between 2% and 6%. A further indication in this sense came from theoretical verification through stoichiometric calculation of the different compounds from REDOX reaction (3): this indicates that 0.469 g of O_2 react with 1 g of H_2S. Considering the average biogas composition at the two plants herein considered (Tables 1 and 5), and the molecular weights of the compounds involved, the theoretical amount of air necessary to trigger and maintain the reaction were estimated equal to 3.316% for the first plant and about 7% for the second. These values were well within, or close, to the above mentioned literature range (2-6%); furthermore, they were compatible with the wide and well-known variability of gas composition; thus they were selected as a starting point for further experimental verifications.

Air flows, determined according to the previous' day estimated biogas productions, were therefore insufflated into the two reactors while checking process parameters in order to determine both the minimum quantity needed to trigger the biological desulfonation process, and the maximum amount beyond which the process became unstable.

3. Experimental phase

At Plant 1, tests started with a 4% air/biogas ratio and lasted for seven days. At this rate, air addition was effective in starting the biological process, and in reducing the initial H_2S concentration of 2,500 ppm registered in the first sampling day (Table 2) to a final stable value of 1,600 ppm after day 5. From that day, H_2S concentration remained leveled at 1,600 ppm, while O_2 concentration decreased from 0.8% to 0.4%, as it was consumed by *Thiobacillus* in the biologic reactions (2) and (3), (Table 2 and Fig. 1). Average sulfur removal yield during this phase reached therefore 64%.

During this phase, both temperature and methane concentration in the biogas were fairly stable, however digester process temperature was quite low during due to large contributions of cold rinsing water coming from cleaning operations at the farm. These contributions (with lower organic matter concentrations and the lower temperature) probably influenced the reaction rate, slowing it down.

During the following week, with a higher process temperature, this time close to the mesophilic range, the air-to-biogas ratio in the digester was increased to 5%, and H_2S concentration reached a new stable minimum at 900 ppm, with O_2 level close to 0.7% (Table 3, Fig. 2).

Table 2. Process parameters at 4% air/biogas ratio

Day	*T [°C]*	*O_2 [%]*	*CH_4 [%]*	*H_2S [ppm]*
1	16	0.5	72	2,500
2	17	0.6	72	2,100
3	16	0.5	71	2,000
4	18	0.7	73	1,800
5	18	0.8	72	1,600
6	17	0.7	71	1,600
7	17	0.4	73	1,600

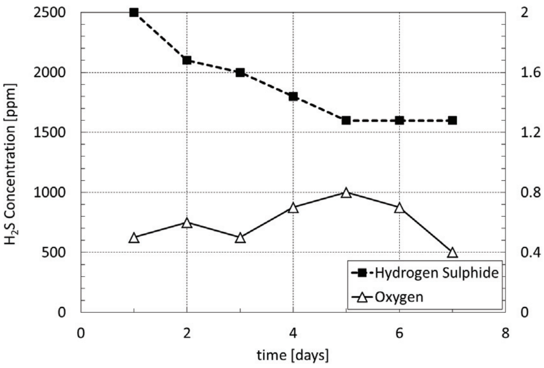

Fig. 1. H_2S and O_2 concentrations – 4% air/biogas ratio

Table 3. Process parameters at 5% air/biogas ratio

Day	*T [°C]*	*O_2 [%]*	*CH_4 [%]*	*H_2S [ppm]*
1	32	0.7	72	1,100
2	32	0.65	73	1,100
3	33	0.75	72	1,000
4	34	0.75	72	900
5	33	0.7	72	900
6	33	0.7	72	900

In the following weeks, increasingly higher air-to biogas ratios (namely 7, 10 and 15%) lead at first to an observed maximum of sulphates removal efficiency (80%), corresponding to a minimum observed concentration of 500 ppm (at 7% air-to-biogas ratio). After this maximum observed removal, process efficiency degraded progressively with increasing air-to-biogas ratios, returning quickly to H_2S concentration levels up to 1,600 ppm, likely due to inhibition. Moreover, variable O_2 and methane concentrations, recorded during the latter phase of the experimentation, showed how the process had departed from steady-state conditions (Table 4, Fig. 3).

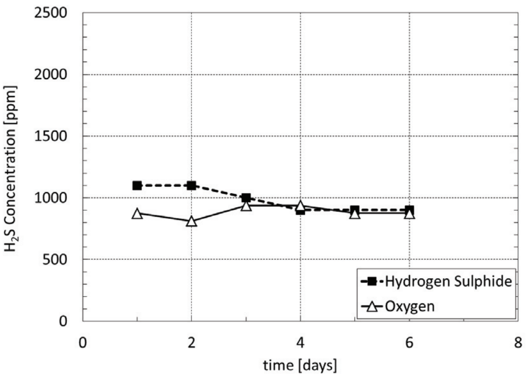

Fig. 2. H_2S and O_2 concentrations – 5% air/biogas ratio

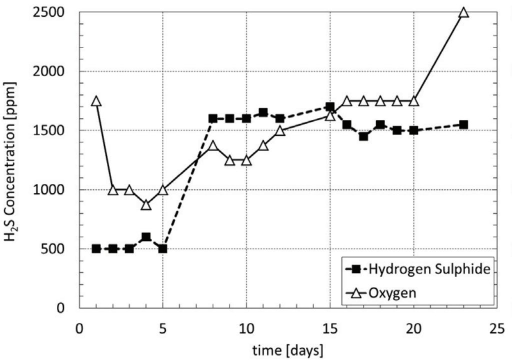

Fig. 3. H_2S and O_2 concentrations – 7, 10 and 15 % air/biogas ratios

Table 4. Process parameters at 7, 10 and 15% air/biogas ratios

Day	*Air-O_2 [%]*	*T [°C]*	*O_2 [%]*	*CH_4 [%]*	*H_2S [ppm]*
1	7%	31	1.4	70	500
2	7%	32	0.8	70	500
3	7%	30	0.8	70	500
4	7%	34	0.7	73	600
5	7%	32	0.8	70	500
8	10%	30	1.1	71	1,600
9	10%	30	1.0	70	1,600
10	10%	31	1.0	68	1,600
11	10%	31	1.1	69	1,650
12	10%	30	1.2	68	1,600
15	15%	30	1.3	67	1,700
16	15%	31	1.4	70	1,550
17	15%	31	1.4	70	1,450
18	15%	31	1.4	68	1,550
19	15%	31	1.4	68	1,500
20	15%	32	1.4	69	1,500
23	15%	30	2.0	66	1,550

Globally, results from the tests on Plant 1 confirmed the potential for the application of biological removal of sulphides, although the maximum efficiency achieved in this instance only reached 80%.

Tests carried out on the second plant were made in the same period (Oct. - Jan.) and with similar modalities. In this case, against reasonable expectations, the theoretically calculated value of air-to-biogas contents necessary to trigger the process (7%) did not work as expected. Recorded daily results were far from those hoped for, as shown in the following Table 5, due to high process instability.

Table 5. Obtained H_2S concentrations at 7% air/biogas ratio

Day	*Sewage T [°C]*	*O_2 [%]*	*CH_4 [%]*	*H_2S [ppm]*
1	13.6	0.6	79	1,500
2	15	0.8	84	900
3	16	0.8	82	700
4	15	1.0	80	600
5	19	1.0	67	2,000
6	21	1.0	64	2,000

Data show an initial reduction of H_2S concentrations correlated mostly with a progressive increase of sewage temperature, and a subsequent unexplained "explosion" of H_2S contents. The first part can be reasonably related to an increasing biologic activity with warmer conditions inside the digester, while in the last two days process inhibition of some sort may have occurred. After restoring steady-state process conditions, a 10% air-to-biogas ratio was applied. These conditions led to the better results, shown in Table 6 and Fig. 4.

Table 6. Obtained H_2S concentrations with 10% air/biogas ratio

Day	*Sewage T [°C]*	*O_2 [%]*	*CH_4 [%]*	*H_2S [ppm]*
1	23	0.6	66	1,800
2	25	0.8	70	1,200
3	26	0.8	73	1,000
4	27	0.8	70	900
5	29	0.8	71	850
6	29	0.8	70	800

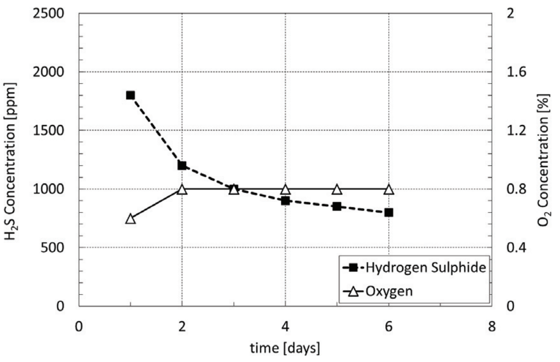

Fig. 4. H_2S and O_2 concentrations – 10% air/biogas ratio

At 10% a/b ratio, an over-all removal yield of 78% for H_2S was obtained. After this, it was not possible to further continue the tests due to a mechanical failure that forced a prolonged maintenance shut-down of the system.

4. Discussion

Although the observed sulphur removal yields in the two treatment plants were distant (78-80%) from those reported in literature (95-98%), the test allowed to gain useful indications to validate the possibility of switching from physico-chemical H_2S removal to biological process removal in both sites. The process showed that it could work fairly satisfactorily even in non-optimal and loosely controlled conditions. Tests proved that it is fundamental to determine the correct amount of air to maintain the biological reaction in a steady-state condition: indirect evaluations, based on engine consumption and running times, led to estimate errors that may have been the main cause of unattainment of the expected removal yields. Exceeding air dosages can determine process inhibition and therefore a reduction of H_2S removal; this could be explained with the appearance, at higher O_2 concentrations, of other aerobic groups of bacteria in competition with Thiobacillus. On the other side, a less-than-adequate air supply will also lead to process failure and a quick return to initial H_2S concentrations.

As it is well known, the daily amount of biogas produced in a digester is strongly variable and bound to different environmental, operational and technical parameters; factors such as periodical washing of livestock's beddings with cold water or the administration of antibiotic compounds with food, can trigger quantitative and qualitative variations in the sewage and consequently in the biogas production rate and composition. For those and other reasons it is necessary that a biological desulfonation process be supported by an accurate online biogas flowrate measurement system, therefore it has been suggested to the operators of both facilities to install such meters. Process temperature can also play an important role in the process, as shown by the first set of tests. In the case of adoption of a biological desulphonation process, operators will have to be careful with the handling of wash water in order not to excessively alter operating temperatures. Finally, better control of air insufflation conditions and more accurate air-phase mixing in the digesters are also required to achieve higher process efficiencies.

Even with the added instrumentation needed for process control, it appears that the cost of biological desulfonation would be in both cases lower than that of a traditional physico-chemical process in the long run. The biological desulphonation process has shown several advantages: it was cheaply implemented, required minimum hardware and did not generate additional waste streams. It also requires a minimum training of the plant personnel and can achieve high efficiency in just a few days.

5. Conclusions

The biological desulphonation process was applied on a trial basis at two biogas producing facilities associated with pig farms in Northern Italy. The purpose of the tests was to determine whether the process could be easily and economically applied in view of a revamping of both facilities.

While obtained results do not replicate the maximum removal yields obtained in the literature, they appear interesting, as they show achievement of relatively good removal efficiencies by means of biological desulfonation, even in the presence of suboptimal process facilities. It is believed that after their due structural and technological updates, its application can result in much higher yields.

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