Plasma Supported Odour Removal from Waste Air in Water Treatment Plants:
An Industrial Case Study

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ABSTRACT

Effects of plasma assisted waste air treatment from a water treatment plant have been investigated in several field tests. In particular the off-air for a thermal sludge dryer was investigated and treated. The intention of this study was to prove whether plasma assisted technologies are a possible solution for the removal of odour from waste air emitted by wastewater treatment facilities. The plasma treatment was combined with a catalytic (copper-manganese) unit, a scrubbing unit, or a bio filter in order to demonstrate the abilities for waste air deodorization. The inlet and outlet gas was analysed by means of FTIR, FID, and chemical sensors and the odour removal was investigated by standardized olfactometry. A significant reduction of hydrogen sulphide and methane by means of combined plasma-catalyst-treatment has been measured, but the removal of hydrogen sulphide leads to the formation of unwanted by-products. Main effects of plasma treatment in the field tests can be compared to the results of laboratory studies published in the literature. A significant odour reduction up to about 90% was measured. Aldehydes and other hydrocarbons are marginally removed by plasma treatment as well as by the bio filter. The bio filter released sulphur containing substances (DMS, CS2, DMDS) which can be destroyed by plasma-catalytic treatment. Based on the results of the field tests a reliable concept for an industrial after treatment installation has been designed as described. Due to the high content of H2S a scrubber as the first treatment unit is desired. Downstream the scrubber the plasma/catalytic unit combined with the existing bio filter is proposed for the removal of the hydrocarbons and other odorous constituents.

Keywords: Non-thermal plasma; DBD reactor; Odour removal; Deodorization; Atmospheric pressure discharge; Air treatment technology.

INTRODUCTION

In many industrial processes exhaust gases with chemical contaminants are released to the atmosphere. Beside the environmental effects the local population near emitting facilities often complaints regarding unpleasant odour emissions. Thus odour management is a major issue for many industrial operators which have traditionally been maintained by the use of buffer distances between industrial sites and receptors or by the installation of odour abatement systems in the exhaust installations (Stuetz and Frechen, 2001). Due to the population growth and increasing global urbanization residents and industry are coming into closer proximity which has increased the needs for more strict regulations of odour emissions. Since the 1970’s most industrial countries began to develop odour emission regulations which standardize the methods of odour measurement and require the application of state-of-the-art technology for prevention.

Several deodorization methods are available. These can be classified as physical, chemical and biological techniques, respectively. The odor substances are either adsorbed and subsequently removed or directly converted to harmless substances, like CO2 and water. Chemical deodorization processes include scrubbing and combustion. In both cases after treatment of the effluent water or NOx-containing combustion gases (e.g. by means of catalysts) is required. Physical processes are based on the adsorption of odor molecules at synthetic zeolites or activated carbon. The adsorption material requires regeneration by thermal processes (e.g. steam) after a certain time of loading. Bio filtration uses living material to capture and biologically degrade pollutant molecules. In bio scrubbers biologically active, nutrient-rich scrubbing solution is sprayed or
Species are generated without a significant increase of the gas enable synergetic effects with catalysts (Van Durme et al., 2007; Kim et al., 2007; Mizuno, 2007). Non-thermal plasma can be generated in the main exhaust gas flow or in a bypass by means of a gas discharge, e.g., corona or barrier discharge. The plasma generates active molecules, like radicals and ions as well as ozone which oxidize odorous substances. In non-thermal plasmas the active species are generated without a significant increase of the gas enthalpy. Such process can be controlled by the electrical operation parameters of the discharge arrangement (amplitude and frequency of the applied voltage). Furthermore, plasma species interact with disposed surfaces giving the possibility to regenerate subsequent adsorbing agents or enable synergetic effects with catalysts (Van Durme et al., 2008). Thus plasma supported methods are an attractive alternative to the classical deodorization processes in particular for low contaminated gas flows (Kim et al., 2007). Every industrial exhaust gas situation is complex and specific but the efficiency and ability of plasma assisted treatment methods depends on many conditions, e.g., type and concentration of pollutants, temperature and humidity of the gas. Thus the question whether a plasma based method is well suited for the deodorization of a wastewater treatment plant cannot be answered without a study at realistic conditions. In order to carry out the possibilities of plasma technology for such a task the following case study was performed. It contains the application of plasma arrangement at different sites of the water treatment installation together with the study of the effects of the plasma-supported catalytic treatment on the gas composition. Gas analyses (Fourier-transform infrared spectroscopy FTIR, flame ionisation detection FID, gas chromatography coupled with mass spectrometry GC/MS, electro chemical sensors) as well as offactometric studies were conducted in parallel. The description of the detailed plasma chemistry including mass-balance etc. is outside the scope of this contribution. The conditions at the field tests sides did not allow required systematic studies for such a task. In particular the humidity and temperature are fluctuating and the number of involved chemical constituents can be large while the time of plasma operation and number of samples is limited in a facility under regular operation. However the field tests presented here can proof whether there is an effect by plasma assisted methods on the gas composition, and the odour status as well as provide information about the formation of unwanted by-products. Such information shall stimulate more systematic work in the laboratory but also gives important hints for the design of a full exhaust treatment installation as discussed at the end of this contribution.

The paper is outlined as follows: the first section will summarize the state of knowledge and technology regarding gas depollution by means of plasmas. The following section will describe the materials and methods used for field test at a wastewater treatment plant in Poznan/Poland. Section three will contain the main results and present the deduced concept for a plasma supported deodorization installation at a selected water treatment plant.

**Odor Removal by Means of Non-Thermal Plasmas**

Plasmas have been demonstrated to be able to decompose volatile organic compounds (VOCs) and thus odour molecules very efficiently for low decontamination levels (<< 1 gCorg/Nm³; i.e., 100 ppm or lower; see e.g., Müller and Zahn, 2007; Kim, 2004; Kim et al., 2007; Mizuno, 2007; Chang, 2008). Many VOCs, e.g., aldehydes, fatty acids, alkanes, formic acid, amines, esters, or thiols have a strong and unpleasant odour (so-called OVOCs - Odour Active Volatile Organic Compounds).

In non-thermal plasmas the chemical processes are based on non-thermal activation of particles via collisions. The quality and quantity of collisions is determined by the density of species and the kinetic parameters (e.g., mean velocity, collision frequency). During electrical breakdown of the gas free electrons with high kinetic energies are produced via ionizing collisions. Electrons undergo further electron-molecule collisions with quite different reaction rates determined by the corresponding energy thresholds and gas temperature. A multitude of inorganic reactions follows due to the formation of radicals. In air plasmas at low gas temperatures reactive oxygen species like ozone (O₃), O and OH as well as HO₂ as strong oxidizing agents are formed. Many molecules are readily attacked by free radicals (Kogelschatz, 2003; Fridman, 2008). To give an example the removal of saturated hydrocarbons starts with the dehydrogenization followed by the oxidation of the remaining organic radical. The latter reaction result in the formation of peroxy radicals (R-HO₂) which are further oxidized down to CO₂ and H₂O (total oxidation) or trigger a radical chain reaction with alkyl hydro peroxide radicals (R-HO₂). In case of unsaturated hydrocarbons additionally radical addition following oxidation, radical chain reaction or polymerization of hydrocarbons take place (Storch and Kushner, 1992; Kogelschatz, 2003; Kim, 2004).

In many situations, e.g., water treatment plants, sulphur containing molecules like hydrogen sulphide (H₂S), dimethyl sulphide (DMS, (CH₃)₂S) or other thiols are responsible for bad smell of exhaust gases. A comparative study of the
decomposition of H2S, DMS and ethanethiol (C2H5SH) was presented by Jarrige and Vervisch (Jarrige and Vervisch, 2007). All three pollutants could be completely removed when a sufficient energy density was deposited in the plasma. The efficiency of the process increased with decreasing the initial concentration of sulphide compounds, while the energy yield (mass of removed compounds per kWh) remained almost unchanged. SO2 was the only identified by-product of H2S decomposition, but the sulphur balance suggested the formation of undetected SO3. The by-products analysed during the degradation of DMS and C2H5SH enabled to propose a reaction mechanism, starting with radical attack and breaking of C-S bonds (Jarrige and Vervisch, 2007).

Laboratory studies, field test results and an industrial plasma deodorization system in a rubber manufacturing factory with H2S as the main pollutant were presented by Mizuno (Mizuno, 2007). The H2S removal performance in a laboratory system consisting of pulsed driven corona with a downstream catalytic adsorbent layer was investigated with H2S concentrations more than two orders of magnitude higher concentration as in the real industrial situation. The pulsed plasma system had better deodorization performance than the traditional adsorption method and the lifetime of the catalytic adsorbent was three times longer than that without plasma operation. Field tests made for rubber and spice factories with direct treated sample gas flows of up to 60 m3/h demonstrated significant and temporally stable odour removal by means of olfactometric measurements. A reasonable energy consumption of about 0.36 J/L was required. The industrial installation at the rubber manufacturing factory is able to treat gas flows of up to 42,000 m3/h.

In water plant exhausts many different pollutant molecules are present. Beside sulphur compounds and other VOCs, ammonia (NH3) must be considered. Simultaneous treatment of H2S and NH3 using non-thermal plasma was investigated by Ma et al. (2001). Beside a barrier discharge arrangement in plane-to-wire arrangement (direct treatment) an additional ozone generation chamber before the plasma reactor was investigated. The decomposition efficiency of H2S or NH3 decreased with increasing initial concentration of pollutants, and increased with increasing amount of injected ozone (up to 25 ppm) and relative humidity. The injection of NH3 into H2S stream (concentration up to 80 ppm) did not improve the H2S decomposition efficiency but was necessary for the removal of other sulphite-containing compounds in the discharge exhaust.

Plasma has been demonstrated to be well suited for low contaminated gas flows (Kim, 2004; Kim et al., 2007; Mizuno, A. 2007). Today processes are applied for industrial purposes, which use medium- to high-frequency alternating currents between 400 Hz and 18 kHz at voltage amplitudes of 4 to 12 kV (pulsed or frequency controlled; Holub and Kalisiak, 2010). The plasmas are generated in discharge vessels that can be constructed in a lot of ways. Barrier discharges are the most typically used, since they enable easy operation and power control. Due to its compactness plasma devices can be easily integrated in existing systems and processes, but special attention must be paid to the reactor geometry since it determines the residence time as well as the back pressure which must be as low as possible in certain cases (Müller and Zahn, 2007; Rafflenbeul, 2008). The direct treatment of the full exhaust gas flow is often not possible due to the high waste air mass flows. In practice only a small waste gas flow or fresh air mass flow (usually 3 to 5% of the total waste air mass flow) is treated with the plasma device and admixed to the total waste air mass flow. This method of indirect treatment has the disadvantage that the effects of transient reactive components on the pollutant degradation are limited. Undesired by-products can be formed since the plasma-chemical conversion which can be quite un-selective. In industrial practice, plasmas are usually combined with catalysts, adsorbing agents and other methods of depollution. Compounds not yet oxidised in the plasma zone may be retained on the surface of the catalyst or adsorbing agent. In such case the catalyst or adsorbing bed is considered as a storage reactor which is regenerated by plasma species and simultaneously decomposes the residual ozone. Such installations are successfully used in gastronomy as well as in the food processing industry (Müller and Zahn, 2007; Rafflenbeul, 2008). Rafflenbeul Engineers presented a commercial plasma process combined with a bio filter as pre-filter and oxidation catalyst as after-filter (Rafflenbeul, 1998). Biodegradable compounds in higher concentrations are decomposed in the bio filter, while the subsequent plasma unit partially oxidizes non-biodegradable pollutants which are finally decomposed in the oxidation catalyst section at moderate temperature. Several commercialised combinations of non-thermal plasmas with catalysts or molecular sieves for waste management facilities, paint shops and other industrial applications generating exhaust streams of up to 300,000 m3/h have been described (Rafflenbeul, 1998).

PROCEDURE OF FIELD TESTS, MATERIALS AND METHODS

The treatment of waste water proceeds in several steps, namely floatation, sedimentation, biologic tanks, filtration, sludge removal and drying. Thus waste treatment plants can have numerous emission fields. The current study was focussed on the emission at the thermal sludge dryer as the most odorous site in the proposed wastewater treatment facility (Aquanet/Poznan). Currently the waste air after the thermal sludge dryer station is treated by a bio filter which showed partly not satisfying results in the past. The main problem was that the bio filter can be hardly controlled by operation parameters which would be beneficial in a real situation with fluctuating odour emissions.

Plasma Device and Mobile Test Facility

A mobile facility with different reaction units (Rafflenbeul Anlagenbau, Germany) has been used for the field tests. A partial gas flow was extracted from the main exhaust flow by a ventilator placed in the mobile test facility and guided to this by flexible tubes. The mobile facility further contained the plasma reactor, catalytic stages, a FID device for gas analysis and ozone detection devices. The plasma reactor
was based on the principle of the dielectric barrier discharge, i.e., the discharge arrangement consisted of several plates of dielectric material with mesh electrodes in between. High voltage with amplitudes of 7–8 kV (rms) and frequencies between 350 and 400 Hz was applied to generate the plasma. The total power of the plasma reactor was controlled between 300 and 600 W. The plasma was operated with a gas flow of fresh air (so-called reaction air), which was then admixed to thepartial sample gas flow from the emission source (so-called indirect treatment or bypass installation). The temperature of the sample gas flows (and thus relative humidity) could be controlled in the range from 20 to 65°C with a serially mounted electro heater. Downstream of the plasma stage a catalyst (copper-manganese) was installed. Its maximum possible temperature was 350°C. An additional reaction chamber with a residence time of about 12 s for the conditions being considered could be installed after the catalysts section. Furthermore a scrubber unit was used in some experiments prior to the plasma stage. Figs. 1–3 show photos of the mobile facility. A more detailed schematic measurement arrangements are described in following sections.

Gas Analysis

Exhaust air of the thermal dryer was analysed using olfactometry, FTIR, FID and a handheld H₂S analyser. The FTIR ("alpha", Bruker) with a resolution of 1 cm⁻¹ and equipped with a 4.8 m long heated gas path cell was used to investigate the presence and relative change of infrared-active gases. The sensitivity of this device is about 2 ppm. The H₂S concentration was measured with the electrochemical handheld device “GasAlertMicro 5 IR” with an integrated IR sensor for the CO₂ monitoring (sensitivity 0.1 ppm or 0.15 mg/m³). Furthermore samples were taken with thermo desorption tubes which were analysed by gas chromatography – mass spectrometry device (GC/MS; GC: 2010 with TD-20 and QP 2010, Shimadzu with column Phenomenex ZB-5) afterwards (about 1 µg/m³ sensitivity). The task of the
GC/MS screening was to detect chemical agents present in the off gas, but below the detection limit of the FTIR as well as an identification of produced and reduced agents at the inlet and outlet of the plasma reactor. The main scope hereby was the detection of compounds including sulphur (e.g., thiols, sulphides etc.). Ammonia and thiols were measured with Dräger tubes. The concentration of total organic carbon was determined by means of FID (Ratfisch Type RS 53, 2 ppm sensitivity). The volume flow was adjusted with a windmill type anemometer from Testotherm. The ozone concentration was measured with the Ozone Monitor (Model 450, Teledyne API).

The measurements of odour concentration were conducted before and after the plasma-catalytic treatment according to the EN 13725:2003 “Air quality - Determination of odour concentration by dynamic olfactometry”, by the specialized team referred to as the odour panel, meeting the selection criteria for olfactory sensitivity. Dynamic predilution with a clean and dry air was applied during sampling (UPP-2 of LAT sampling system). Olfactometric samples were collected to bags made of Nalophan (the seamless casing made of polyethylene terephthalate) for about 15 minutes. Olfactometric measurements of odour concentration [OU/m^3] were conducted in the mobile olfactometric laboratory of the Laboratory for Odour Quality of Air. The conditions inside the olfactometric laboratory were controlled (such as temperature, humidity and CO₂ concentration) by means of air conditioning and odour concentration was measured using an olfactometer (Ecoma TO7 dynamic).

RESULTS AND DISCUSSION

First studies were conducted with the plasma-catalyst arrangement as shown in Fig. 4 (arrangement 1). The following components beside N₂ and O₂ were identified in the thermal sludge dryer outlet by means of different gas analytic techniques: carbon dioxide (CO₂), carbon monoxide (CO), water (H₂O), methane (CH₄), H₂S, NH₃, dimethyl sulphide (DMS, (CH₃)₂S); dimethyl disulphide (DMDS, CH₃SSCH₃), dimethyl trisulphide (DMTS, CH₃S₃CH₃), thiols, aldehydes, and other organic compounds. The largest contribution was due to H₂S (up to 50 ppm or 70 mg/m³). Taking into account the odour thresholds and measured concentrations H₂S and DMDS (concentration about 1.4 mg/m³) can be identified as the two main odour contributors. Other gases such as DMS, toluol, DMTS, limonene and acetic acid have been detected as well, but with much lower concentration (below 0.2 mg/m³). The odour strength in the exhaust gas varied between 96300 and 265100 OU/m³ (odour unit per cubic meter).

An partial gas flow of 160 m³/h was extracted and mixed with a reaction air (fresh air) gas flow of 36 m³/h (total power of plasma unit 300 W). The ozone concentration in the reaction air was measured at about 4 ppm. After the mixing of reaction air and partial exhaust gas flow, the O₃ concentration was below 0.3 ppm. The mixed gas flow was then fed to the catalyst unit which was operated at a temperature of 105°C and a GHSV of 15,000 h⁻¹. After the catalytic stage the gas was subjected to the additional reaction path. Test samples for olfactometry and gas analyses were taken from the dryer exhaust and after the reaction path. The odour strength measured over a total time range of 46 hours is shown in Fig. 5 together with measured data of H₂S. It is clearly shown that the odour strength and the H₂S emission correlate with each other. The plasma-catalytic treatment had a significant effect on odours and H₂S emission. About 50% reduction was achieved. By means of FTIR SO₂ could be identified as a product of H₂S conversion, similar as in laboratory studies mentioned above. The analysis by means of GC/MS (mean value of two samples) shows the reduction of DMDS (from 1.4 mg/m³ to 0.5 mg/m³) and other VOCs (DMS, Toluol, DMTS, limonene and formic acid), but also the slight increase of carbon disulphide CS₂ (from 0.04 to 0.1 mg/m³).
Fig. 4. Flowchart of the first field test experiment (arrangement 1).

Fig. 5. Odor strength and H₂S concentration measured over 36 hours in the raw gas and at the reaction path outlet.
The removal of H₂S is via the formation of the HS radical which is generated by the collision of electrons or the reaction between H₂S molecules and gas-phase radicals (OH, O). The HS radical further reacts with primary or secondary reactive oxygen species (O, O₃, OH, HO₂) forming SO₂ and SO₃ (Ma et al., 2001; Liang et al., 2011). This process might be enhanced by the presence of additional organic radicals formed from hydrocarbons present in the waste air. The formation of CS₂ from H₂S and CH₄ has been found in argon plasma jets, too (Vastola and Stacy, 1967) and is probably supported by the catalyst. Carbon disulphide is a poison with characteristic smell and known as a polymer forming precursor in plasma technology (Hirotsua, 1981). Thus its formation or emission must be avoided since it can inactivate the catalyst or deposit on the electrode surface.

The unwanted by-products were thus mainly caused by conversion of H₂S and efficiency of plasma-catalytic removal at the present concentrations was low. Taking this into account the process design was modified as follows. NH₃ and H₂S should be mainly reduced by a scrubber system upstream to the plasma-catalytic section. Non-soluble compounds should than be converted by means of plasma-catalytic treatment. To test this approach the set-up was changed as shown in Fig. 6 (arrangement 2). The partial gas flow was feed through a scrubber unit and subsequently mixed with plasma treated reaction air. For testing of the removal of NH₃ the scrubber was operated in an acid ambience by using sulphuric acid (chemisorption). For the elimination of H₂S the scrubber was operated by sodium hydroxide (NaOH) and hydrogen peroxide (H₂O₂). Non-soluble compounds which can be not removed by scrubbing, e.g., thiols, alkylsulphids and organic compounds will remain in the gas flow.

In the set of experiments realizing this concept the after-treatment test plant arrangement consisting of scrubber, plasma, catalyst and reaction path was installed after the thermal sludge dryer and before the existing bio filter (see Fig. 6). Again a part of the waste air gas flow was sampled directly after the thermal sludge dryer through a pipe. The concentration of the exhaust gases was measured in-situ by means of FID, H₂S sensor and FTIR in the raw gas (original waste air), after the scrubber and after the plasma/catalyst-treatment in the end of the downstream reaction path. Additional samples were used for ex-situ GC/MS screening.

In order to investigate the combination with the bio filter a second set of experiments was led with the plasma section installed after the existing bio filter, as shown in Fig. 7 (arrangement 3). The scrubber was not used and the concentrations of substances were measured in the raw gas (after the bio filter) and after the plasma/catalyst-unit.

The herein displayed results do not refer to all operated investigations and results are only exemplary. All corresponding experiments were performed with a total plasma power of 500 W, 107°C catalyst temperature and a partial sample gas flow of about 160 m³/h (about 10% added from the plasma unit as reaction air). The scrubber was operated with NaOH solution (pH = 12.5). Contrary to the first series of experiments carbonyl sulphide (OCS or COS) was detected in the waste air by means of FTIR, as shown in Fig. 8. COS is known for its unpleasant odour, poisonous character and leads to sulphate aerosol formation. It was not removed by the bio filter, but a significant reduction of COS was found after the plasma-catalyst treatment (see FTIR-spectra in Fig. 8). The conversion was influenced by the temperature of the catalyst (the higher the temperature the higher the decrease of COS). Even though a decrease of COS could be found after the plasma stage it is not significantly influenced by the plasma power. Surprisingly no thiols could be measured. Possibly their concentration was below the quantification limit of Dräger tubes. Table 1 summarises main results of the olfactometric analyses of measurement arrangements mentioned above.

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**Fig. 6.** Experimental arrangement for experiments on direct thermal dryer outlet exhaust including scrubber unit (arrangement 2).
Fig. 7. Experimental arrangement for experiments on existing bio filter exhaust with plasma-catalytic treatment (arrangement 3).

Fig. 8. FTIR-spectra of waste gas (a) at the inlet to the plasma/catalytic unit, sampled after thermal dryer and bio filter; (b) treated gas at the outlet of the plasma/catalytic unit.
Table 1. Results of olfactometry (n.m. not measured).

<table>
<thead>
<tr>
<th>No.</th>
<th>Arrangement</th>
<th>Total power plasma unit [W]</th>
<th>Temp. Cat. [°C]</th>
<th>Scrub-bing pH</th>
<th>Odor strengths raw gas [OU/m³]</th>
<th>after scrubber or biofilter [OU/m³]</th>
<th>purified gas [OU/m³]</th>
<th>Odor reduction scrubber or biofilter [%]</th>
<th>Plasma/ cat. total [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>before biofilter, only plasma/catalyst</td>
<td>500</td>
<td>108</td>
<td>-</td>
<td>86900</td>
<td>-</td>
<td>24800</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>before biofilter, scrubber and plasma/catalyst</td>
<td>500</td>
<td>107</td>
<td>13</td>
<td>97900</td>
<td>46700</td>
<td>20000</td>
<td>52</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>after biofilter, only plasma/catalyst</td>
<td>500</td>
<td>107</td>
<td>-</td>
<td>n.m.</td>
<td>58000</td>
<td>6700</td>
<td>-</td>
<td>88</td>
</tr>
</tbody>
</table>

The plasma-catalyst treatment alone (arrangement 1) results in odour reduction of about 72%. The combination with the upstream scrubber (arrangement 2) increases the odour reduction to 80%, while already 52% of odour strength units were removed by the scrubber alone. The treatment of waste air with the plasma-catalyst unit after the passage of the bio filter (arrangement 3) resulted in odour removal of about 88% relating to the odour strength after the bio filter. The raw gas odour strength was not measured in this arrangement. If a value of 93,000 is assumed (taking the mean value of arrangements 1 and 2) the total odour reduction would be 92%, whilst the larger reduction is due to the plasma-catalytic treatment. Table 2 shows the results of FID, H₂S-sensor and Dräger tube analyses.

Plasma-catalyst treatment leads to a complete removal of H₂S (note that the concentration was only about 4 ppm during the conductance of this field tests), a moderate reduction of Corg and about 50% NH₃ reduction. Using the scrubber upstream to the plasma/catalyst unit about 35% of H₂S are already removed by NaOH scrubbing but has nearly no effect on NH₃ and Corg. The bio filter seems to have an effect on Corg and H₂S as well as NH₃ - these substances are removed. Still the plasma-catalytic treatment enhances these effects significantly. The results of the GC/MS analysis for arrangements 2 and 3 are shown in the Table 3.

It must be mentioned that more than 50 compounds have been delivered from the GC/MS screening. The following discussion is restricted to compounds which have been measured with a concentration of at least 100 µg/m³ in the raw gas for simplicity. Due to the fact that measurements have been performed on different days with different exhaust conditions the following statements have only a general character.

Aldehydes and other hydrocarbons are significantly removed. Since there is almost no effect of scrubbing on Corg this effect is mainly caused by plasma-catalyst treatment. However, the bio filter removes the aldehydes completely and reduces other hydrocarbons, too. Significant concentrations of sulphur containing compounds are released from the bio filter, but plasma-catalytic treatment removes them significantly. These results are in agreement with the olfactometric results. Better effects on sulphurous substances (DMS, CS₂, DMDS) by plasma-catalytic treatment might be responsible for the higher odour reduction efficiency. The bio filter gives unsatisfying results due to lower effects on several odour molecules.

CONCLUSIONS

Effects of a plasma-catalytic treatment of waste air from a wastewater treatment facility (thermal sludge dryer emissions) have been studied in field tests in order to demonstrate its feasibility for deodorization. The plasma-catalytic treatment was combined with scrubbing or existing bio filters. A significant odour reduction was concluded by means of standardized olfactometric analysis. The conversion of H₂S as one of the main odorous compounds was found, but resulted in the formation of other unwanted by-products e.g., SOₓ and CS₂. Concluding this results, the waste gas treatment of a given wastewater treatment plant...
Table 3. Results of the GC/MS analysis for arrangements 2 and 3 (mean value from 3 samples).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Arrangement no. 2</th>
<th>Arrangement no. 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>scrubber and plasma/catalyst; sampling before biofilter</td>
<td>plasma/catalyst without scrubber; sampling after biofilter</td>
</tr>
<tr>
<td></td>
<td>raw gas [μg/m³]</td>
<td>purified gas [μg/m³]</td>
</tr>
<tr>
<td>Aldehydes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methylbutanal</td>
<td>400</td>
<td>29</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>1160</td>
<td>199</td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>1327</td>
<td>616</td>
</tr>
<tr>
<td>Other HCs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>655</td>
<td>238</td>
</tr>
<tr>
<td>2-Methylfuran</td>
<td>144</td>
<td>-</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>1087</td>
<td>593</td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butanone (MEK)</td>
<td>135</td>
<td>172</td>
</tr>
<tr>
<td>Dimethyl sulphide</td>
<td>129</td>
<td>-</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>675</td>
<td>201</td>
</tr>
<tr>
<td>Dimethyl disulphide</td>
<td>433</td>
<td>121</td>
</tr>
<tr>
<td>2-Methylfuran</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

should be a combination of at least two techniques. Due to the high content of H₂S a scrubber unit (NaOH with H₂O₂ admixture) is used for the reduction of H₂S emissions with reliable operation cost. Downstream the scrubber the plasma-catalytic stage downstream can be utilized for the removal of remaining sulphides and hydrocarbons. A similar system has already been installed in Switzerland and gave reliable and stable results (about 95% odour strength reduction) for several years. In the given installation in Poznan it is recommended to remain with the existing bio filter but with a scrubber and a plasma-catalyst unit upstream. The bio filter may provide a long retention time for the reaction with plasma generated species (e.g., O₃ as an oxidizing agent) while the plasma treatment leads to the enlargement of bio filter lifetime and activity due to prior reduction of hydrocarbons.

The presented study has been performed at real conditions, in an industrial plant with limited access and without systematic variation of operation parameters as well as the evaluation of long time effects. Therefore further studies would be necessary to support the stated conclusions and to explain the involved effects in detail.

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