The control of mercury vapor using biotrickling filters

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Abstract

The feasibility of using biotrickling filters for the removal of mercury vapor from simulated flue gases was evaluated. The experiments were carried out in laboratory-scale biotrickling filters with various mixed cultures naturally attached on a polyurethane foam packing. Sulfur oxidizing bacteria, toluene degraders and denitrifiers were used and compared for their ability to remove Hg^0 vapor. In particular, the biotrickling filters with sulfur oxidizing bacteria were able to remove 100% of mercury vapor, with an inlet concentration of 300–650 $\mu g\,m^{-3}$, at a gas contact time as low as six seconds. 87–92% of the removed mercury was fixed in or onto the microbial cells while the remaining left the system with the trickling liquid. The removal of mercury vapors in a biotrickling filter with dead cells was almost equivalent to this in biotrickling filters with live cells, indicating that significant abiotic removal mechanisms existed. Sulfur oxidizing bacteria biotrickling filters were the most effective in controlling mercury vapors, suggesting that sulfur played a key role. Identification of the location of metal deposition and of the form of metal was conducted using TEM, energy dispersive X-ray analysis (EDAX) and mercury elution analyses. The results suggested that mercury removal was through a series of complex mechanisms, probably both biotic and abiotic, including sorption in and onto cellular material and possible biotransformations. Overall, the study demonstrates that biotrickling filters appear to be a promising alternative for mercury vapor removal from flue gases.
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1. Introduction

Mercury (Hg) is a hazardous chemical and one of the priority pollutants. It is emitted to the atmosphere from a variety of natural and anthropogenic sources (Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2002). Anthropogenic sources of mercury emissions include coal and oil combustion for energy generation, incinerators, chlor-alkali industries, mining, processing/refining of mercury ore and gold mining (Pacyna et al., 2000; Pirrone et al., 2001, 2003; Pacyna and Pacyna, 2002). Estimates of global mercury emissions to the atmosphere indicate that the contribution from industrial sources ranges between 1600 t yr^{-1} and 2200 t yr^{-1} (Carpi,

1997; Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2002). In coal combustion flue gases, concentrations of mercury typically ranges from 1 to 35 $\mu g\,m^{-3}$, whereas the mercury concentration in exhaust gases of incinerators can be as high as 400–700 $\mu g\,m^{-3}$ (Kolkar et al., 2006; Liuzzo et al., 2007).

Exposure to mercury leads to serious health effects and therefore, EPA was compelled to put stringent regulations for mercury emission from various activities. Though there are many traditional mercury removal methods based on absorption in wet scrubbers, or adsorption onto activated carbon or other adsorbents injected into the gas stream (Sjostrom et al., 2002; Pavlish et al., 2003), there is currently no single technology that can be broadly applied for the complete removal of mercury from flue gases. Combinations of available control technologies may provide up to 90% control of total mercury in some plants but not in others depending on the makeup of mercury vapors. Of the different forms of mercury in combustion gases, elemental

mercury, Hg^0 poses the greatest challenge for effective treatment as it does not sorb well to current sorbents and is difficult to scrub (Carpi, 1997; Sjostrom et al., 2002; Pavlish et al., 2003; Kolkar et al., 2006; Gutiérrez Ortiz et al., 2007).

In this context, alternative treatment options are needed. In particular environmentally friendly methods and methods that offer the potential to be developed as multi-pollutant (NO_x, SO_x, particulate matter, and Hg) treatment systems should be developed. One such system may be biological treatment, which holds promise for multi-pollutant treatment (Lee and Sublette, 1991; Devinny et al., 1999; Philip and Deshusses, 2003; Higuchi et al., 2004; Jinsiriwanit, 2006). However, the use of bioreactors for the treatment of mercury vapor from flue gases needs first to be proven and optimized.

Many microorganisms are capable of concentrating heavy metals from their aqueous environment (Nakajima and Sakaguchi, 1986; Volesky, 1990). Microorganisms like *Phanerochaete chrysosporium, Fusarium floccciferum, Rhizopus arrhizus, Trametes versicolor* are reported to exhibit high mercury adsorption capacity. It is also reported that dividing, non-dividing and dead cells of *Chaetoceros costatum*, a marine diatom can take up significant amount of mercury (Glooschenko, 1969). Dead cells showed better metal accumulation capacity compared to active and resting cells. Mercuric ion and organo-mercurial transformation in bacteria from mercury contaminated environments results in the less toxic Hg^0 (Nakajima and Sakaguchi, 1986; Volesky, 1990; Chen and Wilson, 1997; Hobman et al., 2000). Certain other strains like *Enterobacter aerogens* reduce the toxicity of Hg ions by complex formation with extra cellular polymers. Hg ions also have a high affinity to sulfhydral and amino-nitrogen ligands in proteins and other important biological molecules. Recently it has been reported that Hg^0 can pass through the cell wall of certain types of soil bacteria and *Escherichia coli* and be oxidized to Hg^{2+} which is more toxic than elemental mercury (Chen and Wilson, 1997; Smith et al., 1998). Moreover, Levchenko et al. (1997) reported the accumulation of colloidal gold by living bacteria. In this case membrane proteins were mainly responsible for the gold accumulation and different quinines played the main role in the redox transformation of gold. Unfortunately most of the biosorption studies were concentrated on the removal of Hg^{2+} from aqueous solutions.

In the present paper, the possibility of using biosorption/bio-precipitation as an alternative technology for the removal of mercury vapor from flue gases was explored. The removal of mercury from synthetic flue gases in a biotrickling filter was studied and attempts were made to understand the mechanisms of mercury removal.

2. Materials and methods

2.1. Biotrickling filter setup

A schematic of the experimental setup is shown in Fig. 1. All reactors were made out of clear Schedule 40 PVC pipe,
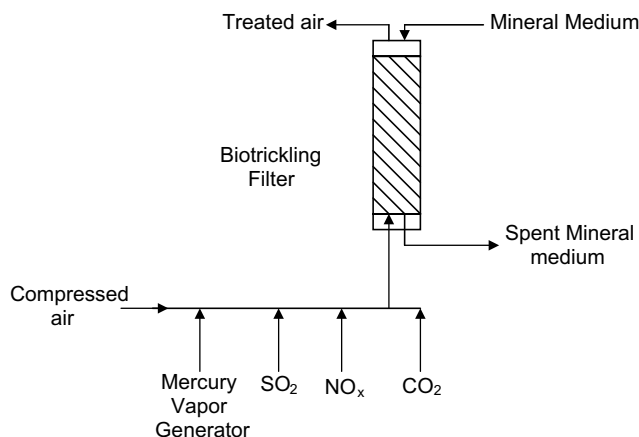

Fig. 1. Schematic diagram of the biotrickling filter treating mercury contaminated flue gases.

fittings and caps (ID = 4 cm). The total height of each reactor was 60 cm and the bed height was 50 cm. The reactor contained 0.57 l of packing made of open pore polyurethane foam cubes ($4 \times 4 \times 4$ cm, specific surface area of 600 $m^2\, m^{-3}$, density of about 35 kg m^{-3} from EDT, Germany (Philip and Deshusses, 2003; Gabriel and Deshusses, 2003)) cut to a cylindrical shape to fit the reactor internal diameter. The trickling liquid (see composition below) was sprinkled over the packed bed at a axial rate of 0.8 m h^{-1} (i.e., 1000 ml h^{-1}) from the top of the reactor. The biotrickling filter liquid effluent was collected from the bottom of the reactor and analyzed for mercury prior to disposal. All the biotrickling filters except one were operated at room temperature (20–24 °C). To simulate the flue gas conditions, one reactor was operated at 65–70 °C, which is the usual temperature of combustion gases after desulfurization in a lime scrubber. The trickling liquid (pH = 7.0 ± 0.5) consisted of a mineral medium with the following composition (in g l^{-1} in deionized water) K_2HPO_4 (1), KH_2PO_4 (1), NaCl (1), $MgCl_2$ (0.25), $CaCl_2$ (0.52), KNO_3 (1) $Na_2S_2O_3$ (0.50) and trace element solution 1 ml l^{-1} (Philip and Deshusses, 2003). Simulated flue gas was prepared by mixing a metered flow of 10% vol. compressed air, 15% CO_2, 75% N_2 and, in some experiments NO and SO_2 gases. The total gas flow rate was varied to achieve empty bed residence times (EBRTs) in the reactor ranging from 6 to 70 s. To generate Hg^0 contaminated air, a small side stream of compressed air was diverted through a 40 ml vial containing metallic mercury at room temperature. This stream was then mixed with the main air stream. The resulting inlet Hg^0 concentrations were in the range of 250–700 µg m^{-3}. Changing the airflow rate through the vial allowed to vary the concentrations of mercury in the synthetic flue gas stream.

2.2. Microbiological protocol

Three types of mixed bacterial cultures namely: sulfur oxidizing bacteria (SOB) from a hydrogen sulfide treating biotrickling filter, autotrophic denitrifying bacteria (DNB) collected from a nitrogen oxides treating biotrickling filter,

and toluene degraders (TND) collected from a bioreactor treating toluene were used in the present study. In the case of SOB and DNB, the bacteria were already immobilized on the polyurethane foam as the packing was taken from active bioreactors (Kim and Deshusses, 2005). To kill the cells for abiotic controls, the polyurethane foam cubes with bacteria attached were exposed to 254 nm UV radiation for 12 h while changing the UV exposed face of the foam cube periodically. Separate viable cell counts of cells removed from the foam cubes indicated that such UV exposure resulted in greater than three log reductions of viable cells. The NO_x treating bioreactor used as a source for the DNB was operated under anaerobic condition with an EBRT of 70 s (Jinsiriwanit, 2006). The toluene degrading bioreactor was similar in size to the mercury treating biofilter. To establish a biofilm on the foam support, a mixed culture collected from a bubble column treating toluene vapors was allowed to trickle through the bioreactor for 6 h. The medium was then replaced by fresh mineral medium to provide optimum growth environment for the bacteria. The composition of the mineral medium was the same as listed above except that there was no thiosulfate. A gaseous toluene concentration of 0.5–1.7 g m^{-3} was supplied to the reactor. Prior to exposure to mercury, the reactor was operated for 10 d to develop sufficient biomass on the foam support.

2.3. Analyses

The analysis of Hg^0 in the gas phase was carried out using a mercury vapor analyzer (MVI Mercury Vapor analyzer, Shaw City Limited, UK). The lower detection limit for the mercury analyzer was 1 μg m^{-3}. Selected grab samples were analyzed for verification purposes using Hg^0 Draeger tubes (Fisher Scientific, USA). Sulfate/sulfite, sulfide and thiosulfate analyses in liquid samples were carried out as per Standard Methods (APHA, 1994). Sulfate analysis was based on a spectrophotometric method. Sulfite was determined by titration using standard potassium iodide–iodate titrant and a starch indicator, with careful precautions to avoid any interference. Elemental sulfur analysis was done as described by Schedel and Trueper (1980) by reacting the elemental sulfur with cyanide to produce thiocyanate, which was quantified spectrophotometrically as $Fe(SCN)_6^{3-}$. pH measurements were carried out using a regular pH meter (Fisher Scientific, USA). Gaseous toluene concentrations were measured by gas chromatography (HP 5890) and a FID detector. Analysis of SO_2 and NO_x were carried out using a combustion gas analyzer (IMR-1400 Gas Analyzer, IMR Environmental Equipment International Inc., USA).

The amount of mercury in the matrices was measured after dismantling the reactors. Mercury concentration in the trickling liquid also was measured. A Bacharach Coleman model – 50 B mercury analyzer system (New Kensington, PA) was used for mercury analyses in liquid samples. Bacteria immobilized on polyurethane foam were digested in a mixed acid solution (HCl:HNO$_3$ at a 3:1 molar ratio) at 90 °C for 2 h then cooled and filtered.

Microbial density immobilized in the matrices was measured in terms of total protein. A calibration curve was made using bacterial concentration (dry weight) vs. total protein content. The total protein of intact cell was determined according to the method of Herbert et al. (1971). This method is essentially a modification of Lowry's method (Lowry et al., 1951) adapted for bacterial cells.

For the quantitative analysis of methyl and ethyl mercury, one cylinder of polyurethane foam from the biotrickling filter was immersed in 100 ml of 1:1 (HCl:DDI water) and sonicated for 30 min. After cooling, the samples were centrifuged at 1000g for 15 min, the supernatant was extracted twice with 5 ml of toluene. The moisture content was removed by filtering the extract through anhydrous sodium sulfate. The final filtrate volume was analyzed using a GC–MS (Ipolyi et al., 2004). For the analysis of liquid samples, acidified samples were used for extraction.

Extraction and classification of highly mobile, semimobile and non-mobile species of mercury from the biotrickling filter material was carried out as per the procedure suggested by Han et al. (2003). The target mercury species include methyl and ethyl mercury as well as inorganic mercury species that have great mobility in the environment, such as soluble Hg^{2+} ions and mercuric oxide (HgO). The mercury loaded polyurethane cubes with biomass were placed in a beaker containing 2% HCl and 10% ethanol as the extraction liquid, and mixed thoroughly for 2 min. Concentrated HCl was added dropwise until the pH of the mixture was between 1.5 and 3. The sample was sonicated for 7 min and was centrifuged to separate the supernatant. The extraction was repeated for three additional times and the extract was analyzed for Hg. The matrix material remaining after the ethanol extraction was further divided into semi-mobile and non-mobile mercury fractions. The semi-mobile mercury species include mainly Hg and mercury metal amalgam. The non-mobile mercury species mainly include HgS and Hg_2Cl_2. For the extraction of semi-mobile species 1:2 HNO$_3$:DDI water was used as eluent and heated at 95 °C in a water bath for 40 min. For the extraction of non-mobile mercury species, 1:6:7 HCl:HNO$_3$:DDI water was used as the extraction solution and heated at 95 °C in a water bath for 40 min.

For TEM observations, cells were fixed in 2% glutaraldehyde in phosphate buffer (0.1 M, pH-7.2–7.4) for 1 h at room temperature, dehydrated in ethanol and embedded in Spurr's epoxy medium. Unstained ultra-thin sections (70–90 nm) were mounted on 100 mesh copper grids and placed in a Philips CM 12 TEM microscope fitted with an energy dispersive X-ray spectrophotometer (EDAX).

3. Results and discussion

3.1. Mercury vapor removal in the biotrickling filters

For the initial experiment, the gas stream consisted of mercury vapor (300–650 μg m^{-3}) in air which was treated in the reactor containing SOB and operated at room
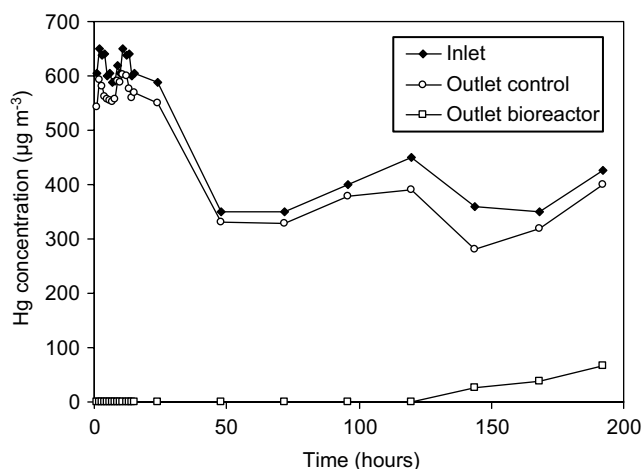
Fig. 2. Inlet and outlet concentrations of mercury vapor in the SOB packed biotrickling filter and in the cell-free control. Conditions: Air as carrier gas: EBRT = 70 s (0–1 h), 35 s (1–9 h), EBRT = 15 s (9–48 h), EBRT = 6 s (48–192 h).

temperature. Under these conditions, the biotrickling filter exhibited complete removal of mercury vapor at an initial EBRT of 70 s. Subsequently, the gas residence time was gradually reduced to 35 s, 20 s and to 6 s (Fig. 2) until breakthrough was observed after 5 d. Once the outlet concentration exceeded more than 10% of the inlet concentration, the operation of the reactor was stopped. Mercury concentration in the trickling water was analyzed periodically and it was observed that at any given time 8–13% of the inlet mercury concentration was leaving the system through trickling water. Inorganic and organic mercury have some affinity to thiosulfate. The trickling liquid used in the experiments with SOB had high concentrations of thiosulfate (500 mg l^{-1} as Na$_2$S$_2$O$_3$). To find whether mercury was removed by the trickling liquid only, a control reactor with all the conditions kept the same but without any microorganism was also operated in parallel to the biotrickling filter. Mercury removal in the control reactor was only about 8–10% (Fig. 2), indicating that that majority of mercury removed in other experiment was by sorption and or bio-precipitation onto microorganisms attached to the packing.

Next, the efficiency of the system for the removal Hg vapor in presence of multipollutants, i.e., SO$_x$ and NO$_x$ as in real flue gased was evaluated. The gas stream treated consisted of 10% compressed air, 15% CO$_2$, 75% N$_2$ and various percentages of NO and SO$_2$ gases. The SO$_x$ concentration varied from 300–500 ppm$_v$ whereas NO$_x$ concentration was below 300 ppm$_v$ most of the time. The biotrickling filter was able to remove SO$_x$ completely irrespective of the inlet concentration or the EBRT, though there was no significant NO removal (SO$_x$ and NO results not shown). This was expected as SO$_2$ is highly soluble and can be easily scrubbed, whereas NO has a high Henry's law coefficient and therefore is not removed during wet scrubbing. The mercury vapor removal efficiency of the system

was very high and breakthrough was not observed before 35 d (see Fig. A in Supplementary Information). Unlike other adsorbents like activated carbon (Yan et al., 1998), the presence of sulfur dioxide did not affect the mercury removal efficiency of the system. In fact, it had a positive effect. Consistent with earlier work (Philip and Deshusses, 2003), SO$_2$ was converted to sulfite and sulfate which presence must have improved conditions for mercury capture. Although sulfide could not be measured in the effluent of the trickling filter, after a few days of operation a yellow/white sulfur-like precipitate was observed on the packing. Even after 17 d of operation in the presence of SO$_2$, the biotrickling filter was not completely exhausted for mercury removal (see Fig. A in Supplementary Information).

The actual flue gas temperature can be very high. To evaluate the applicability of the new system in power plants or hot exhausts, experiments were conducted at elevated temperature of 65–70 °C, which corresponds to the lower limit of economical heat recovery. The results are presented in Fig. 3. During the experiment, fluctuations of the inlet concentration of mercury occurred. However, there was no visible impact on the outlet concentration of mercury. This was due to load equalization achieved by the biotrickling filter similar to the effect described by Moe and Li (2005) for variable toluene loads in granular activated carbon. At an EBRT of 6 s, mercury removal was above 95%, and the system was able to sustain efficient removal for more than 5 d. The specific adsorption capacity as calculated based on breakthrough point (an outlet concentration of 25 µg m^{-3}) for the system was 50.7 mg g^{-1}. This was about 60% of the capacity observed at room temperature (83.8 mg g^{-1}) under similar conditions. At the higher temperature, some bacterial cell components undergo denaturation and there may be many conformational changes in the adsorption sites. This might have reduced the adsorption capacity. Even though there was a reduction in adsorption capacity of the biosystem at elevated tempera-
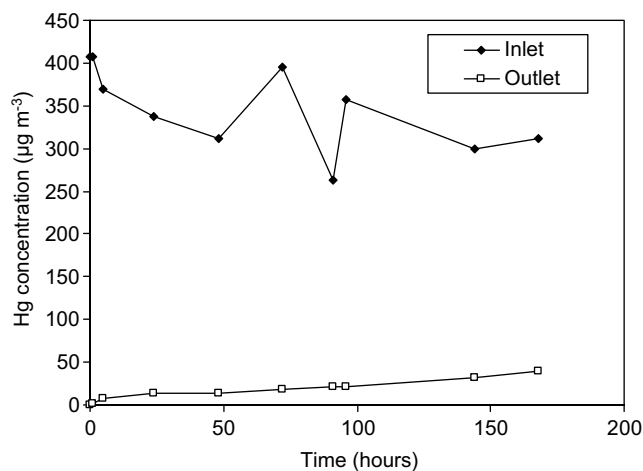

Fig. 3. Inlet and outlet concentrations of mercury vapor in the high temperature biotrickling filter. Conditions: air as carrier gas, temperature ∼65–70 °C, live SOB. EBRT = 6 s.

tures, the capacity was 10 to 750 times greater than the other commonly used adsorbents (Table 1). The adsorption capacity of powdered activated carbon, which is the most commonly used adsorbent for mercury control from flue gases is in the order of 0.2–5 mg g^{-1} (Yan et al., 1998; Sjostrom et al., 2002).

Since mercury contaminated flue gases may be toxic to the SOB or treatment may be at temperatures promoting cell death, investigations on the removal of mercury using dead cells were conducted. It is worth noting here that cells were treated with UV (see Methods section) which disrupts the cells' ability to replicate DNA. However some biological transformations may remain effective, at least for some time, in UV treated cells. The specific mercury removal capacity of UV treated cells was better than that of the living cells with sustained removal for over 18 d (see Fig. B in Supplementary Information). On the other hand, minor breakthrough of Hg occurred earlier and dead cells were not able to remove mercury vapor with 100% efficiency at any time, indicating some kind of mass transfer limitation. This suggests that system design based on dead cells would require a taller bed, in order to achieve the required percentage removal.

Mercury vapor removal in a reactor operated as a biofilter was also examined. The reactor was operated at the same conditions as the biotrickling filter except that there was no trickling of water. The inlet air was humidified before entering in the reactor to avoid drying of the packed bed. The reactor size was half that of the biotrickling filter. Compared to the biotrickling filter, breakthrough occurred

sooner (see Fig. C in Supplementary Information) in part because all the mercury had to be removed in the bed compared to the biotrickling filter in which roughly 10% of the mercury was removed by scrubbing. However, the specific mercury removal capacity was about twofold lower (Table 1) which indicates that the presence of trickling liquid had some effect on the cells' affinity to mercury.

A comparison of the mercury removal capacity of all the different reactors packed with sulfide oxidizing bacteria and operated under various conditions is given in Table 1. The sorption capacity was based on a breakthrough concentration of 25 μg m^{-3}, hence the actual maximum capacity of the various systems is higher than reported here. A comparison with current conventional adsorbents used for mercury control reveals that the specific adsorption capacity of the sulfide oxidizing bacteria is 10–750 times greater than the best adsorbents currently used for mercury control (Yan et al., 1998; Sjostrom et al., 2002).

An attempt was made to close the mercury balance in all the systems studied (Table 1). The calculation was made as follows. The difference between the time-weighed average inlet and outlet concentrations of mercury gave the average concentration of mercury that was removed in μg m^{-3}. This was then multiplied with air flow rate (in m^3 h^{-1}) and duration of experiment (h) to give the amount of mercury removed from the gas phase. This value was compared with the mercury assay value in the immobilized matrix after the termination of the experiment. Specific mercury uptake was calculated based on the biomass concentration on the matrix which was measured by protein determination. The average dry biomass amount in 1 l of polyurethane foam was 200–220 mg$_{dw}$ for SOBs and DNB. For toluene degraders it was in the range of 400–500 mg$_{dw}$ l^{-1}. Around 8–13% of the total adsorbed mercury left the system through the trickling liquid. Except for the biofilter experiment for which excellent closure of the mercury balance was obtained, the recovery was lower (63–82%) than the calculated adsorbed value. The variation of air flow rate, the non uniformity of mercury adsorption on the biomass due to possible air short circuiting, and experimental uncertainties might have caused this disparity.

Further studies were carried out with denitrifying bacteria and toluene-degrading bacteria to evaluate whether the type of microbes could be used for mercury vapor removal. Mercury vapor removal by autotrophic denitrifiers was

Table 1
Specific Hg^0 removal capacity based on breakthrough point (25 μg m^{-3}) and recovery of the removed mercury in the matrix

Type of reactor/nature of microbes	Specific Hg^0 removal capacity, mg$_{Hg}$ g^{-1}$_{cell\ dry\ weight}$	% Mercury recovery by desorption from the matrix[a]
Live cells of SOB, air, biotrickling filter, room temperature	84 ± 5	82 ± 4
Dead cell of SOB, air, biotrickling filter, room temperature	91 ± 5	75 ± 5
Live cells of SOB, synthetic flue gas, biotrickling filter, room temperature	148 ± 8	63 ± 10
Live cells of SOB, air, biotrickling filter, 65–70 °C	51 ± 5	68 ± 7
Live cells of SOB, air, biofilter, room temperature	35 ± 5	123 ± 5
Literature reports on the best conventional adsorbents (9, 30)	0.2–5[b]	NA

[a] Except for biofilter operation, 8–13% of the mercury left the system via the trickling water.
[b] Maximum adsorption capacity in mg$_{Hg}$ g^{-1}$_{adsorbent}$.

Table 2
Sequential elution and analysis of mercury species

Type of reactor/bacterial system	Highly mobile mercury species (%)	Semi-mobile (%)	Immobile (%)
Live cells of SOB, synthetic flue gas, biotrickling filter, room temperature	47	22	31
Live cells of SOB, air, biotrickling filter, 65–70 °C	21	63	16

Percentages are based on total desorbed mercury from the packing.

insignificant while toluene degraders were able to remove 20–50% of the mercury with an inlet concentration range of 80–500 μg m^{-3} under the same conditions as those used for mercury removal by SOB (results not shown). However their specific Hg removal capacity was low (6 ± 2 mg$_{Hg}$ g^{-1}$_{cell\ dry\ weight}$) compared to this of the SOB. There was little effect of mercury on toluene removal. These results suggest that the presence of sulfide oxidizing bacteria is a required component for success. This was confirmed by studies on the mechanisms of Hg removal.

3.2. Mechanism of mercury removal and fate of mercury

Bacterial cells are negatively charged and have a high affinity for cations. Transport of non-ionic metal molecules through the cell walls is known to be difficult. But it has been reported that genetically modified and wild species of certain bacteria were able to take up Hg^0 through the cell wall and oxidize it to Hg^{2+} by a catalase which is a cytosolic enzyme (Hobman et al., 2000). Once Hg^{2+} was formed it rapidly combined with sulfhydral and imino-nitrogen ligands in proteins and other important biological molecules. Aiking et al. (1985) reported that *Klebsiella aerogens* NCTC 418 produced HgS when grown in continuous aerobic culture with the addition of 2 μg HgCl$_2$ ml^{-1}. Others reported that the mechanisms for mercury removal are the aerobic precipitation of ionic Hg^{2+} as insoluble HgS as a result of H$_2$S production and biomineralization of Hg^{2+} as an insoluble mercury sulfur compound other than HgS. This may be due to the aerobic production of a volatile thiol compound which is effective at different pH and salinity levels (Essa et al., 2002). In the case of the present biotrickling filter, the same phenomenon is likely to be taking place. Hg^0 probably passes through the cell wall and gets oxidized to Hg^{2+} and is then adsorbed in the cellular components.

Analysis of organic mercury species by GC–MS after extraction of trickling liquid and biofilms, confirmed that no methyl or ethyl mercury was formed in the system, which would have been a serious health and safety concern. It is likely that the mercury control was mediated by a combination of biotic and abiotic uptake and transformations. As shown earlier (Table 1), dead cells were able to remove considerable amount of mercury, though significant differences existed between reactors packed with dead and live cells indicating that both biotic and abiotic mechanisms are involved in the removal of Hg vapors. Another means of mercury removal must be through HgS or Hg–sulfur compound production and precipitation. Thiosulfate also has high affinity to mercury compounds (Pandit et al., 1997). The sequential elution and analysis of mercury species from the immobilized matrices (Table 2) showed that the biotrickling filter operated at elevated temperature had more mercury in semi-mobile species (63%), i.e., metallic mercury compared to mobile (Hg^{2+} 21%) or non-mobile species (HgS or Hg$_2$Cl$_2$, 16%). The system operated with live cells and flue gases showed more mobile species of mercury compared to semi-mobile species, while the non-mobile mercury concentration (31%) was comparable to that of highly mobile one (47%). It may be concluded that in the live cell system, elemental mercury is converted to Hg^{2+} by biological means and mercury ions thus formed are getting attached to bacterial cell components.

A significant portion of mercury (31%) may be forming insoluble HgS or Hg$_2$Cl$_2$ precipitates whereas elemental mercury concentration in the system is reduced (22%). At elevated temperature, the microbial cells probably lost most or all activity and oxidation of mercury by cytosolic enzymes probably did not happen. Transmission electron microscopy (TEM) pictures of SOBs before and after mercury exposure were taken (Fig. 4). The live cells show mercury accumulation both inside the cells and on the cell walls, whereas in dead cells and the cells from the biotrickling filter operated at elevated temperature most of the mercury was accumulated on the cell walls. There was no mercury either inside or on the cell walls of TND (not shown). EDAX of the dark spots revealed peaks of mercury and sulfur (see Fig. D in Supplementary Information). Cells of SOB, which were not exposed to mercury, lacked both the peaks providing further evidence of the key role of sulfur in the effective treatment of mercury vapor in biotrickling filters. Even so, much greater detailed studies will be needed to fully elucidate the exact mechanisms of Hg removal and firmly identify the fate of mercury in the biotrickling filters.

4. Conclusions

Alternative methods for the treatment of mercury vapors in combustion gases are needed, in particular
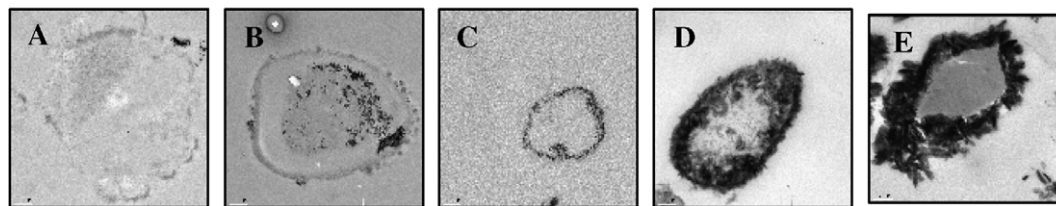

Fig. 4. TEM pictures of microorganisms from the various bioreactors. (A) Fresh SOB cells, (B) living SOB exposed to mercury vapor for 1 d, (C) living SOB cells exposed to mercury vapor until breakthrough, (D) dead SOB exposed to mercury vapor, (E) living SOB cells exposed to mercury vapor at elevated temperature. EDAX on dark spots confirmed presence of mercury (see Supplementary Information).

environmentally friendly methods and methods that offer the potential to be developed as a multi-pollutant (NO_x, SO_x, particulate matter, and Hg) treatment systems. In the present paper, early results on the control of mercury vapors in biotrickling filters were presented and discussed. The results highlight the highly complex nature of the mechanisms involved in mercury capture in biotrickling filters. At the same time, they illustrate the potential of novel biosystems for the control of mercury vapor from flue gases. Further process optimization and detailed engineering of the best way to integrate the proposed mercury vapor control with existing or novel flue gas treatment are required.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere. 2007.06.073.

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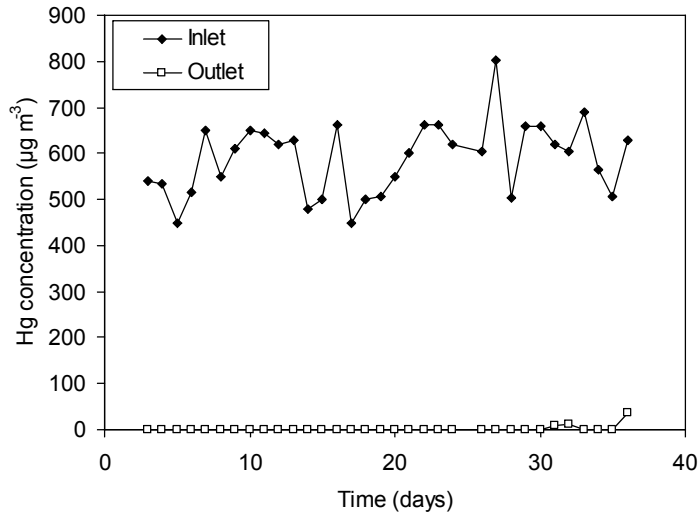
SUPPLEMENTARY INFORMATION

Figure A. Inlet and outlet concentrations of mercury in the biotrickling filter. Conditions: Synthetic flue gas (75% N_2 and 15% of CO_2 and 10% of air), live SOB cells, EBRT = 70 s (day 1-27), EBRT = 20 s (day 28-31), EBRT = 6 s (day 32-37). SO_2 (300 ppm_v) was added to the flue gas on day 28.
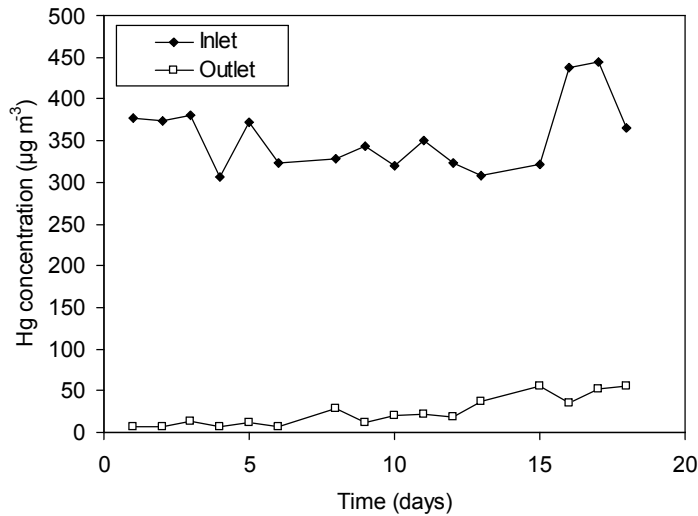

Figure B. Inlet and outlet concentrations of mercury in the biotrickling filter. Conditions: air as carrier gas and reactor packed with dead SOB. EBRT = 6 s.
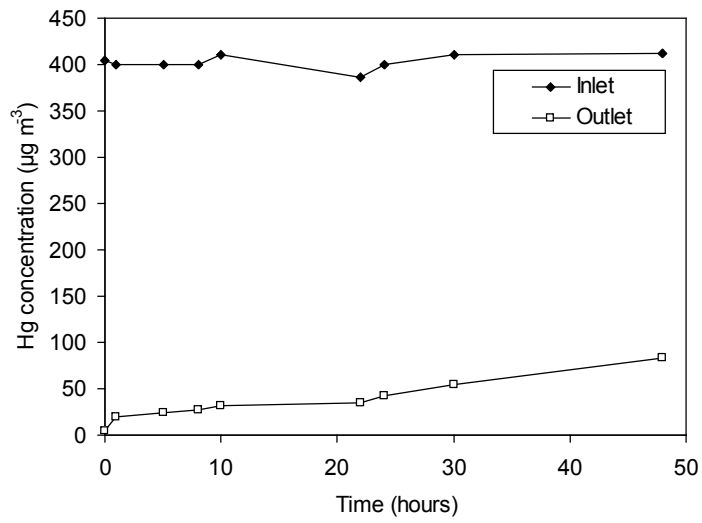
Figure C Inlet and outlet concentrations of mercury vapor during operation as a biofilter.
Conditions: air as carrier gas and live SOBs. EBRT = 6 s.
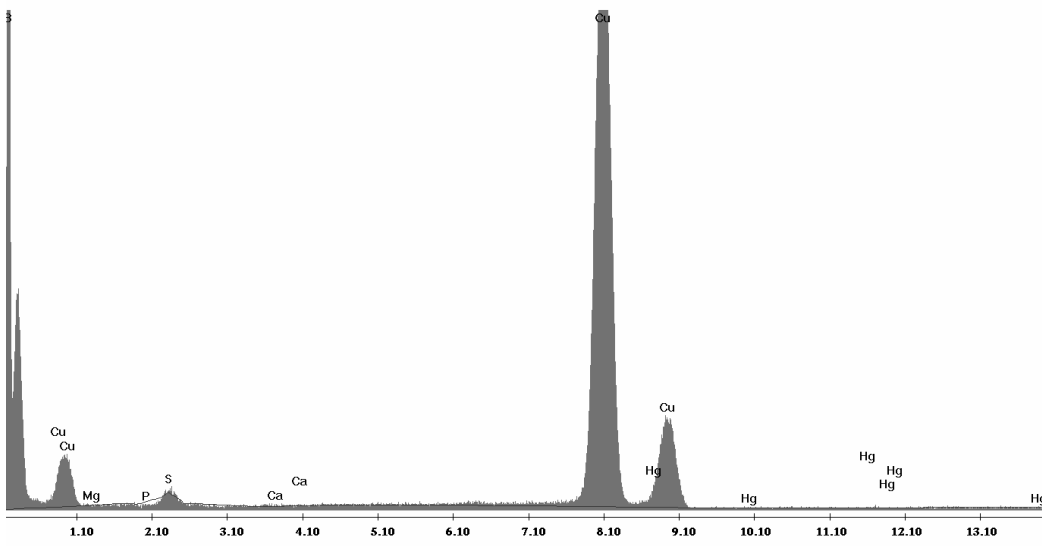
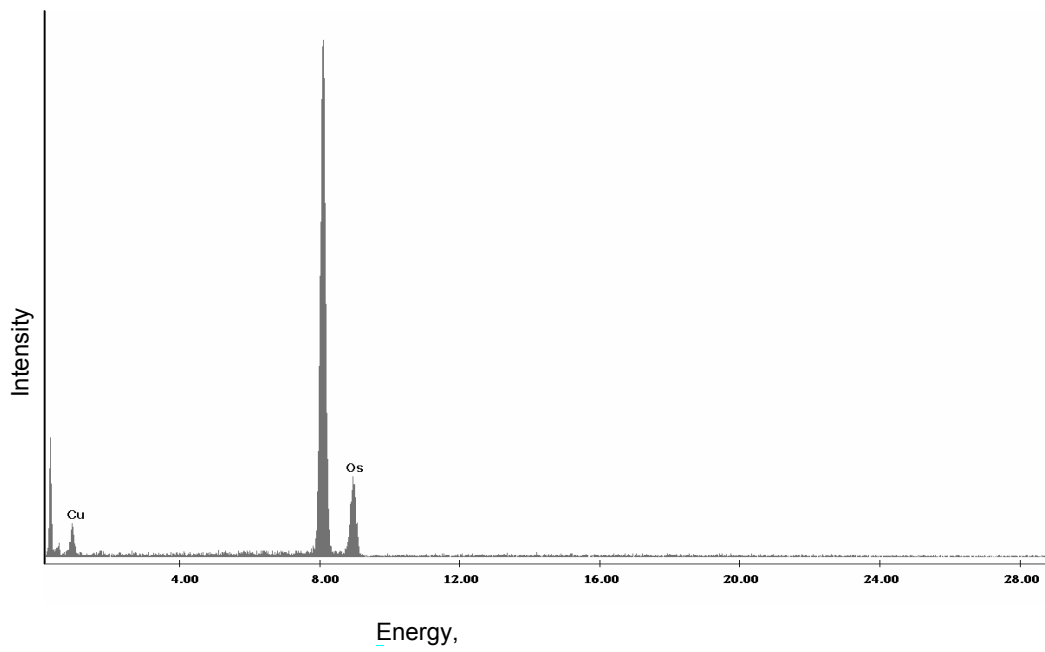Figure D1. EDAX of mercury laden biomass.
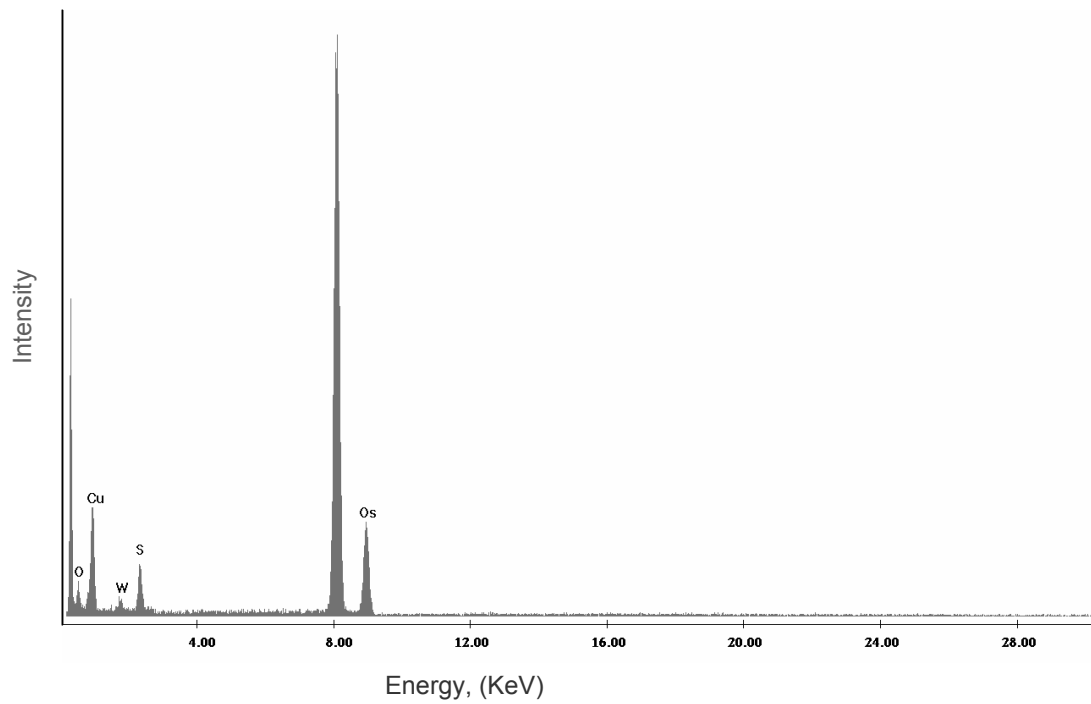

Figure D2 EDAX of control without any biomass.

Figure D3 EDAX of cells not exposed to mercury.