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Chemisorption of hydrogen sulphide and methanethiol by light expanded clay aggregates (Leca)

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HIGHLIGHTS

- Leca was studied with respect to sorption and chemisorption of H_2S, MT and DMS.
- DMS is not degraded but H_2S and MT are removed with variable efficiency.
- O_2 is not necessary for chemisorption of H_2S and MT.
- Moisture content has an influence on removal of H_2S and MT.
- Dimethyl disulphide and dimethyl trisulphide are observed as gaseous by-products.

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ABSTRACT

Removal of volatile sulphur compounds from livestock waste air by biological air filtration may be enhanced by application of packing materials with reactive properties. In this study, light expanded clay aggregates (Leca®) was tested with respect to sorption and potential chemical degradation of H_2S, Methanethiol (MT) and Dimethyl sulphide (DMS). Leca was selected due to its content of minerals, including iron, and due to its high specific surface area. The performance of Leca was evaluated based on breakthrough curves and by comparing the difference between the inlet and outlet gas concentrations. Whereas DMS did not appear to be removed by Leca, both H_2S and MT were removed with variable efficiency depending on the specific conditions. Dimethyl disulphide (DMDS) and dimethyl trisulphide (DMTS) were demonstrated to be produced during the degradation process in relatively high yields. A comparison between ambient air and nitrogen gas conditions showed that the chemisorption of H_2S and MT did not necessarily need oxygen to be present. X-ray analysis of Leca showed an abundance of Fe_2O_3. It is therefore hypothesized that Fe_2O_3 in Leca can remove H_2S and MT by chemisorption. Both air velocity and moisture content clearly affected the capacity of Leca for removal of H_2S and MT. Lower removal is seen at higher air velocities, whereas higher moisture content enhances removal. However, chemisorption of MT by Leca appears to be limited above a threshold moisture level. Potential reaction mechanisms are discussed in relation to the observed effects. The results implicate that Leca can be used as a filter material with reactive properties provided that moisture content is controlled and that an adequate air velocity is used.

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1. Introduction

Odour nuisance from intensive livestock production can reduce the well-being of residents living close to the production facilities through discomfort and may also lead to health related symptoms such as headache, and vomiting (Schiffman et al., 2005; Wing et al., 2008). These problems have been reported to be a source of conflicts between farmers and residents (Reisner and Taheripour, 2007). Odour emanating from intensive livestock housing consists of a range of compounds such as sulphur-containing compounds, nitrogen-containing compounds, volatile fatty acids, indoles, and phenols. Sulphur-containing compounds such as H_2S, Methanethiol (MT) and Dimethyl sulphide (DMS) are expected to be key contributors to perceived odour due to their low odour detection thresholds compared to other compound emitted from intensive livestock housing (O'Neil and Phillips, 1992; Feilberg et al., 2010b).

There are several available technologies for treatment of volatile sulphur compounds (VSC), but with conditions of low concentrations and high flow rates from livestock housing, biofiltration is considered as one of the most appropriate waste gas treatment technologies: it is regarded to be cost-efficient and does not

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produce toxic by-products during treatment (Devinny et al., 1999). Biofiltration rely on physical processes such as absorption and adsorption for the supply of odorants to be degraded (Chen and Hoff, 2009); therefore, adsorbents with good physical properties can increase the efficiency of biofilters. Adsorbents such as compost, soil, and perlite, have relatively low sorption capacities for waste gases, which reduces the efficiency of biofilters (Dorado et al., 2010). Other adsorbents such as activated carbon with high sorption capacity lose some of the capacity when they are humidified (Devinny et al., 1999). They are also associated with high cost (Dorado et al., 2010) compared to other adsorbents.

Low mass transfer of VSCs, as a result of the high air–water partition, has been identified as a major challenge to efficient removal of VSCs using biofiltration (Feilberg et al., 2010a). A packing material with a high adsorption capacity may enhance the mass transfer process and therefore the removal efficiency of VSCs in biofilters.

Light expanded clay aggregate (Leca) is traditionally used as a construction and hydroponic material, but has recently been used as a biofiltration packing material for treating odour (Fogarty and Curran, 2008; Feilberg et al., 2010a) and aqueous organic waste treatment (Dorado et al., 2010). Leca has been observed to have a high surface area, excellent mechanical properties and higher removal efficiencies of VSCs compared to other materials (Feilberg et al., 2010a).

Leca is composed of several metal oxides (Dorado et al., 2010), which is predicted to contribute to degradation of H_2S and MT during adsorption (Lahava et al., 2004; Tamai et al., 2011) in addition to biological degradation during biofiltration. It is therefore important to investigate the potential adsorption and degradation of VSCs by Leca and to further investigate the mechanisms of removal and the conditions that favour the degradation of VSCs on the surface of Leca.

In this study, the chemisorption of volatile sulphur compounds on Leca has been investigated under different conditions: (1) presence of gaseous oxygen (air vs. N_2) (2) air velocity and (3) moisture content (in air and in the Leca material). It is hypothesized that metal oxides (especially iron oxides) in Leca are involved in one or more surface-catalyzed reactions with H_2S and MT.

2. Materials and methods

2.1. Leca pellets (burnt clay particles) and preparation

Specially manufactured Leca pellets, 2–4 mm from Saint-Gobain Weber A/S, Randers (Denmark) was used in this study. The pellets have an external surface area of 1000 $m^2\ m^{-3}$ and internal surface area of 580 $m^2\ kg^{-1}$ with corresponding external pore volume of 48% and internal pore volume of 81%. They have a very porous internal structure with a wide range of pore sizes.

In this study, a mass of 11.2 g of Leca was used for each test. Dry Leca (drying Leca in oven with 100 °C overnight) had a moisture content of 0.2% after a gravimetric measurement. Wet Leca was prepared by soaking 11.2 g of Leca in 100 mL de-ionized water in a 250 mL tightly closed glass bottle for 3 d. The moisture content of Leca before each wet Leca test was measured to be 52% w/w. Measured pH of Leca soaked in deionized water was 8.4 ± 0.1.

2.2. Preparation of gas mixture in Tedlar bags

Gas standard mixtures (Linde Gas, Germany) containing H_2S (5.06 ppm ± 0.51), MT (5.20 ppm ± 0.26) and DMS (5.45 ppm ± 0.55) was used as the source of volatile sulphur compounds. Experiments were carried out under ambient air and nitrogen gas environments. The gas phase environment was simulated by using charcoal-filtered ambient air or standard nitrogen gas (Air liquid, Horsens, Denmark) containing nitrogen (⩾99.999%), H_2O (⩽3 ppm), O_2 (⩽2 ppm) and C_nH_m (⩽0.5 ppm) for dilution of the volatile sulphur gas mixture in Tedlar bags. A mass flow controller (Smart-Trak 2, Series 100, Sierra instruments, The Netherlands) was used to control the flow of gases to the Tedlar bags.

The diluted gas mixtures were filled in a 10 L bag for adsorption tests at 25 mL min^{-1} and 50 mL min^{-1} flow and 24 L bag for adsorption tests at 150 mL min^{-1} flow. Flow rates between 25 mL min^{-1} and 150 mL min^{-1} were selected to achieve a considerable removal and not too fast breakthrough. The choice of the flow was also due to the limitation of the time resolution of the measurements. The air or nitrogen gas and sulphur gas mixture dilution are as follow; a volume of 7.5 L of air or nitrogen gas was diluted with 2.5 L of the sulphur gas mixture for the 10 L bags and a volume of 15 L of air or nitrogen gas was diluted with 5 L of sulphur gas mixture in the 24 L bags (which were not filled completely). A recent study showed that VSCs (H_2S, MT and DMS) are well recovered even after 24 h (Hansen et al., 2011) and loss of VSCs in the Tedlar bags was therefore considered to be insignificant.

Initial long-term experiments (up 28 h) were carried out with a dynamic dilution system instead of the bags. The required relative humidity of the gas mixtures for the experiments under humid gas condition was obtained by injecting a known volume of water into a Tedlar bag (with known volume of gas). The expected relative humidity was calculated from psychometric charts from Perry et al. (1984) before injection. The relative humidity of the gas mixture after evaporation in the Tedlar bags was confirmed with a digital hygrometer. The measured relative humidity of dried charcoal filtered ambient air was 5% while the relative humidity of the nitrogen gas was 2%.

2.3. Gas chromatograph (GC) sulphur chemiluminescence detector (GC-SCD)

Gaseous sulphur compounds were analyzed by a GC-SCD. The GC-SCD was made up of two main units; a GC (GC 7890A) and a 355 SCD, with sample a loop of 1.0 mL. The detection limits of H_2S, MT and DMS were 1.7, 1.5 and 1.5 ppb respectively. Detailed operation principle of the GC-SCD can be found in Yan (2006). The GC column (length = 60 m and id = 0.53 mm) has a capillary column with a stationary phase of dimethylpolysiloxane (DB-1, Agilent Technologies A/S, Horsholm, Denmark). Helium was used as the carrier gas at a flow rate of 10 mL min^{-1}. The oven temperature was held for 4 min at 40 °C ramped at 10 °C min^{-1} up to 200 °C. A gas standard (Air liquid, Horsens, Denmark) containing H_2S (5.33 ± 0.16 ppm), MT (5.37 ± 0.27 ppm) and DMS (5.84 ± 0.29 ppm) was used as a one-point calibration. The GC-SCD was programmed to automatically inject the outlet gas at 20 min intervals.

2.4. X-ray fluorescence scan

The elemental composition of Leca was obtained by X-ray fluorescence analysis of crushed Leca pellets. Four sets of Leca samples were prepared for the analysis: fresh Leca, used Leca after a dry test, used Leca after a wet test and used Leca after desorption. The X-ray analysis was carried out by wavelength dispersive X-ray fluorescence (WDXRF; PW2400/Uniquant, Philips Analytical, The Netherlands).

2.5. Experimental set-up

Leca was packed in a 13.5 cm long acrylic tube with 2 cm id. Teflon tubes were used for all the gas transport to the GC-SCD. A pump connected to the GC-SCD outlet and loop drew the gas mixture from the Tedlar bag via the column of Leca. A control

measurement was performed with an empty tube before and after each test. The experimental conditions are presented in Table 1.

Triplicate tests were carried out for run 1a, 1b, 4a, 4b, 7a and 7b (see Table 1). Single test was run for subsequent tests due to low standard errors observed in the above runs. In an initial test for 28 and 20 h at 50 and 180 mL min^{-1}, respectively (shown in Fig. 1), no saturation was seen. Therefore, it was decided to focus on differences in the initial phase of the breakthrough curve in order to avoid excessively long test periods. Hence, all experiments were run for 150 min except for run 3a and 3b, which were run for 350 min because no breakthrough of H_2S was observed after 150 min.

Dimethyl disulphide (DMDS) and dimethyl trisulphide (DMTS) peaks were detected in reference to detection time of authentic samples. Concentrations of DMDS and DMTS in the outlet of the tube were quantified using the equimolar detection of sulphur compounds by the GC-SCD. A response factor was calculated by dividing the peak area and concentration of a standard of DMS. Peak areas of DMDS and DMTS were then divided by the calculated response factor (of DMS) divided by the number of sulphur atoms in the compound.

3. Results and discussion

3.1. Overall mechanism

In order to gain insight into the mechanism (physical sorption or chemisorption) of the removal, a comparison between sorption of H_2S, MT and DMS was carried out together with an attempt to identify sulphur-containing volatilized products by GC-SCD. In addition, sorption tests were performed in air and pure nitrogen at different Leca moisture contents and gas phase relative humidity.

Fig. 1a and b shows the breakthrough curves of H_2S, MT and DMS by dry Leca in ambient air at 50 and 180 mL min^{-1} flow rates for 28 and 20 h respectively. Both figures show that Leca retains more H_2S and MT than DMS. In Fig. 1a gradual increases were observed for the outlet concentrations of H_2S and MT from the start of the test to 28 h when the test was stopped. DMS instantly broke through with an outlet concentration similar to the inlet concentration. In Fig. 1b, a test run at a higher flow rate of 180 mL min^{-1} showed more rapidly increasing outlet concentrations of H_2S and MT during the first 2 h, which was followed by slowly increasing outlet concentrations of H_2S and MT until around 20 h when the

Table 1
Experimental conditions.

Run no.	Gas phase environment	Flow rate (mL min^{-1})	Gas phase relative humidity (%)	Leca moisture content (%)	Inlet concentration (ppb) ± standard deviation (SD)				Mass loading rate (μg min^{-1})		
					Hydrogen sulphide (H_2S)	Methanethiol (MT)	Dimethyl sulphide (DMS)	SD (n)	H_2S	MT	DMS
1a	Air	25	5	0.2	983 ± 75	1000 ± 93	986 ± 92	5	0.034	0.049	0.063
1b	Nitrogen gas	25	2	0.2	916 ± 70	940 ± 77	931 ± 87	11	0.032	0.046	0.059
2a	Air	25	74	0.2	975 ± 85	1043 ± 108	1020 ± 111	2	0.034	0.051	0.065
2b	Nitrogen gas	25	71	0.2	907 ± 27	925 ± 35	911 ± 36	3	0.032	0.046	0.058
3a	Air	25	74	52	865 ± 32	874 ± 34	885 ± 36	4	0.030	0.043	0.056
3b	Nitrogen gas	25	71	52	878 ± 44	907 ± 56	892 ± 41	4	0.031	0.045	0.057
4a	Air	50	5	0.2	978 ± 90	1027 ± 80	1027 ± 85	10	0.068	0.101	0.130
4b	Nitrogen gas	50	2	0.2	885 ± 75	926 ± 88	906 ± 88	6	0.062	0.091	0.115
5a	Air	50	74	0.2	796 ± 146	896 ± 178	892 ± 184	3	0.055	0.088	0.113
5b	Nitrogen gas	50	71	0.2	900 ± 10	940 ± 23	920 ± 25	3	0.063	0.092	0.117
6a	Air	50	74	52	830 ± 50	852 ± 56	840 ± 63	3	0.058	0.084	0.107
6b	Nitrogen gas	50	71	52	807 ± 19	813 ± 17	795 ± 16	4	0.056	0.080	0.101
7a	Air	150	5	0.2	1224 ± 181	1307 ± 160	1340 ± 156	9	0.256	0.386	0.511
7b	Nitrogen gas	150	2	0.2	1137 ± 55	1168 ± 42	1171 ± 38	7	0.238	0.345	0.446
8a	Air	150	74	0.2	884 ± 26	884 ± 16	870 ± 16	3	0.185	0.261	0.332
8b	Nitrogen gas	150	71	0.2	924 ± 144	930 ± 120	927 ± 113	2	0.193	0.274	0.353
9a	Air	150	74	52	816 ± 38	832 ± 43	811 ± 38	2	0.171	0.246	0.309
9b	Nitrogen gas	150	71	52	764 ± 12	768 ± 24	751 ± 28	2	0.160	0.227	0.286

n = Number of samples.

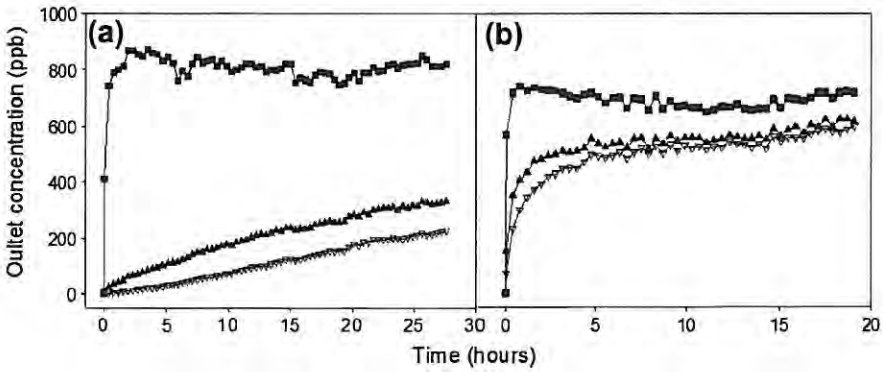

Fig. 1. Breakthrough curves of H_2S, MT and DMS by dry Leca at 50 mL min^{-1} flow for 28 h (a) and 180 mL min^{-1} flow rate for 20 h (b) in a preliminary experiment. (■) DMS, (▲) MT, (▽) H_2S. DMS-inlet concentration (886 and 775 ppb), MT-inlet concentration (905 and 780 ppb) and H_2S-inlet concentration (600 and 715 ppb) for a and b respectively.

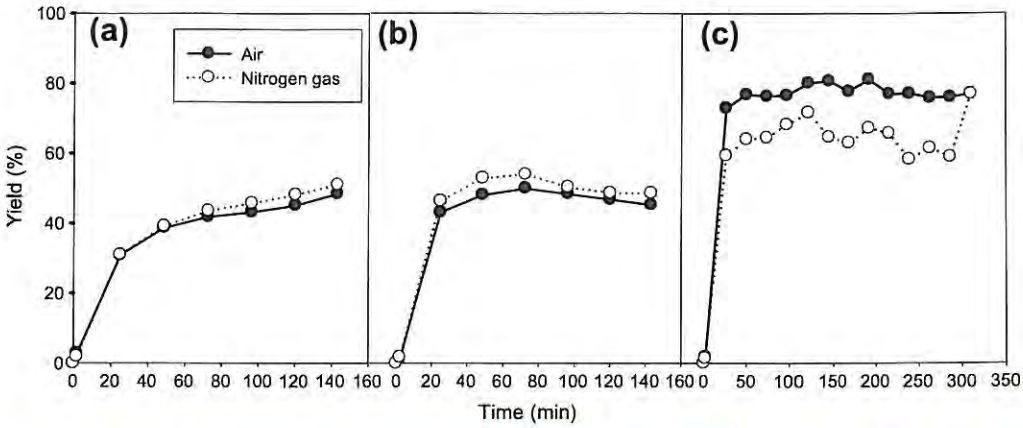

Fig. 2. Sum of DMDS and DMTS yields from the removal of MT in air and nitrogen gas environment by (a) dry Leca, (b) dry Leca at 74% gas RH and (c) wet Leca at 74% gas RH.

test was stopped. Similar to the adsorption test at 50 mL min^{-1}, H_2S and MT could not saturate Leca after 20 h of adsorption while the outlet concentration of DMS was almost the same as the inlet concentration just after the start of the test.

According to theory, sorption of adsorbates on solid surfaces is inversely related to their vapour pressures in physisorption processes (Pankow and Bidleman, 1992; Goss and Schwarzenbach, 1998). This suggests that more DMS should have been adsorbed on Leca than H_2S and MT since DMS has a lower vapour pressure (Table SM-1 of Supplementary material (SM)). On the contrary, Leca removed more H_2S and MT than DMS in our study. This most likely is due to H_2S and MT being more reactive towards Leca, while DMS is non-reactive and only physically sorbed to Leca. This is in accordance with the findings of Katoh et al. (1995) in a test with H_2S, MT, and DMS gas mixture adsorbed to carbon adsorbents. This apparently indicates that the removal of H_2S and MT in our study is related to the presence of one or two –S–H groups.

To verify the assumption that H_2S and MT are removed through chemisorption by Leca while DMS is only physisorbed on Leca, an adsorption–desorption test was run on dry Leca in ambient air condition. The test was performed by first carrying out an adsorption test with H_2S, MT and DMS at inlet concentrations of 1100, 1370 and 1455 ppb respectively. The adsorption test was stopped after 2 h and immediately followed by a desorption test. During the desorption test, non-detectable concentrations of H_2S and MT were observed after 30 min of desorption but detectable concentrations of DMS were still observed at 2 h when the test was stopped. Both adsorption and desorption tests were run at 50 mL min^{-1} flow rate. Masses of H_2S and MT removed and recovered from the adsorption and desorption tests were 1.8 and 0.08 μg and 4.2 and 0.15 μg, respectively. Due to the fast breakthrough of DMS during the adsorption test and still low detectable concentration of DMS when test was stopped, the recovery of DMS could not be determined accurately and is therefore not included.

DMDS and DMTS were detected during the experiments, which also support the assumption of chemisorption of MT by Leca (the potential and suggested reaction mechanisms are discussed in a SM). Whereas production of DMDS from MT is relatively straightforward, formation of DMTS requires a third sulphur atom. This is most likely provided by elemental sulphur either from oxidation of H_2S or from native elemental sulphur from the Leca material (Van Leerdam et al., 2011). Fig. 2 shows the yield of total DMDS and DMTS (assumed to be by-products of MT) obtained from Fig. 3b,d,g,h,k,l. Yields of DMDS and DMTS in Fig. 2 were calculated as (with [x] indicating gas concentration):

$$Y(\%) = \frac{[\mathrm{DMDS}]_{out} + [\mathrm{DMTS}]_{out}}{([\mathrm{MT}]_{in} - [\mathrm{MT}]_{out}) \times 2} \times 100$$

in which the change in MT concentration was multiplied by 2 to take into account that it takes two MT molecules to create on DMDS or DMTS. By this definition, the yield is calculated with respect to the methyl groups, assuming that the third S-atom in DMTS is provided by elemental sulphur either from H_2S (or MT) oxidation or from the filter material. No significant difference in the yields of DMDS and DMTS were observed under air condition compared to nitrogen condition. This apparently indicated that gaseous oxygen is not necessary for the production of DMDS and DMTS from oxidation of MT by Leca. At the same time, similar amounts of H_2S were removed by Leca under air and nitrogen gas condition as shown in Fig. 3a,c,e,f,i,j. Greater amounts of MT were removed by Leca under nitrogen condition from Fig. 3a,c,i,j while an opposite trend was observed from Fig. 3e and f. Calculated mass fraction of sorbed H_2S and MT to Leca to the total inlet mass of H_2S and MT during adsorption showed (0.54 and 0.48) from Fig. 3a (air condition) and (0.65 and 0.82) from Fig. 3c (nitrogen condition) for H_2S and MT respectively. For Fig. 3e (air condition) and Fig. 3f (nitrogen condition), mass fractions of (0.63 and 0.72) and (0.95 and 0.59) were calculated for H_2S and MT respectively while in Fig. 3i (air condition) and Fig. 3j (nitrogen condition), (0.5 and 0.5) and (0.31 and 0.31) were found for H_2S and MT respectively. It is difficult to explain why greater amounts of MT was sorbed to Leca in air condition than nitrogen condition from Fig. 3f, however the overall trend indicates that the removal of H_2S and MT is not necessarily oxidized by oxygen. It is important to mention that calculated DMDS/DMTS ratios from Fig. 3a,c,e,f,i,j showed nearly the same amount of DMDS and DMTS from Fig. 3a,c,e,f with greater production of DMDS than DMTS as adsorption progressed from Fig. 3i and j (DMDS/DMTS ratio curves can be found in Fig. 1 in Supplementary material).

It is seen from X-ray analysis that Leca contains substantial amounts of iron and other metals in oxidized form (Table SM-2). This means that the Leca material has an oxidation potential in itself and does not necessarily require gaseous oxygen (see also discussion on removal mechanisms in Supplementary information).

In addition, fresh Leca, Leca after dry adsorption without desorption and desorbed Leca after wet adsorption were analyzed by X-ray with respect to sulphur content with the results showing a sulphur content of 0.84%, 0.55% and 0.68% (mass percentage) for fresh Leca, dry Leca without desorption and wet Leca after desorption respectively. It is hypothesized that intrinsic sulphur compounds in Leca reacted with MT to form DMDS and DMTS, thus

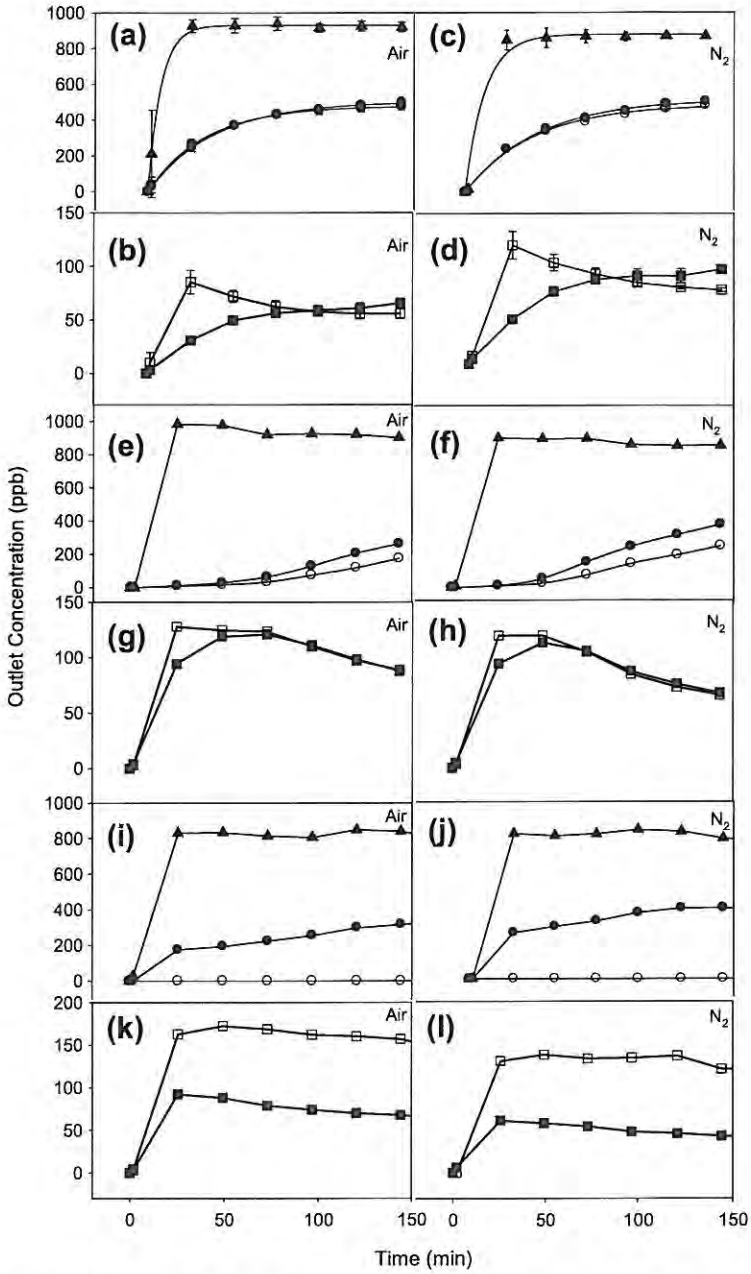

Fig. 3. Breakthrough curves of H_2S, MT and DMS by dry Leca figures; (a–d); 74% gas relative humidity by dry Leca figures; (e–h) and at 74% gas relative humidity by wet Leca (52% moisture content) figures; (i–l) all at 25 mL min^{-1} flow rate in ambient air and nitrogen gas environments and detected DMDS and DMTS by-products during adsorption (▲) DMS, (●) MT, (○) H_2S, (□) DMDS, (■) DMTS.

resulting to the reduction of elemental sulphur in the used samples (suggested reactions can be found in Sections SM 1.1 and 1.2).

To summarize, the following observations are best explained by chemisorption of H_2S and MT: (i) Dry Leca removed more H_2S and MT than DMS, which is contrary to the inverse relation between sorption of compound to solid surfaces and their vapour pressure, (ii) H_2S and MT are poorly recovered from Leca after exposure, (iii) DMDS and DMTS are identified as by-products after the exposure of the sulphur compound mixture to Leca, and (iv) Leca is observed to contain a large amount of metal oxides, e.g., Fe_2O_3 that may be involved in surface oxidation. Since DMS appear not to be permanently degraded by interaction with Leca, the discussion in the following is mainly focused on H_2S and MT.

3.2. Effect of relative humidity and moisture

Fig. 3a,e,i shows the removal of H_2S, MT and DMS by Leca at dry conditions as well as under conditions of humidified air and pre-soaked material. Fig. 3c,f,j shows the removal of H_2S, MT and DMS by Leca under similar conditions, but in a nitrogen atmosphere. The experimental conditions in the study are shown in Table 1. It is worth noting that all adsorption were run at 25 mL min^{-1} gas flow rate.

Under humid conditions (Fig. 3e and f), Leca had a higher removal of H_2S and MT when compared to dry conditions (Fig. 3a and c). The presence of moisture is hypothesized to facilitate the sorption and dissociation of H_2S and MT. It is also assumed that

moisture on Leca makes it more reactive compared to dry Leca. Leca lost its chemisorption ability gradually over time (Fig. 3e and f), and this could be due to formation of a bulk water film by continuous sorption of water from the gas phase to the Leca surface. As the thickness of this layer increased, a diffusion resistance for H_2S, MT may have been built up. It could also partly be due to oxidation products of H_2S and MT that increasingly occupy the active sorption sites on Leca and prevent further chemisorption of H_2S and MT. As shown in Fig. 3e and f, Leca adsorbed more H_2S than MT, which may be due to the fact that the pH of Leca (pH = 8.4 ± 0.1) is higher than the pK_a value of H_2S (pK_a = 7.04 at 25 °C; Smet et al., 1998) but lower than the pK_a value of MT (pK_a = 9.6; Smet et al., 1998). Thus, H_2S is mainly in the form of HS^- but MT remains mainly neutral in the presence of water.

In Fig. 3i and j, no breakthrough of H_2S was observed even when the test was extended to 330 min (Fig. 3i and j shows results for only 150 min). Less MT was retained by wet Leca (Fig. 3i and j) compared to dry Leca (Fig. 3e and f). Again, more H_2S than MT was observed to be removed.

Fig. 4a,c,e shows the effect of the gas phase moisture content and the wetness of Leca on the removal of H_2S and Fig. 4b,d,f for MT at 25, 50 and 150 mL min^{-1} flow rates. All data in Fig. 4 were obtained from tests under ambient air conditions. Results from tests in a nitrogen atmosphere showed similar trends as under ambient air condition (data not shown). Removal of H_2S increased with increasing gas phase moisture content and water content of Leca. The highest removal occurred with pre-humidified gas combined with water-soaked Leca, which was followed by sorption with the pre-humidified gas on dry Leca. As discussed above, moisture on Leca might have helped adsorb gaseous H_2S by dissociation into HS^- (enhanced by the water film pH).

On the other hand, adsorption of MT on Leca with different gas phase moisture content and wetness of Leca did not show a straightforward trend as was seen for H_2S. Leca retained MT mostly when it was pre-humidified and adsorbed on dry Leca. Pre-humidification of MT followed by adsorption onto wet Leca resulted in similar or lower removal compared to the former although these semi-wet conditions gave better performance compared to completely dry conditions (without pre-humidification). This indicates that the breakthrough of MT critically depends on a specified moisture content of Leca. For both H_2S and MT there is a clear trend in the breakthrough curves with respect to air flow through the column. In all cases, a concentration plateau is reached.

A careful look at removal of pre-humidified MT on dry and wet Leca at 25 mL min^{-1} flow in Fig. 4d and f suggests that the former, which performs better initially, seems to lose its removal capability quicker after 80 min. This is seen by comparing the breakthrough concentration in Fig. 4d and f (open triangles) after 140 min exposure. It could result from the formation of a bulk water film (due to the accumulation of water vapour) on the surface of Leca, which may create a diffusion resistance for MT to Leca. The existence of a moisture content threshold for optimal MT removal below water saturation is suggested.

Increasing the relative humidity and moisture content of Leca resulted in an increased formation of DMDS when comparing Fig. 3b and d and Fig. 3k and l, but reduced the production of DMTS using wet Leca as shown in Fig. 2k and l when compared to Fig. 3e and f. This could be a result of the reduction in the amount of MT sorbed to Leca during wet conditions.

In summary, the presence of moisture increased the removal of H_2S and MT by Leca compared to under dry conditions. Whereas for H_2S removal is increasing with increasing moisture content, MT removal appear to be less enhanced at the highest water content (Leca pre-soaked in water). Differential dissociation can be a part of the explanation of this difference between the two compounds.

3.3. Implications for practical application

The results of the present study confirm that Leca is a unique material with potential reactive properties in relation to

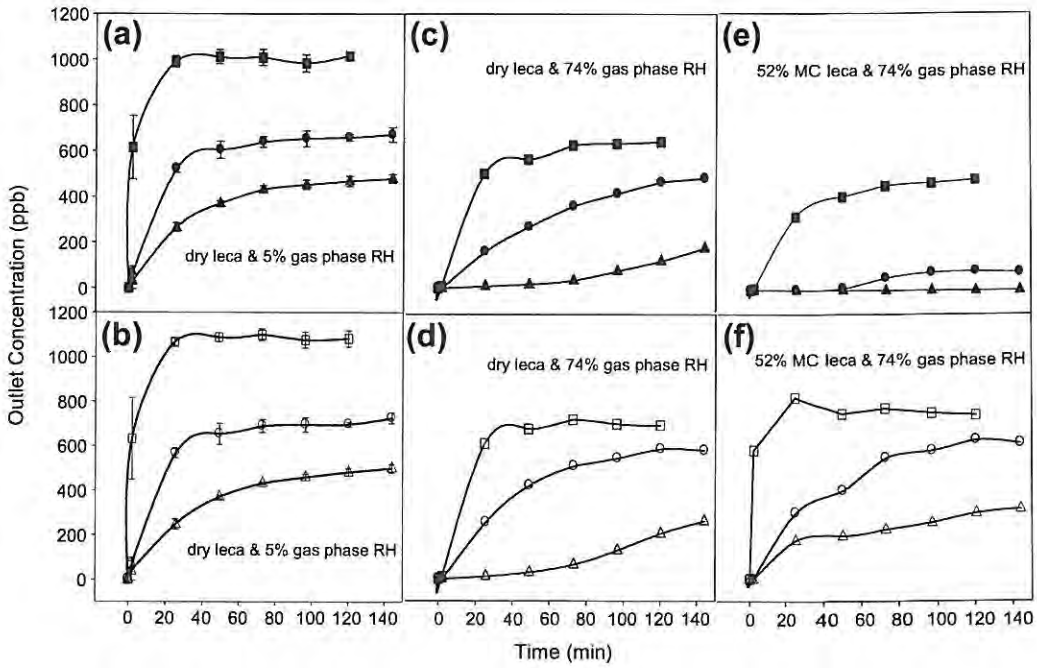

Fig. 4. Breakthrough of H_2S and MT at 25, 50 and 150 mL min^{-1} flow rate in ambient air condition by dry Leca at 5% and 74% gas relative humidity and adsorption by wet Leca (52% MC) at 74% gas relative humidity. (■) 150 mL min^{-1} (H_2S), (●) 50 mL min^{-1} (H_2S), (▲) 25 mL min^{-1} (H_2S), (□) 150 mL min^{-1} (MT), (○) 50 mL min^{-1} (MT), (△) 25 mL min^{-1} (MT).

degradation of gaseous sulphur compounds. Leca is particularly effective towards H_2S at low flow rates and high water contents at which no breakthrough is observed. Under such conditions, Leca may be used as a purely chemical air treatment. In addition, Leca may be used in biological air treatment systems as a material, which will enable chemical reactions in addition to biological reactions. In a biological filter based on Leca, the micro-organisms could be involved in continuous removal of soluble reaction products and in re-generation processes. The fact that DMDS and DMTS were produced as by-products during the adsorption of H_2S, MT and DMS indicates in practical application that the use of Leca as a biofiltration might not result in the total removal of gas mixtures of reduced sulphur compound. However, it is expected that the odour levels would be reduced significantly because the odour activity value (calculated as the ratio of typical concentration of an odorant to its odour threshold value) of DMDS and DMTS are much lower than H_2S, MT and DMS. Further experiments are required to investigate the application of Leca in a full scale filter unit with biological activity.

4. Conclusions

Breakthrough tests have demonstrated that DMS is poorly retained by Leca under all conditions tested, which indicates a physical sorption mechanism of this compound, whereas H_2S and MT were subject to chemisorption. Comparison between tests in ambient air and nitrogen conditions showed that the chemisorption of H_2S and MT did not necessarily require the presence of oxygen. DMDS and DMTS were detected by GC-SCD and are assumed to be derived from the reaction between MT and elemental sulphur intrinsically in Leca or elemental sulphur from the oxidation of H_2S since a reduction in the mass fraction of elemental sulphur in Leca was observed from an X-ray analysis.

Pre-humidification of H_2S and MT increased the adsorption performance of Leca compared to dry conditions. Adsorption on wet Leca (52% moisture content) further increased the adsorption performance of Leca for H_2S but not for MT.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.07.068.

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