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Dependence of Sulphurous Odorants Reduction on Loading Rates in Inoculated Biofilter Columns

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Odour emission from intensive pig production is a major source of local nuisance and sulphur-containing odorants (e.g. hydrogen sulphide and methanethiol) have been recognized as key odorants. Biological air filter has emerged as a cost-effective technique to remove odorants from ventilation air. However, low removal efficiencies for sulphurous odorants have been observed when a large volume of air has been applied with low concentrations. Recent kinetic studies on full scale biological air filters indicate that the removal of odorants is related both to mass load and air load of odorants but the dependence of sulphurous odorants on loading rates are not clear due to the very low and highly varying removal efficiencies. In the present study, two inoculated biofilter columns were applied to test the dependence of sulphurous odorants (hydrogen sulphide, methanethiol and dimethylsulfide) removal on air loading rate, mass loading rate or concentration. Specially designed commercially available ceramic saddles and cellulose pads were selected as biofilter media for the experimental tests. Whereas the air loading rate varied from around 10 to 1300 m^3 m^{-3} h^{-1}, the mass loading rate varied from approximately 10 to 500 mg m^{-3} h^{-1} for hydrogen sulphide. Concentration levels varied from around 10 to 3000 ppbv for hydrogen sulphide, covering the typical concentration range of H_2S emitted from pig facilities. The results indicated that the removal of hydrogen sulphide and methanethiol was closely dependent on air loading rate for both biofilter columns. Whereas the removal of hydrogen sulphide was observed to be also dependent on mass loading rate and concentration for the ceramic saddles packed biofilter column, the removal efficiency of H_2S was independent on mass loading rate or concentration for cellulose packed biofilter column. Further, significant competition between methanethiol and hydrogen sulphide was observed for the ceramic packed biofilter column, when the mass load of hydrogen sulphide was increased. On the other hand, no such competition was observed for the cellulose packed column. Kinetics analysis indicated that both Grau second-order kinetics and Stover-Kincannon model can generally be applied to describe the degradation of both hydrogen sulphide and methanethiol in biofilters, except a small deviation observed for methanethiol, when applied to Stover-Kincannon model.

1. Introduction

Recently global pig production increased rapidly with a 50% increase over the previous 15 years (Best, 2010). Odour emission from the intensive pig production is a major source of local nuisance (Nimmermark, 2004). Thus it is vital to develop efficient odour reduction techniques ensuring low emissions of odorants to the surroundings. Sulphur-containing odorants (e.g., H_2S and methanethiol) have been recognized as key odorants (Feilberg et al., 2010b; Hansen et al., 2012). Biofiltration has emerged as a cost-effective way to remove odorants from ventilation air (Nicolai and Janni, 2001; Melse and Ogink, 2005; Chen and Hoff, 2009). However, generally low removal efficiencies (RE) for sulphurous odorants (with low concentrations) have been observed when a large volume of air has been applied with low empty bed residence time (EBRT < 10 s) (Feilberg et al., 2010a; Hansen et al., 2012). A recent kinetic study on a full-scale biotrickling filter (packed with structured cellulose pads) indicated that the removal of odorants are both related to mass load and air load of odorants but the dependence of sulphurous odorants on loading rates are not clear due to the very low removal efficiencies and large variations of RE except for H_2S (Liu et al.,

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2012). Another study on full-scale biotrickling filter (packed with random Leca® pellets: light-weight Expended Clay) indicated the less dependence of sulphurous odorants removal on mass load than air load, with a conducted ventilation controlled on-site experiment (Liu et al., 2014b).
In the present study, an experimental biofilter column inoculated from a full-scale biological air filter (structured cellulose pads) was applied to test the dependence of sulphurous compounds removal on air loading rate, mass loading rate or concentration and thereby the removal kinetics of sulphurous odorants. Specially designed commercially available ceramic packing (ceramic saddles) and cellulose pads were selected as biofilter media for the experimental tests. These two packing materials showed potential of normalized mass transfer coefficients to pressure drop for sulphurous odorants and therefore may have advantages for the sulphurous compounds removal in biofilters (Liu et al., 2014a).

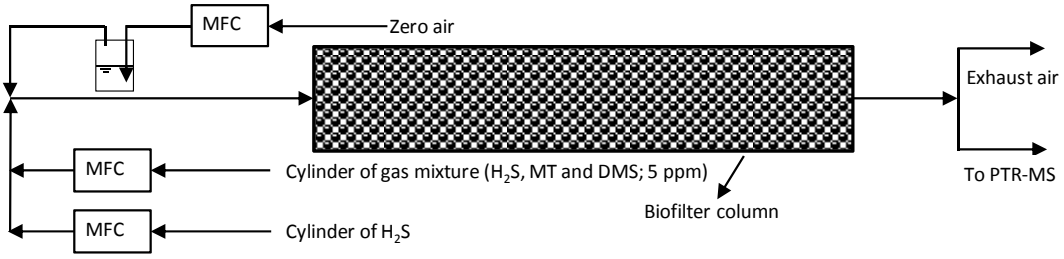

Figure 1: Scheme of experimental set-up. MT: methanethiol; DMS: dimethyl sulphide.

2. Methods

2.1 The full-scale three stage biological air filter and inoculation of biofilter columns

A full-scale three-stage biological air filter manufactured by SKOV A/S (SKOV, Roslev, Denmark) was installed next to a pig production facility feeding growing-finishing pigs (Hansen et al., 2012). The packing material used in all three stages was made of vertical walls of cellulose pads. The specific surface area of cellulose pads is 383 m^2 m^{-3} (Ottosen et al., 2011). Stage 1 and stage 2 was 15 cm wide and stage 3 was 60 cm wide. Stage 1 and 2 were irrigated with recirculated water from the water pond beneath the filter and thus could be regarded as biotrickling filter stages. Stage 3 was supplied only by the humidified air after the stage 2 with no water irrigation and thus could be regarded as a biofilter stage (Liu et al., 2012). Previous study demonstrated that the stage 3 was responsible for most of the reduction of H_2S (Hansen et al., 2012). Thus the stage 3 was chosen for the inoculation of the experimental biofilter columns. Two pieces of column cores (ID 10 cm, 60 cm length) containing cellulose pads and ceramic saddles, respectively, were placed into the stage 3 for two and half months in the early summer. It was assumed that both packing columns were inoculated completely and contained comparable microbiology environment as in stage 3. Both columns were soaked in the biotrickling filter liquid for one week before putting into the stage 3. After the inoculation, each column core was collected from the stage 3 and performed the experiments immediately within one day.

2.2 Experimental set-up

The scheme of the experimental set-up is shown in Figure 1. The biofilter column contained ceramic saddles or cellulose pads from the stage 3 of the 3-stage biological air filter. Two gas cylinders were used for the experiments. One cylinder contained a gas mixture of H_2S, methanethiol (MT) and dimethyl sulphide (DMS) (all with 5 ppmv). The other gas cylinder contained only hydrogen sulphide (5 ppmv or 1000 ppmv) in order to obtain a higher concentration of hydrogen sulphide. Humidified zero air was introduced for making dilution. Different levels of air load and mass load of sulphurous chemicals were performed for the experiments. Humidity level was controlled through weighing of the biofilter column frequently and a controlled volume of liquid collected from the three stage biological air filter was added to the front of the biofilter column when it was necessary.

2.3 PTR-MS

A high-sensitivity PTR-MS (Ionicon Analytik, Innsbruck, Austria) was applied for the experiments. Standard drift tube conditions was used with the drift tube pressure of 2.1~2.2 mbar, the drift tube voltage of 600 V and the drift tube temperature of 60 °C. The calibration for H_2S measurements was performed under different humidity levels (Feilberg et al., 2010b).

2.4 Data analysis

The removal efficiency (RE) of an odorant in a biofilter is a common used performance indicator and can be expressed as follows:

$$RE = 100\% \times (C_{in} - C_{out}) / C_{in} \quad (1)$$

where C_{in} refers to odorant inlet concentration (g m^{-3}) and C_{out} refers to outlet concentration (g m^{-3}).

Kinetics study can be an essential tool for investigation of the removal pattern and mechanisms and for design purpose. Previously two macrokinetic models (Stover-Kincannon model and Grau 2nd order kinetics) were observed to be more suitable for simulation of odorants removal performance in the full-scale biological air filter but the performance on sulphurous odorants needs to be further investigated (Liu et al., 2012). Specifically, it is interesting to test if the Stover-Kincannon could still be applied for the sulphurous compounds removal simulation, with which the mass transfer might be limited in the biotrickling filters. These two macrokinetic models were therefore chosen in this study to simulate the removal of sulphurous odorants under controlled conditions. The Stover-Kincannon model was built as a connection between removal rate and mass load of a contaminant and could be expressed as follows after linearization (Kincannon and Stover, 1983):

$$\frac{V}{Q\left(C_{in} - C_{out}\right)} = \frac{K_S}{U_{\max}} \cdot \frac{V}{Q\,C_{out}} + \frac{1}{U_{\max}} \quad (2)$$

where V and Q refer to the bulk volume of the biofilter column (m^3) and supplied air flow rate to the biofilter column (m^3 h^{-1}), respectively, while U_{max} and K_s denote maximum utilization rate constant (g m^{-3} h^{-1}) and saturation constant (g m^{-3} h^{-1}), respectively. Grau 2nd order kinetics (Grau et al., 1975), on the other hand, was based on the assumption of decrease of removal rate along the biofilter bed while the contaminant passing through it. This model could be linearized as below with m and n as constants:

$$\frac{EBRT}{RE} = n \cdot EBRT + m \quad (3)$$

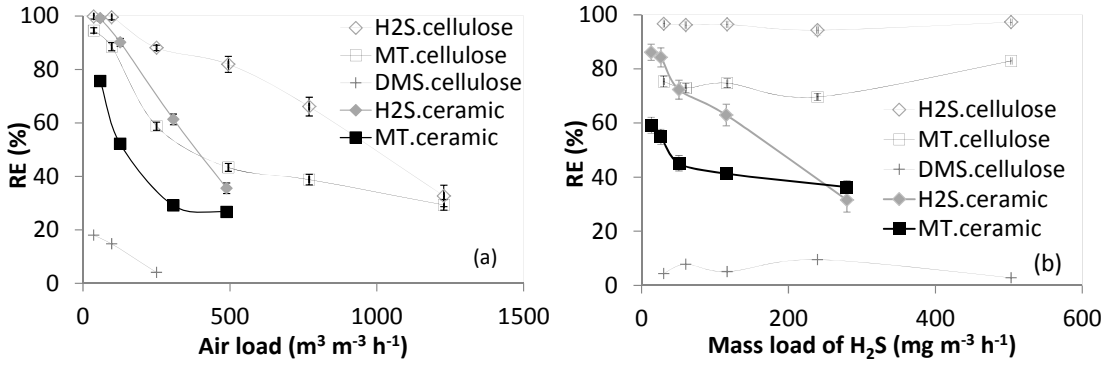

Figure 2: (a): Under fix mass load, removal efficiencies (RE) of H_2S, methanethiol (MT) and dimethyl sulphide (DMS) as functions of air load; Mass load is 130, 5 and 5 mg m^{-3} h^{-1} for H2S, MT and DMS for cellulose packed biofilter column and 65, 5 and 5 mg m^{-3} h^{-1} for H_2S, MT and DMS for ceramic saddles packed biofilter column; (b): RE of H_2S, MT and DMS as functions of mass load of H_2S under fix air loading rate (130 m^3 m^{-3} h^{-1}) for cellulose packed and ceramic saddles packed biofilter columns. The mass loads of MT and DMS (5 mg m^{-3} h^{-1}) were kept unchanged under different mass load of H_2S. DMS for ceramic saddles was excluded in both (a) and (b) since no removal was observed in all conditions.

3. Results and discussion

The experiments for both biofilter columns were mainly performed under controlled conditions of fix mass load, fix air load and fix concentration. Since these three parameters are not independent, other two parameters would change simultaneously while one was fixed. Results showed in general a better removal performance of H_2S and MT for cellulose pads biofilter column than ceramic packed biofilter column.

Figure 2(a) shows the removal efficiencies (RE) of sulphur compounds as functions of air load for both biofilter columns under fixed mass load of these sulphur compounds. In general cellulose packed biofilter column had better performance for sulphurous odorants removal than ceramic saddles packed biofilter column when the data from the same level of air load were compared. DMS was not removed much except when very low air loading rates were applied and specifically no DMS removal was observed for ceramic saddles packed biofilter under all conditions. While the RE of H_2S for cellulose packed biofilter column was decreased steady by increased air load, the RE of H_2S for ceramic packed biofilter column was decreased rapidly when the air load was increased. For the removal of MT, on the other hand, a similar trend was observed for both biofilter columns, except lower RE of MT was observed for ceramic packed biofilter column. The data obtained on another level of mass load for both columns showed similar trend (data not shown). These results indicated that the ceramic saddles packed biofilter column did not show higher removal performance as expected from the previous measured higher mass transfer coefficients (Liu et al., 2014a), probably due to the low biodegradation rate in this column. As mentioned in the method section, the two biofilter columns were inoculated in a full-scale cellulose biological air filter. Since the higher resistance of the ceramic saddles packed column than the cellulose, it could be possible that the attached biofilm on ceramic saddles were not the same as the cellulose parts.

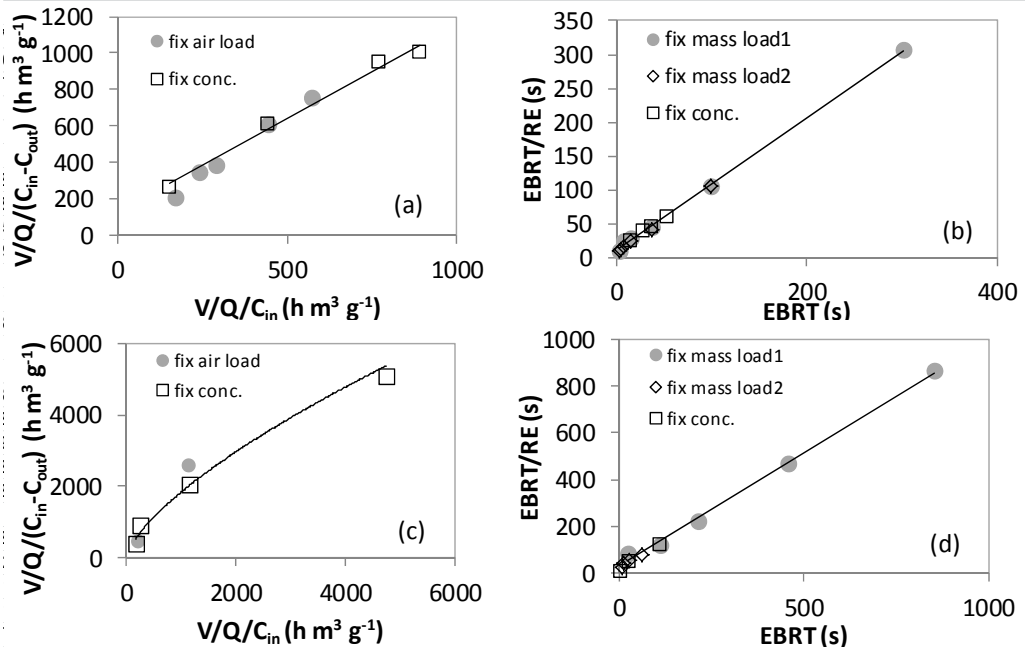

Figure 3: Kinetics analysis for methanethiol removal in the inoculated biofilter column. (a) Stover-Kincannon model for cellulose packed column; fix air load = 130 m^3 m^{-3} h^{-1}; fix conc. = 12 ppbv; (b) Grau second-order kinetics for cellulose packed column; fix mass load1 = 1.3 mg m^{-3} h^{-1}; fix mass load2 = 6 mg m^{-3} h^{-1}; fix conc. = 12 ppbv; (c) Stover-Kincannon model for ceramic saddles packed column; fix air load = 130 m^3 m^{-3} h^{-1}; fix conc. = 5 ppbv; (b) Grau second-order kinetics for ceramic saddles packed column; fix mass load1 = 0.2 mg m^{-3} h^{-1}; fix mass load2 = 4.5 mg m^{-3} h^{-1}; fix conc. = 5 ppbv.

Another test of fix air load revealed the dependence of the RE on mass load of sulphurous compounds. For example, Figure 2(b) showed the dependence of RE of H_2S, MT and DMS on the mass load of H_2S under fix air loading rate. For cellulose packed biofilter column, no apparent change of RE of H_2S, MT and DMS were observed while the mass load of H_2S were increased. This indicated that the RE of H_2S in cellulose packed biofilter column was independent on the mass load of H_2S and the MT removal was not

influenced by the different mass load of H_2S. For ceramic saddles packed biofilter column, on the other hand, the RE of H_2S and MT was reduced when higher mass load of H_2S was applied. This observation revealed that the RE of H_2S in the ceramic packed biofilter column was dependent on the mass load of H_2S. Further, the lower RE of MT indicated a competition of MT removal and H_2S removal when higher mass load of H_2S was applied. This again may indicate that the low biodegradation rate (low biomass) in the ceramic packed biofilter column. Thus further study is needed in order to compare the removal performance of sulphurous odorants thoroughly between the two biofilter columns.

Figure 3 showed the kinetics analysis for the MT removal in the two biofilter columns under different conditions. For cellulose packed biofilter column, both the Stover-Kincannon model and the Grau 2nd order kinetics were confirmed to be well applied to MT removal, as shown in Figure 3(a) and 3(b). Similar results were obtained for H_2S and DMS. While the Stover-Kincannon model indicated that the removal rate of MT in cellulose packed biofilter was dependent on MT mass load, the Grau 2nd order kinetics demonstrated that the RE of MT was only dependent on the air load. For ceramic packed biofilter column, however, only the Grau 2nd order kinetics were well applied to MT removal, as shown in Figure 3(d). The Stover-Kincannon model showed a small deviation for MT removal application (Figure 3(c)), although no such deviation was observed for H_2S removal application (Figure 4(a)) which demonstrated the increase of removal rate of H_2S under increased H_2S mass load, although the increase of H_2S removal rate might not compensate the increased H_2S mass load and thus the RE of H_2S decreased, as compared to Figure 2(b). Still, the final conclusion is kept temporarily due to the few data obtained in this study. Further, a previous field biotrickling filter (packed with lightweight expanded clay aggregates) study indicated the failure of application of Stover-Kincannon model for removal of H_2S, MT and DMS (Liu et al., 2014b), and thereby indicated the mass transfer limitation of these compounds in that filter, although this didn't seem to happen in the two innoculated biofilter columns in this study.

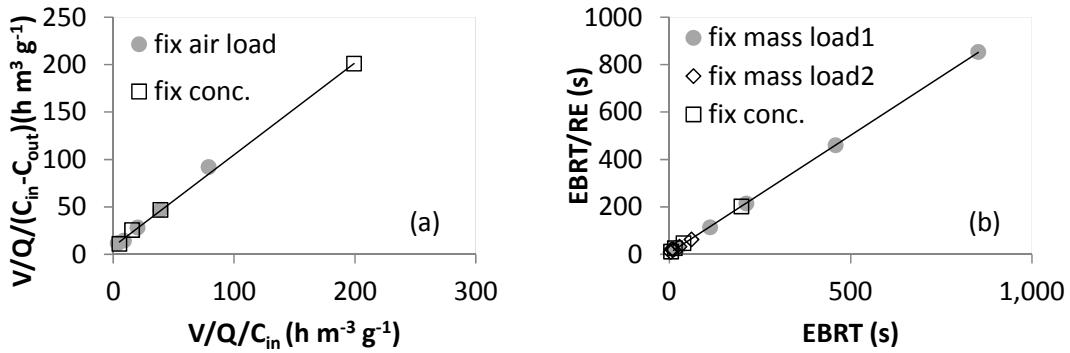

Figure 4: Kinetics analysis for hydrogen sulphide removal in the ceramic saddles packed inoculated biofilter column. (a) Stover-Kincannon model application; fix air load = 130 m^3 m^{-3} h^{-1}; fix conc. = 150 ppbv; (b) Grau second-order kinetics application; fix mass load1 = 5 mg m^{-3} h^{-1}; fix mass load2 = 60 mg m^{-3} h^{-1}; fix conc. = 150 ppbv.

4. Conclusions

In this study, the dependence of removal of selected sulphurous odorants on air load and mass load was investigated through two inoculated biofilter columns. Ceramic saddles and cellulose pads were selected as biofilter media for the experimental tests due to the mass transfer potential in previous study. Whereas the air loading rate varied from around 10 to 1300 m^3 m^{-3} h^{-1}, the mass loading rate varied from ca. 10 to 500 mg m^{-3} h^{-1} for hydrogen sulphide. Concentration of H_2S varied from ca. 10 to 3000 ppbv. The results indicated that the removal of hydrogen sulphide is only dependent on air loading rate in cellulose packed biofilter column, while the removal of hydrogen sulphide was both dependent on air load and mass load of H_2S in ceramic packing biofilter column. Significant decrease of methanethiol removal efficiency was observed for the ceramic packed biofilter column, when the mass load of hydrogen sulphide was increased, while it was not the case for the cellulose packed biofilter column. While Grau 2nd order kinetics could be well applied to describe the degradation of both hydrogen sulphide and methanethiol, Stover-Kincannon model was only applied well for hydrogen sulphide removal, and a small deviation was observed for methanethiol removal application.

References

Best P., 2010, World pork output grows again, in: Pig international, 8-9, WATTAgNet.com, accessed 20.03.2014.

Chen L., Hoff S.J., 2009, Mitigating odors from agricultural facilities: A review of literature concerning biofilters, Appl. Eng. Agric., 25, 751-766.

Feilberg A., Adamsen A.P.S., Lindholst S., Lyngbye M., Schäfer A., 2010a, Evaluation of Biological Air Filters for Livestock Ventilation Air by Membrane Inlet Mass Spectrometry, J. Environ. Qual., 39, 1085-1096.

Feilberg A., Liu D., Adamsen A.P.S., Hansen M.J., Jonassen K., 2010b, Odorant emissions from intensive pig production measured by online proton-transfer-reaction mass spectrometry, Environ. Sci. Technol., 44, 5894-5900.

Grau P., Dohanyos M., Chudoba J., 1975, Kinetics of multicomponent substrate removal by activated sludge, Water Res., 9, 637-642.

Hansen M.J., Liu D., Guldberg, L.B., Feilberg, A., 2012, Application of Proton-Transfer-Reaction Mass Spectrometry to the assessment of odorant removal in a biological air cleaner for pig production, J. Agric. Food Chem., 60, 2599-2606.

Kincannon D. F., Stover E. L., 1983, Design methodology for fixed film reaction-RBCs and biological towers, Civil Eng. Pract. Des. Eng., 2, 107-124.

Liu D., Andreasen R.R., Poulsen T.G., Feilberg A., 2014a. A comparative study of mass transfer coefficients of reduced volatile sulphur compounds regarding packing materials for biotrickling filters, Submitted to Chem. Eng. J., under review.

Liu D., Løkke M.M., Leegaard R.A., Mortensen K., Feilberg A., 2014b, Evaluation of clay aggregate biotrickling filters for treatment of gaseous emissions from intensive pig production, J. Environ. Manage., 136, 1-8.

Liu D., Hansen M.J., Guldberg L.B., Feilberg A., 2012, Kinetics evaluation of remoal of odorous contaminants in a three-stage biological air filter, Environ. Sci. Technol., 46, 8261-8269.

Melse R.W., Ogink N.W.M., 2005, Air scrubbing techniques for ammonia and odor reduction at livestock operations: Review of on-farm research in the Netherlands, Trans. ASABE, 48, 2303-2313.

Nicolai R.E., Janni K.A., 2001. Biofilter media mixture ratio of wood chips and compost treating swine odors, Water Sci. Technol., 44, 261–267.

Nimmermark S., 2004, Odour influence on well-being and health with specific focus on animal production emissions, Ann. Agr. Environ. Med, 11, 163-173.

Ottosen L.D.M., Juhler S., Guldberg L.B., Feilberg A., Revsbech N.P., Nielsen L.P., 2011, Regulation of ammonia oxidation in biotrickling airfilters with high ammonium load, Chem. Eng. J., 167, 198-205.