

Environmental odour control by atmospheric dielectric barrier discharge

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Abstract: Hydrogen sulphide (H₂S) removal was studied using a non-thermal plasma process generated by a coaxial dielectric barrier discharge. Starting from the development of a numerical model including the main chemical process for hydrogen sulphide removal in O₂-N₂ mixture, hydrogen sulphide has been treated experimentally in order to verify the numerical predictions and to analyze the influence of O₂-N₂ mixtures. H₂S was initially dissociated and then oxidized in order to form SO₂ and, finally, sulphuric acid. High removal efficiencies in a synthetic odour mixture were rated close to 100% in the case of a H₂S – O₂ mixture.

Keywords: non-thermal plasma process, environmental applications, dielectric barrier discharge.

1. Introduction

Dielectric barrier discharge (DBD) cells with sharp electrodes are widely used devices in the generation of atmospheric pressure cold plasma for ozone generation and pollution control [1] namely, to eliminate toxic and dangerous compounds such as hydrogen sulphur (hydrogen sulphide) [2]. The latter is often present in hydrogen and fuel gas systems as an impurity [3]

Noxious gases like ammonia, hydrogen sulphide and odorous organic compounds are produced during waste decomposition in collection pits, swamps and organically contaminated surfaces. These gases and odours pose a considerable public health hazard and a social nuisance on neighbouring properties, straining public relations. Alternative solutions have been put forward, some in the form of additives able to reduce the odour emission. Such substances include masking agents, counteractants, deodorants and adsorbents which can be used for odour control [4]. Technologies like biofiltration are used effectively in reducing concentrations of ammonia, hydrogen sulphide and other sulphur-based compounds found in odours. Ozone-enriched oxygen is used to oxidize undesirable cells or bacteria, whereby reducing odour emissions from e.g., manure [5]. Likewise, a continuous development of new effective technologies to reduce gas emissions from residual bogs could be highly beneficial to the environment.

Non-thermal plasmas have the advantage of enabling the simultaneous treatment of several pollutants. We report on the use of this non-thermal plasma technology by means of a dielectric barrier discharge system. Odours are constituted by a complex mixture of compounds such as volatile organic compounds (VOC's), ammonia,

hydrogen sulphur, methyl mercaptan, dimethyl disulphide and others sulphur based compounds. Hydrogen sulphur was selected as the main target gas in this study given its universal presence in solid-liquid organic decomposition such as the found in the upper reaches of the Lerma River in Mexico [6, 7]. This study departed from a specifically developed numerical model intended to identify the main path to hydrogen sulphide elimination. Later on, synthetic odour samples formed by gas mixtures like H₂S, N₂ and O₂ were treated in a dielectric barrier discharge chamber where composite odour samples extracted from liquid waste of the Lerma River were finally degraded.

2. Experimental Setup

A typical cylindrical DBD reactor geometry has been selected for our purpose. The 23 cm³ reactor is constituted by a 9 mm Pyrex-like glass tube wrapped in a fine metallic mesh as an external electrode. The internal electrode consists of a metallic rod placed inside a thin (~0.8 mm wall thickness) ceramic tube. The reactor is 350 mm long and endowed with 1.2 mm outer diameter concentric ceramic tube. A quasi-sinusoidal voltage [8] was applied to the metallic mesh with peak to peak voltages up to 25 kV at 1.25 kHz as measured by a Tektronics P6015A 1:1000 probe. The power released in the reactor was calculated with the well known Lissajous method. At a constant frequency (1.25 kHz), the voltage was varied to 15, 20 and 25 kV so to obtain the electrical characteristics of the reactor.

As a first stage, a synthetic odour mixture was created in the laboratory mixing nitrogen balanced H₂S in concentrations around 25, 50, 75 and 100 μmol H₂S per mol. The dilution gas was N₂, O₂ and SO₂ in a 1.0 SLPM total flow rate. Afterwards, we tried a two point moisture

effect: 15% HR at 10° and 32% HR at 22°C. The concentrations were monitored using an electrochemical gas analyzer and a gas chromatograph coupled to a Agilent mass detector.

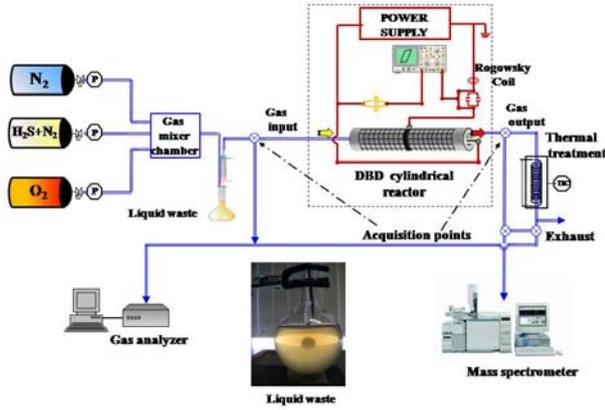


Fig. 1 Dielectric barrier discharge system

At the second stage, a natural odour was collected from liquid waste. The collected fluid was heated in a container at around 25-30°. Then, the emission gas was passed into a condenser while the non-condensable gas was driven to the plasma reactor with a N₂ and O₂ carrier gas. Exhaust gas samples were measured by chromatography and mass spectrometry.

The consumed power in the reactor was calculated employing the typical Lissajous's method. This consists in calculating the area inside a parallelogram formed by the charge – voltage characteristic (Fig 3). The area related to the frequency rate and a constant due to the capacitor set (Fig. 1) represent the power consumed by the reactor in watts.

3. Numerical Model

A specific simple kinetic model containing a group of reactions that take place during the H₂S removal process in N₂ – O₂ mixtures was developed. We considered 25 chemical species and around 90 chemical reactions [9-12]. Denoting the density of a given species by *n*, the following continuity equation can be written:

$$\frac{dn_i}{dt} = S_i(T) \quad (1)$$

where *S_i(T)* is the source term due to chemical kinetics. Equation (1) generates a first order ordinary differential equation system, solved by means of the Rosenbrock's algorithm [13] which is a trustworthy integrator for 'stiff' differential equations.



Fig 2. Water sample aspect for the treatment

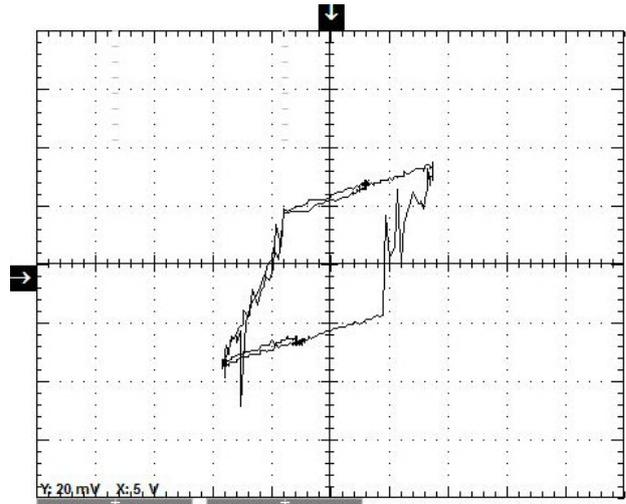
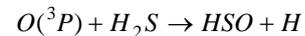
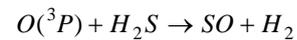
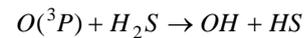


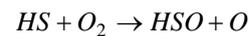
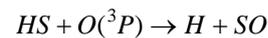
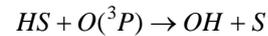
Fig. 3 Charge – voltage characteristic

4. Results

As seen figure 4, the H₂S was immediately dissociated for oxygen radical due to the reactions:



The *HS* radical is then transformed in sulphur oxide, atomic sulphur and an acidic precursor.



Finally, the sulphur is transformed totally into either sulphuric acid or dioxide of sulphur. When water is included in the calculation, the sulphuric acid is formed earlier and the dioxide sulphur is delayed (Fig. 5) the efficiency not being affected. The H₂S theoretical removal efficiency reached 100%.

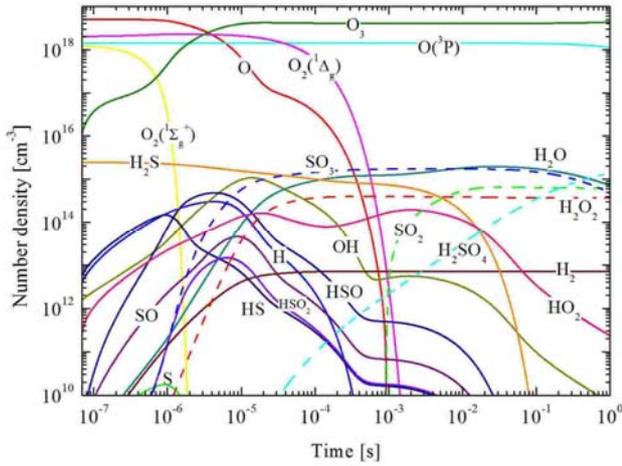


Fig 4. Species time distribution for H₂S removal; O₂: 100%; H₂S: 100 ppm.

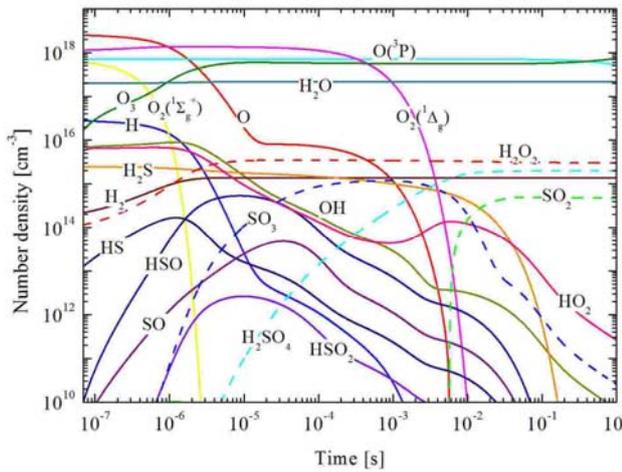


Fig 5. Species time distribution of H₂S removal; O₂: 100%, H₂S: 100 ppm, H₂O: 1% (v/v)

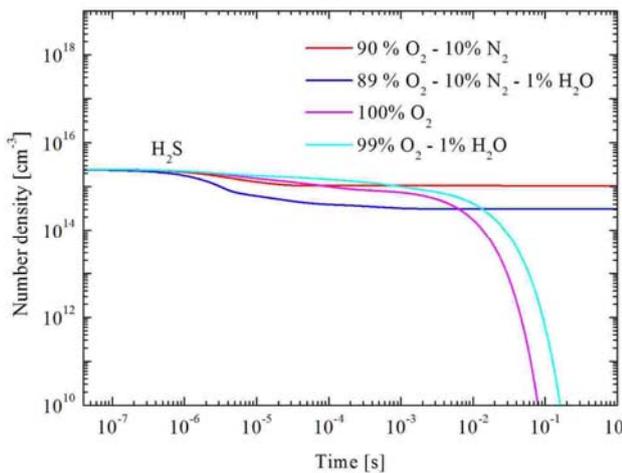


Fig 6. H₂S time distribution; H₂S: 100 ppm, N₂ and H₂O effect.

On the other hand, the nitrogen addition exhibited a negative effect. The oxygen radical apparently reacts better with nitrogen than with sulphur. A quantity of oxygen atoms is dedicated to the formation of nitrogen

oxides. Consequently the H₂S removal efficiency is reduced. The humidity proved to have a favourable effect when nitrogen was added.

We show in Fig. 7 (a), (b) the effect produced by N₂ and O₂ on H₂S removal from the synthetic odour mixture. At high power, the oxygen reacts to produce free radicals able to oxidize hydrogen sulphide. In nitrogen, the tendency is towards a chemical reduction. The direct elimination should take place by electron – molecule collision with the hydrogen sulphide. The efficiency in nitrogen was relatively low (~20-40%) although the moisture contributed to enhance the removal efficiency, in some cases, up to around 90%, Fig. 8(b). Meanwhile, as the oxygen was increased, the removal efficiency was increased, close to 100% as seen in Fig. 8 (a).

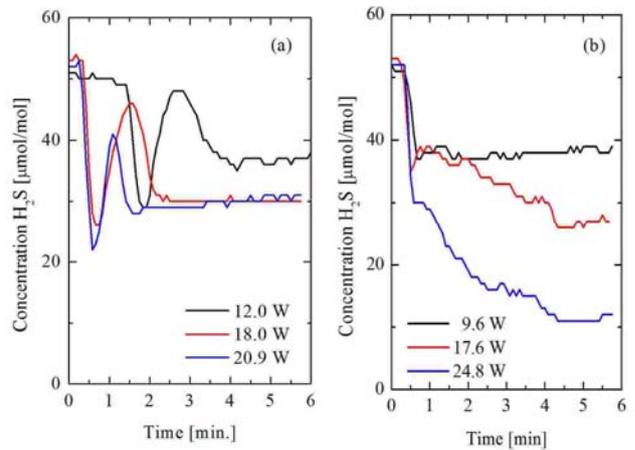


Fig 7. H₂S removal distribution; H₂S: 50 ppm, (a) 100% N₂ and (b) 50%N₂-50% O₂

For the H₂S -N₂-O₂ mixtures, the moisture had a slightly negative effect. The removal efficiency was, for each case, slightly lower than the one shown in Fig. 8(a). This result was also suggested on Fig. 6.

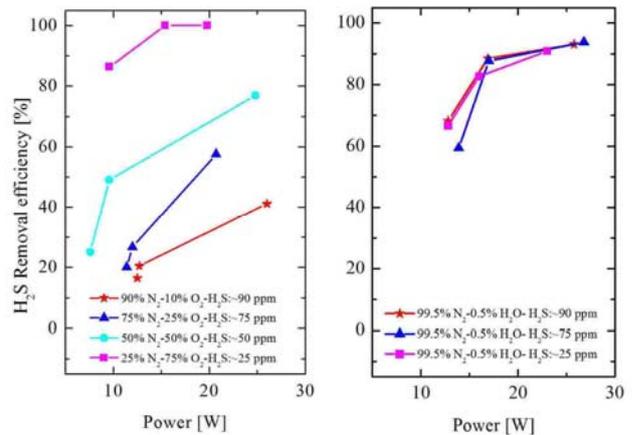


Fig 8. H₂S removal efficiency; a) O₂ and b) H₂O effect

The hydrogen sulphide removal is analyzed by means of gas chromatography in Fig. 9. A removal efficiency close to 78% can be observed, in good agreement with the results presented in Fig. 8(b) with H₂S – N₂ mixtures.

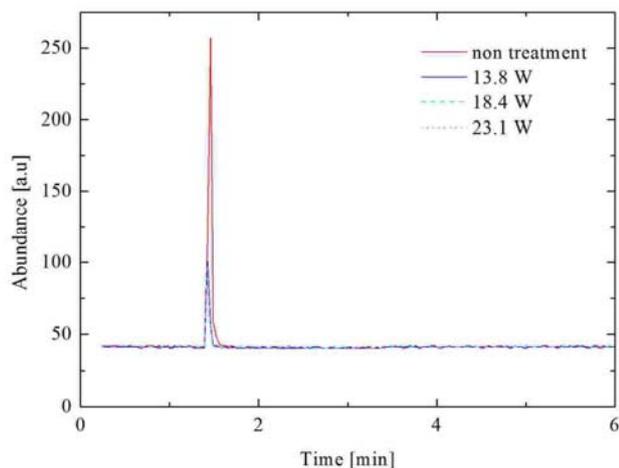


Fig 9. Gas chromatography spectra in synthetic mixture for H_2S

The outcome of the hydrogen sulphide removal from the real odour mixture is seen in Fig. 10. We must remark that other compounds can be present in the gas mixture and can modify the resulting spectrum due to the influence of the other species. Fig. 10 considers only the hydrogen sulphide molecule. In spite of it, a hydrogen sulphide removal around 50% can be seen on Fig. 10(d) which is as considerable as that in the case of the synthetic gas mixture.

5. Conclusions

Hydrogen sulphide has been oxidized and then removed from several gas mixtures as sulphuric acid. The nitrogen presence can decrease the removal efficiency albeit a small quantity of moisture contributed to counter it. The efficiency removal of H_2S from a real odour mixture presented a slight difference with respect to the synthetic case; this fact can be attributed to the presence of compounds like ammonium and distinct sulphured compounds.

Works are under way aimed to study actual complex odour mixtures encompassing other compounds both in the numerical modelling and, when possible, in the experimental synthetic odour mixture.

Acknowledgment

This work was partly supported by CONACyT, Mexico, under contract 060406.

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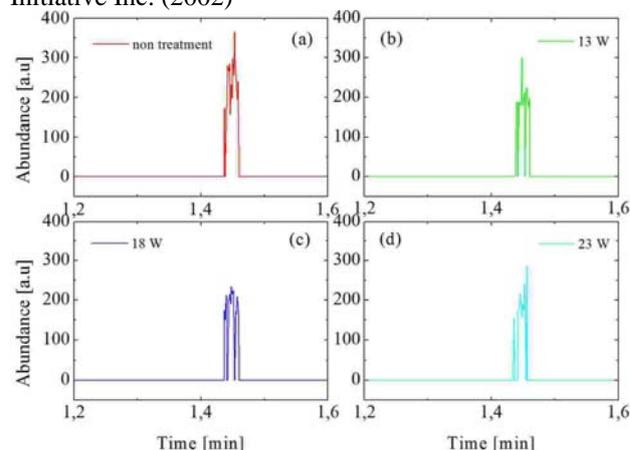


Fig 10. Gas chromatography spectra for H_2S in real odour mixture

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