



The combined removal of methyl mercaptan and hydrogen sulfide via an electro-reactor process using a low concentration of continuously regenerable Ag(II) active catalyst

Govindan Muthuraman, Sang Joon Chung, Il Shik Moon*

Department of Chemical Engineering, Suncheon National University, 315 Maegok Dong, Suncheon 540-742, Chonnam, Republic of Korea

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ABSTRACT

In this study, an electrocatalytic wet scrubbing process was developed for the simultaneous removal of synthetic odorous gases namely, methyl mercaptan (CH₃SH) and hydrogen sulfide (H₂S). The initial process consists of the absorption of CH₃SH and H₂S gases by an absorbing solution, followed by their mediated electrochemical oxidation using a low concentration of active Ag(II) in 6 M HNO₃. Experiments were conducted under different reaction conditions, such as CH₃SH and H₂S loadings, active Ag(II) concentrations and molar flow rates. The cyclic voltammetry for the oxidation of CH₃SH corroborated the electro-reactor results, in that the silver in the 6 M HNO₃ reaction solution significantly influences the oxidation of CH₃SH. At a low active Ag(II) concentration of 0.0012 M, the CH₃SH removal experiments demonstrated that the CH₃SH degradation was steady, with 100% removal at a CH₃SH loading of 5 g m⁻³ h⁻¹. The electro-reactor and cyclic voltammetry results indicated that the removal of H₂S (100%) follows a mediated electrocatalytic oxidation reaction. The simultaneous removal of 100% of the CH₃SH and H₂S was achieved, even with a very low active Ag(II) concentration (0.0012 M), as a result of the high efficiency of the Ag(II). The parallel cyclic voltammetry results demonstrated that a process of simultaneous destruction of both CH₃SH and H₂S follows an H₂S influenced mediated electrocatalytic oxidation. The use of a very low concentration of the Ag(II) mediator during the electro-reactor process is promising for the complete removal of CH₃SH and H₂S.

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1. Introduction

Continuous population increases and raised environmental awareness have seriously stimulated the need to find a more suitable alternative method for the control of odorous emissions following the disposal of urban waste. Indeed, residential developments near urban disposal and waste treatment plants cause exposure to high levels of odorous gases and serious concerns related to their elimination of odorous gases. Of the many odorous gases amines (especially NH₃), H₂S and CH₃SH are the most predominant odorous molecules associated with sewage and food wastes [1,2]. In the removal of these odorous gases, a number of classical processes are implemented, such as biofilters [3,4], chemical reduction [5–8] and by carbon adsorption [9,10], but an alternative would be a wet scrubbing method via the continuous generation of an active catalyst using an electrochemical technique conducted in a packed column [11], because this would minimize the use of excess chemicals as the active catalysts, which in turn

would reduce the production of secondary wastes; the reactions could also be conducted at ambient temperature.

Of the many processes employed for the destruction of odorous gases, wet scrubbing with an active catalyst [12–16] has predominantly been performed because of the intimate contact of the odorous gases with the scrubbing liquid, which is considered as one of the key parameter in degradation process. This approach has shown good results for many years, but also exhibits low removal efficiencies and is associated with the inactivation of the catalyst during the chemical scrubbing process. Indeed, the continuous generation of the catalyst required for sustainable scrubbing, as well as the reactive behavior of the chemicals inside a packed column, indicate the importance of the need for an effective reactive mediator (catalyst). Fairly recently, a few metal ion based mediators for the mediated electrochemical oxidation (MEO) of H₂S [17–19] have gained attention. In these cases; however, although a high amount of odorous gases are removed, these mediators are insufficient for their complete removal. Gendel et al. studied Fe couple with Cl⁻ ions, which showed a 58% current efficiency, low cost and was effective in the H₂S removal process. Indirect electrolysis of H₂S using VO₂⁻ has also been performed, where elemental sulfur and hydrogen were separated, with a current efficiency of 97% (Huang et al.

* Corresponding author. Tel.: +82 61 7503581; fax: +82 61 7503581.

E-mail address: ismoon@suncheon.ac.kr (I.S. Moon).

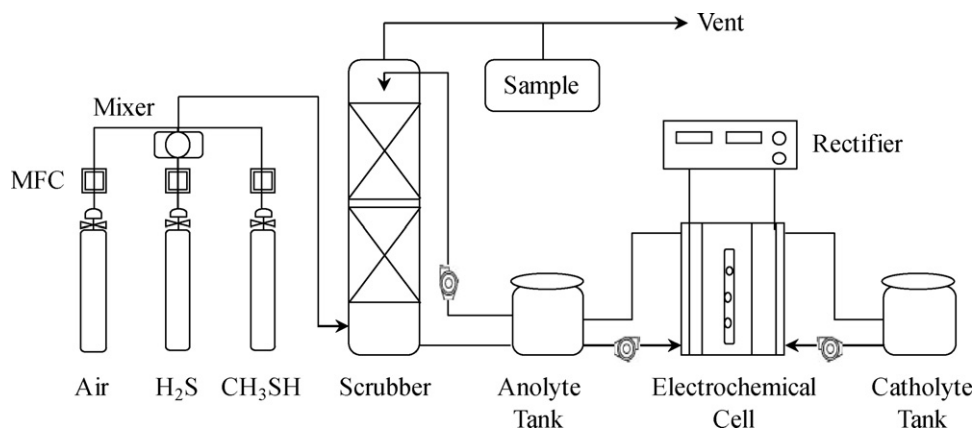


Fig. 1. Schematic of the electro-reactor experimental set-up used in this study for the continuous removal of CH_3SH and H_2S from a synthetic odor-air mixture using the Ag(II)/Ag(I) based combined mediated electrochemical oxidation/wet scrubber column process.

[17]). It has been well documented that high inorganic acid concentrations have been tested in electro-reactors for maintaining high oxidation state free ionic metal species (catalyst); and at the same time, intensify the absorption process into the liquid [20–22]. With these aims in mind, the destruction of H_2S was recently carried out with the aid of Ce(III) as the mediator in a nitric acid medium, which showed a 94% removal efficiency with 0.1 M Ce(III) [19]. As a continuation of the above approach, the present investigation focused mainly on how to simultaneously completely destroy the odorous gases with a very low concentration of the mediator. Also, to the best of our knowledge, no previous studies have been reported on the simultaneous removal of H_2S and CH_3SH using MEO coupled with a wet scrubbing process.

Therefore, it would appear that a new mediator, capable of generating high removal efficiency with a low concentration of catalyst, needs to be introduced for the simultaneous removal of H_2S and CH_3SH . In order to draw conclusions with respect to the electrogenerated Ag(II) catalyst, the removal efficiencies of H_2S and CH_3SH were characterized using a laboratory-scale pilot unit, with the simultaneous removal of hydrogen sulfide and methanethiol successively studied. Initially, the influence of the operating parameters (superficial fluid flow rates, gas flow rates, and compound inlet concentration) was characterized using CH_3SH as the sole odorous compound. Also, separate cyclic voltammetry experiments were carried out to see if the oxidation followed an indirect reaction pathway. Secondly, the complete removal and influence of CH_3SH along with H_2S were analyzed using a mixture of both these sulfur compounds. As economic considerations are vital, the consumption of a low concentration of Ag(I) was followed during this part of the study.

2. Materials and methods

2.1. Materials

Silver(I) nitrate ($\text{Ag(NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%) from TERIO Corporation, China, nitric acid (HNO_3 , 60%) from Sam Chun Chemicals, Korea, and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) from Junsei Chemical Co., Ltd., Japan were used as received, without further purification. A Nafion[®] 324 membrane was purchased from DuPont, USA, and mesh-type Pt-coated-Ti and Ti plate electrodes were from Wesco, Korea. All the solutions were prepared using water purified by reverse osmosis (Human Power III plus, Korea). The cylinder gases, CH_3SH (0.5% CH_3SH in N_2) and H_2S (2% H_2S in N_2), were supplied by P.S. Chem. Co., Ltd., Korea, and the oil free air compressor was supplied by Kyungwon Co., Korea.

2.2. Apparatus and process

The experimental set-up used for the removal of CH_3SH and H_2S consisted of two main units: an electrochemical cell and a wet scrubber reactor column. A schematic diagram of the set-up is shown in Fig. 1. The electrochemical cell used for Ag(II) generation consisted of a plate-and-frame type narrow gap divided flow cell configuration, with a mesh type Pt-coated-Ti anode and Ti cathode, separated by a Nafion 324 membrane. The inter-electrode gap was maintained at 5 mm, with the aid of two Viton rubber gaskets (thickness = 2 mm). The electrode assembly set-up was tightly clamped to Ti end plates, with thicknesses of 5 mm, with the aid of a series of Teflon plates (thickness = 5 mm) and rubber gaskets, using a filter press technique. Provisions were made with separate channel paths, by which the anolyte and catholyte solutions could flow to their respective electrodes. A 2.0L solution of silver(I) nitrate in 6 M nitric acid and 1.0L of 2.0M sulfuric acid, taken into separate anolyte and catholyte glass tanks, respectively, were continuously circulated through the anode and cathode compartments of the electrochemical cell, at different constant flow rates (L min^{-1}), via a magnetic pump (Pan World Co., Ltd., Taiwan). The electrolysis for the generation of the active Ag(II) mediator was conducted galvanostatically by applying a constant current of 10 A via a current source from Korea Switching Instrument. The effective surface area of each electrode exposed to the solution was 224 cm^2 .

The CH_3SH and H_2S removal system was composed of these sulfur compounds, an air supply, scrubbing liquid tank, scrubber reactor column, data logging and gas analysis systems. The scrubber column, 9.5 cm (inner diameter) and an 80 cm (height) glass vessel, was filled with Tri-pak packing material (25.4 mm diameter). The CH_3SH and H_2S -air mixture, obtained by controlled mixing of air, CH_3SH and H_2S , using mass flow controllers (MFC), was introduced at the bottom of the scrubber, at a constant gas flow rate, with the activated catalyst containing solution (6 M HNO_3 with Ag(II)) introduced at the top of the scrubber with a counter current flow pattern, at a given constant liquid flow rate. The outlet scrubbing solution containing the reduced form of Ag (Ag(I)) was passed through the electrochemical cell for the generation of Ag(II) , which was then further re-circulated.

2.3. Analytical methods

The outlet concentrations of the CH_3SH and H_2S gases were measured at regular time intervals using a Sequential Thermal Desorber (STD 1000, DANI Instruments, Italy) and GC/FPD (GC-2010, Shimadzu, Japan). The outlet gas sample was collected for 1 min into an aluminum-layered Tedlar sample bag (Top Trading Eng Co.,

Table 1
Experimental conditions of GC.

Detector	FPD
Column	DB-1 (60 m × 0.25 mm ID × 0.25 μm)
Carrier gas	He 25 mL min ⁻¹
Air flow rate	110 mL min ⁻¹
H ₂ flow rate	90 mL min ⁻¹
Oven temperature	50 °C (9 min) → 40 °C min ⁻¹ → 200 °C
Detector temperature	250 °C

Korea), connected through a Teflon valve to a low volume air sampler (Pulse Pump, AeroVironment, Inc., USA), at flow rates between 1.5 and 2.0 L min⁻¹. After sampling, the bags were immediately analyzed. Based on the GC peak areas of the inlet and outlet gases, the removal efficiencies of CH₃SH and H₂S were calculated. The operating conditions of the GC are given in Table 1. In order to minimize the errors, a sequential thermal desorber (STD) was used prior to the GC column, under the standard operating conditions. Before each successive measurement, pure air from the sampling bag was passed through the STD and GC units under the same operating conditions employed during the CH₃SH and H₂S measurements, to flush out the adsorbed traces of CH₃SH and H₂S from the tubing and column. The reproducibility in the CH₃SH and H₂S measurements with the STD/GC instrument were tested with 5 and 10 ppm samples, respectively, and measured five times, with the coefficient of variation found to be 7.66%. All the CH₃SH and H₂S removal measurements were carried out at 20 ± 1 °C.

Before the start of the removal experiments, the electrochemical cell was first run until the Ag(I) to Ag(II) oxidation conversion attained 25%, as assessed by measuring the Ag(II) in the anolyte via a potentiometric titration with Fe(II). Only then was the scrubbing solution allowed into the scrubber. In order to know the fundamental electron transfer phenomena, the anolyte pH was checked before and after electrolysis (0.30 not stable), but no significant change was observed. Cyclic voltammetry experiments were carried out using a BAS-Epsilon EC instrument, USA. Platinum (2 mm) and a Pt wire served as the working and counter electrodes, respectively, with Ag/AgCl serving as the reference electrode.

3. Results and discussion

3.1. Removal of CH₃SH and H₂S

The effects of removing both CH₃SH and H₂S were studied at a given molar gas flow rate of 15.5 × 10⁻⁶ mol min⁻¹, and a flow rate of the 6 M HNO₃ scrubbing liquid of 70 L min⁻¹, in the absence and presence of Ag(II) (M). Fig. 2 shows the CH₃SH and H₂S removal efficiency profiles with respect to time and under different experimental conditions. The initial CH₃SH removal efficiency was 73%, but this started to decrease when only 6 M HNO₃ was used as the scrubbing solution (Fig. 2 (curve a)). With respect to H₂S removal, the removal efficiency showed a decreasing trend and became almost zero after 90 min (Fig. 2 (curve c)). At the same time, both CH₃SH and H₂S exhibited 100% removal efficiencies in the presence of Ag(II), as shown in Fig. 2 (curves b and d). These comparative results clearly indicate that the direct oxidation of CH₃SH on the platinumized titanium electrode in the 6 M HNO₃ medium was possible, or that its destruction was enabled via a chemical reaction. However, the reason for the almost 100% removal efficiency was solely due to the presence of Ag(II), providing further evidence of the mediated degradation of CH₃SH. In contrast to CH₃SH, H₂S shows no direct oxidation, as shown by the sharp decrease in the removal efficiency over time, which eventually became zero (Fig. 2 (curve c)). An electrochemical study could be expected to provide direct impacts on the electron transfer phenomena that could possibly have occurred in the working solution. Assuming this to be

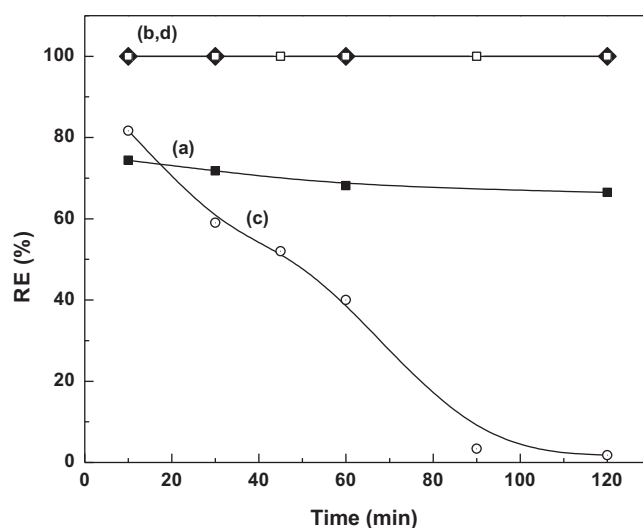
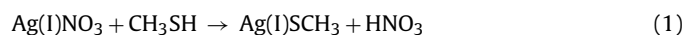


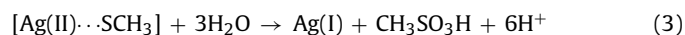
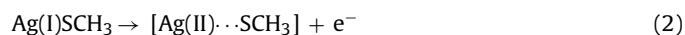
Fig. 2. Comparative plot of the CH₃SH and H₂S removal efficiencies with respect to time in 6 M HNO₃: (a) CH₃SH; (b) Ag(II) (12.5 × 10⁻⁴ M) + CH₃SH; (c) H₂S; (d) Ag(II) (2.5 × 10⁻⁴ M) + H₂S. Experimental conditions: feed concentration of CH₃SH = 5 ppm; H₂S = 10 ppm; gas flow rate = 70 L min⁻¹; liquid flow rate = 4 L min⁻¹.

the case, CV experiments were performed using the Pt electrode in 6 M HNO₃, with various separate experimental solutions.

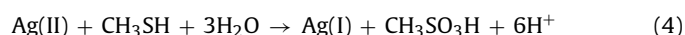
Fig. 3a depicts the cyclic voltammetry response at the Pt electrode in both the absence and presence of 0.005 M Ag(I), with a 200 ppm CH₃SH solution, at a scan rate of 100 mV s⁻¹. A decrease in the oxidation peak current was observed in the presence of 0.005 M Ag(I) compared to that of CH₃SH alone in the 6 M HNO₃ solution, providing evidence of the direct oxidation of CH₃SH at the Pt coated Ti electrode. Also, this decreased oxidation peak current might have been due to complex formation between Ag(I) and CH₃SH in the 6 M HNO₃ solution, which would; in turn, minimize the direct oxidation or favor MEO via an intermediate complex formation. *Note:* There was evidence for complex formation between Ag and CH₃SH in the gas phase [23], which could have occurred via the following reaction:



Also, a mediated oxidation could have occurred via the Ag(I)SCH₃ intermediate complex, along with direct oxidation, because the CH₃SH removal efficiency reached 100% in the presence of silver:



However, as per the MEO mechanism in the electro-reactor, the following reactions could be envisaged for the efficient removal of CH₃SH by the scrubbing liquid (Ag(II)) mediator catalyst ions in 6 M HNO₃:



The CV results corroborated that the oxidation of CH₃SH could follow two different electron transfer paths, but silver plays a major role in attaining the 100% degradation efficiency in the electro-reactor scrubbing system.

With respect to the CV of H₂S both in the presence and absence of silver, as shown in Fig. 3b, there appeared to be an increased anodic peak current at around 1.82 V in the presence of silver, which is the oxidation potential of Ag(II). However, no such peak appeared in the absence of silver. The increase in the peak current due to the mediator, here Ag(II), showed an oxidation potential typical of mediated electrocatalytic oxidation [24]. Here again, the CV behavior indirectly indicated that no direct oxidation of H₂S had occurred under

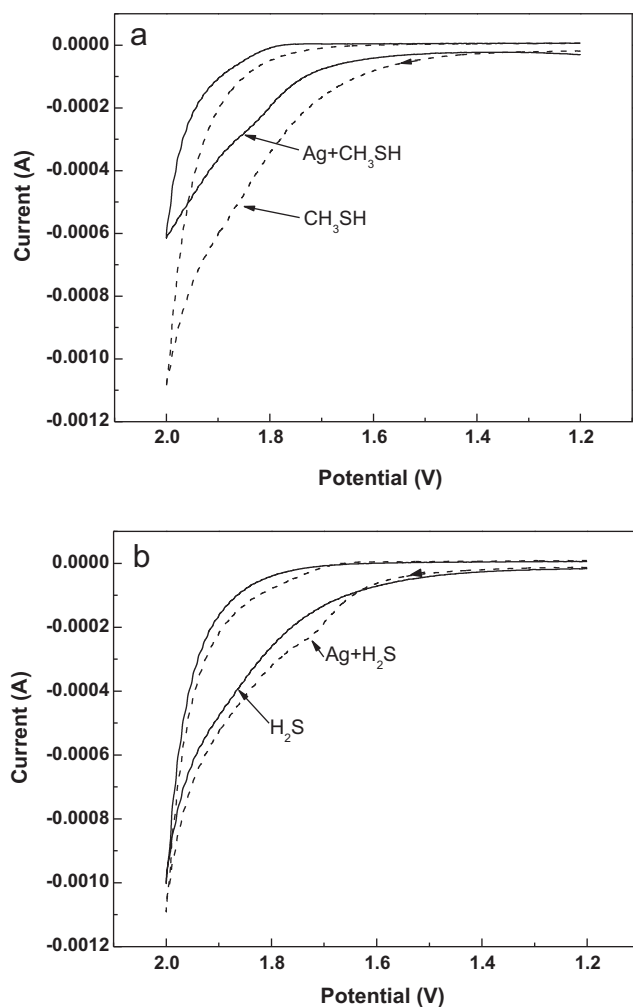
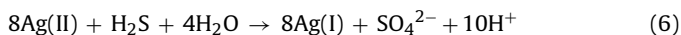


Fig. 3. (a) CV response of CH_3SH in different working solutions (mentioned in figure) in 6 M HNO_3 : working electrode, Pt; scan rate, 100 mV s^{-1} ; silver(I) concentration, 0.005 M; CH_3SH concentration, 200 ppm. (b) CV response of H_2S in various working solutions (mentioned in figure) in 6 M HNO_3 . Working electrode: Pt; scan rate: 100 mV s^{-1} ; silver(I) concentration: 0.005 M; CH_3SH concentration: 200 ppm.

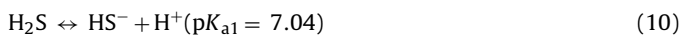
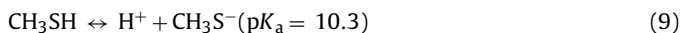
the given experimental conditions. These CV results were well correlated with the electro-reactor process, i.e. the removal efficiency sharply decreased to zero within 120 min., as shown in Fig. 2 (curve c). The reaction path may be:



Considering the absorption of both CH_3SH and H_2S into solution, the gases in the liquid phase could be represented by the following equilibria at the gas–liquid interface:



The dissociation constants ($\text{p}K_{\text{a}}$) of CH_3SH (10.3 [25]) and H_2S (7.04 and 11.96 [26]) are represented by the following dissociations in the liquid phase:



As the scrubbing medium was highly acidic in the present MEO system (6 M HNO_3), both CH_3SH and H_2S gases in solution would

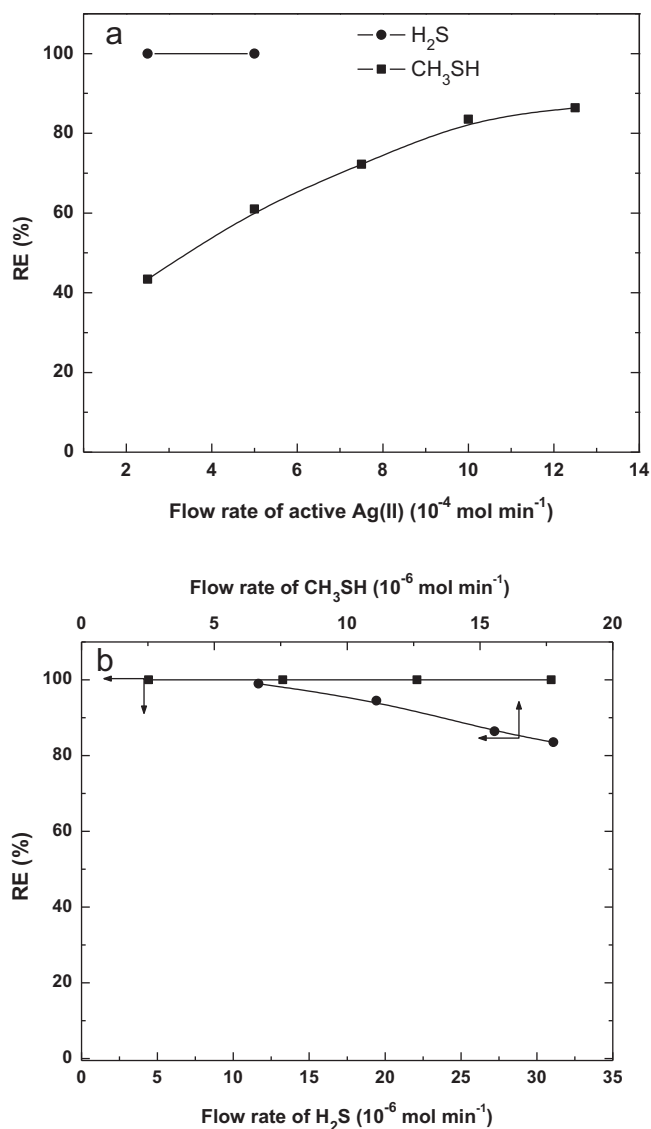


Fig. 4. (a) CH_3SH and H_2S removal efficiencies as a function of the active Ag(II) flow rates (mol min^{-1}). Experimental conditions: Ag(II) flow rate = $((2.5\text{--}12.5) \times 10^{-4} \text{ mol min}^{-1})$; gas flow rate = 70 L min^{-1} ; feed concentration of CH_3SH = 5 ppm; H_2S = 10 ppm; electrolyte 6 M HNO_3 . (b) CH_3SH and H_2S removal efficiencies with respect to the flow rates of CH_3SH and H_2S (mol min^{-1}). Experimental conditions: CH_3SH and H_2S molar flow rates = $((4.4\text{--}30.9) \times 10^{-6} \text{ mol min}^{-1})$; feed concentration of Ag(II) = $12.5 \times 10^{-4} \text{ M}$; liquid flow rate = 4 L min^{-1} ; electrolyte 6 M HNO_3 .

be present entirely in their molecular forms. The absorptivities, in the form of Henry's constant, for both CH_3SH ($267.6 \text{ Pa m}^3 \text{ mol}^{-1}$ [27]) and H_2S ($856 \text{ Pa m}^3 \text{ mol}^{-1}$ [28]) are moderate, but the fast irreversible oxidation reaction, i.e. Eqs. (4)–(6), would favor the solubilities of CH_3SH and H_2S by moving the equilibrium, Eqs. (7) and (8), right, towards the solution solubilized species. The corresponding oxidation reactions that could take place in the bulk solution under this solution condition would favor those given Eqs. (4) and (6).

3.2. Effect of molar flow rates

Fig. 4a shows the variations in the removal efficiencies of both CH_3SH and H_2S as a function of the different molar liquid flow rates of the scrubbing liquid Ag(II) (mol min^{-1}) in the 6 M HNO_3 solution. These data were collected using different active catalyst

Ag(II) flow rates, from 2.5×10^{-4} to 12.5×10^{-4} mol min⁻¹, with constant feed concentrations of CH₃SH (15.5 mol min⁻¹) and H₂S (13.3 mol min⁻¹).

The outlet removal efficiency attained a steady state after 10 min. It was observed that the higher the flow rates of the solution containing the active catalyst, the better the removal of methyl mercaptan; as shown in the Fig. 4a. The 42% outlet removal efficiency with a low active catalyst flow rate of 2.5×10^{-4} mol min⁻¹ increased to 88% when the molar flow rate of the active Ag(II) containing solution was increased to 12.8×10^{-4} mol min⁻¹. Two benefits were associated with the improved removal efficiencies at higher flow rates: one was the greater availability of fresh active catalyst ions, Ag(II), which enhanced the oxidation and removal of CH₃SH. An increase in the mass transfer parameters, viz., the interfacial area and mass transfer coefficient, at the higher liquid flow rates would lead to a higher efficiency, which is the other possible benefit. However, exact measurements of the mass transfer parameters are outside of the framework of the present study.

Contrary to the above, 100% H₂S removal efficiency was (Fig. 4a respective data) attained at a low molar flow rate of 2.5×10^{-4} mol min⁻¹, which was also maintained at high molar flow rates. One possible reason for this could be that such a low Ag(II) concentration was sufficient for the 100% removal efficiency or highly potentiality of the Ag(II) mediator towards the removal of H₂S to be attained. Another reason could be a change in the charge transfer parameters, viz., electron transfer between Ag(II) and H₂S, paving the way for the high removal efficiency, irrespective of the flow rate of the active Ag(II) containing solution used in this study.

In a series of experiments, data on the removal of CH₃SH (5 ppm) and H₂S (10 ppm) were collected using the active catalyst (Ag(II)) in 6M HNO₃ at a flow rate of 12.5×10^{-4} mol min⁻¹, and varying the CH₃SH and H₂S gas molar flow rates from 4.4×10^{-6} to 30.9×10^{-6} mol min⁻¹, the results of which are summarized in Fig. 4b (respective compounds mentioned in the figure) in the form of the removal efficiencies. In contrast to the effect of varying the active catalyst solution flow rate, the final CH₃SH removal efficiency was almost 100% at the lowest flow rate of 6.6×10^{-6} mol min⁻¹, and was reduced with increasing gas flow rate (85% at the highest flow rate 17.7×10^{-6} mol min⁻¹), as shown in Fig. 4b (respective data). In the above case, the supply of the oxidant Ag(II) was kept constant. The decrease in the CH₃SH removal efficiency at the higher gas flow rate was as expected, since the Ag(II) concentration would decrease due to there being a greater amount of CH₃SH to oxidize. Unlike CH₃SH, the removal efficiency of H₂S remained at (Fig. 4b respective data) almost 100%, irrespective of the molar gas flow rate. Therefore, similar charge transfer phenomena to those between H₂S and Ag(II) could also have occurred here, as observed in Fig. 4a (respective compounds).

3.3. Effect of molar feed concentration

In order to minimize the use of silver, with respect to the cost, experiments were performed to observe the influence of the active catalyst Ag(II) concentration on the effective removal of CH₃SH and H₂S in our packed column reactor. For a liquid flow rate of 12.5×10^{-4} mol min⁻¹, the redox ion (Ag(II)) concentration was varied from 0 to 18.8×10^{-4} M in 6M nitric acid solution. Fig. 5a (respective symbols in the figure) shows the effect of the Ag(II) concentration on the CH₃SH removal efficiency. For these measurements, the concentration of CH₃SH was kept at a molar value-cum-gas flow rate of 15.5×10^{-6} mol min⁻¹. The removal of CH₃SH was enhanced at the higher Ag(II) concentration (18.8×10^{-4} M), which was very low compared with previous studies [19]. For example, the steady state removal was 85% with an Ag(II) concentration of 2.5×10^{-4} M, but increased to 100%

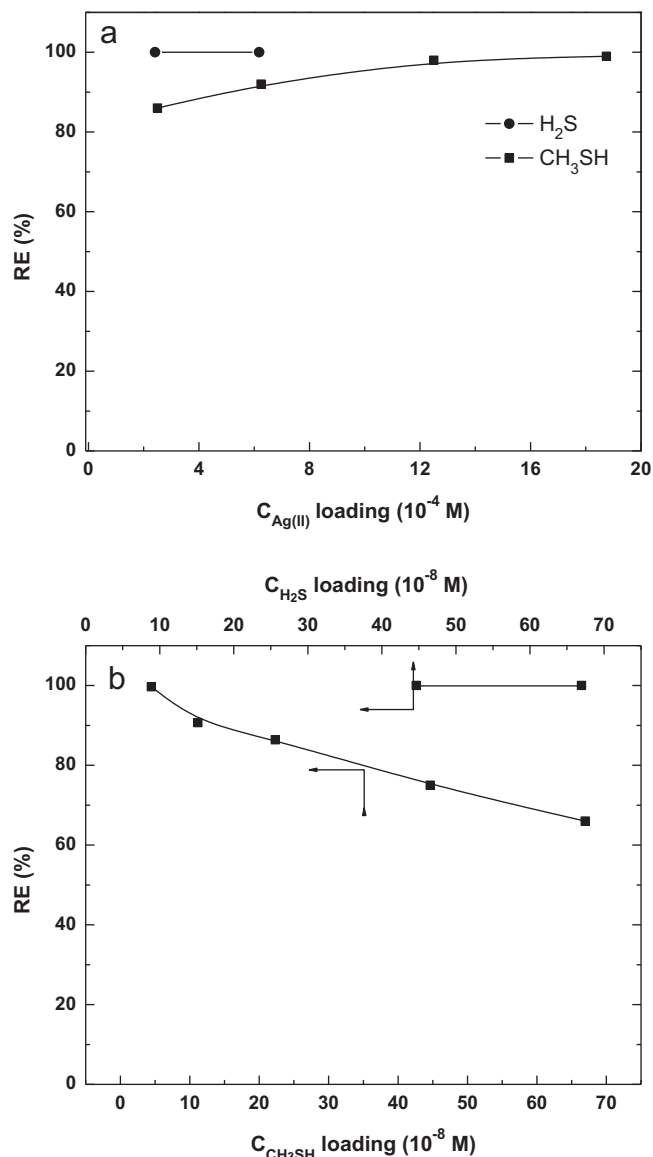


Fig. 5. (a) CH₃SH and H₂S removal efficiencies as a function of the loading concentrations of active Ag(II) (M). Experimental conditions: gas flow rate = 15.5×10^{-6} mol min⁻¹; liquid flow rate = 10×10^{-4} mol min⁻¹; electrolyte 6M HNO₃. (b) CH₃SH and H₂S removal efficiencies with respect to the CH₃SH and H₂S (M) loading concentrations. Experimental conditions: feed concentration of Ag(II) = 12.5×10^{-4} M; liquid flow rate = 4 L min⁻¹; electrolyte 6M HNO₃.

with an Ag(II) concentration of 18.8×10^{-4} M, as shown in Fig. 5a (respective symbols), indicating that a higher (18.8×10^{-4} M) Ag(II) concentration was more advantageous. Fig. 5a (respective curves) shows the removal efficiency of H₂S on varying the feed concentration of active Ag(II) (M). Here, a removal efficiency of 100% was attained, even at a low active Ag(II) concentration (2.5×10^{-4} M), providing further evidence that the reaction pathway follows a charge transfer process.

It is known that more than 1 ppb of CH₃SH and 0.5 ppb of H₂S are malodorous to health [29], but experiments were carried out to check the ability of Ag(II) mediation at very high CH₃SH concentrations. The effect of the initial CH₃SH feed concentration was studied from 1 to 15 ppm, which is toxic level to health, at a gas flow rate of 70 L min⁻¹, with a scrubbing liquid Ag(II) concentration of 2.5×10^{-4} M in 6M HNO₃, at a liquid flow rate of 5 L min⁻¹. Fig. 5b (respective axes marked in the figure) shows the CH₃SH removal efficiency with respect to the different actual loading

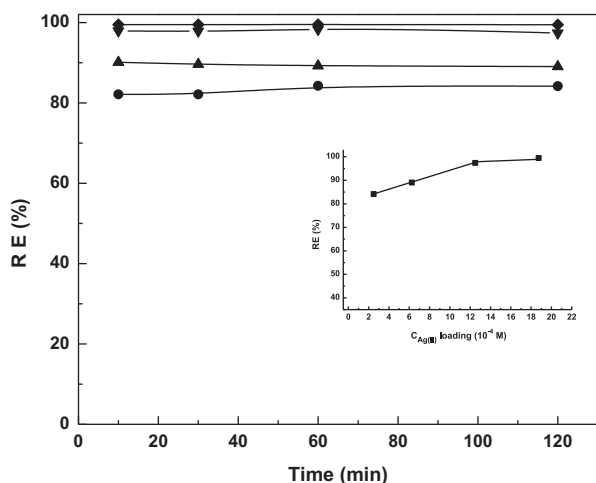


Fig. 6. Simultaneous removal efficiency of CH_3SH and H_2S as a function of time for various concentrations of active Ag(II) (M) in 6 M HNO_3 : (●) 2.5×10^{-4} ; (▲) 6.3×10^{-4} ; (▼) 12.5×10^{-4} ; (◆) 18.3×10^{-4} . *Inset:* Dependence of the CH_3SH and H_2S removal efficiency at 120 min on the initial CH_3SH (5 ppm) and H_2S (10 ppm) feed concentrations with various concentrations of active Ag(II) . Experimental conditions: gas flow rate = 70 L min^{-1} ; liquid flow rate = 4 L min^{-1} .

concentrations (M). It was observed that the removal efficiency decreased with increasing actual CH_3SH loading concentration within the range 4.5×10^{-8} to 70.0×10^{-8} M. While 4.5×10^{-8} M CH_3SH showed 100% removal efficiency, this decreased to 67% with the 70.0×10^{-8} M actual CH_3SH concentration. However, it should be noted that almost 100% removal efficiency was obtained with a high active Ag(II) concentration (18.8×10^{-4} M) at a low gas flow rate of $6.6 \times 10^{-6} \text{ mol min}^{-1}$ (see Fig. 4a respective symbol), revealing that high Ag(II) concentrations and low gas flow rates were more beneficial for the efficient removal of CH_3SH . As previously observed, H_2S showed 100% removal efficiency (Fig. 5b (respective curve)) at high concentrations (10 and 15 ppm). Therefore, this again indicates that the removal efficiency of H_2S follows a charge transfer phenomena dominated pathway.

3.4. Simultaneous removal of CH_3SH and H_2S

The simultaneous removal of CH_3SH and H_2S , with a feed gas containing a mixture of 5 ppm CH_3SH –10 ppm H_2S –air, was also studied. The CH_3SH and H_2S removal profiles measured at the outlet of the scrubber reactor over time are presented in Fig. 6. The Ag(II) in the scrubber reactor removed both CH_3SH and H_2S quite effectively, approaching 100%, for the individual CH_3SH and H_2S gases. Good linearity was also observed for the simultaneous removal efficiency with the Ag(II) concentration, as shown in the inset of Fig. 6. Saturation on eliminations of CH_3SH and H_2S began at an Ag(II) concentration of 12.5×10^{-4} M, providing evidence of the efficiency of such a low concentration of the mediator on CH_3SH and H_2S removal process.

Contrary to the CV of CH_3SH , as shown in Fig. 3a, the current response increased with a 250 mV negative shift in the Ag(I) oxidation potential in the presence of H_2S , as depicted in Fig. 7 (curve b). This is typical of mediated catalysis in a homogeneous solution phase [24]. A further increase in the peak current, with a 270 mV negative shift in the potential, was observed in the presence of both H_2S and CH_3SH (Fig. 7 (curve c)), which may suggest that H_2S influenced the mediated oxidation of CH_3SH in the 6 M HNO_3 solution. As shown by Liu et al. [23], any one of the reaction intermediates of the sulfur compounds formed could be responsible for this increase in the mediated oxidation peak current.

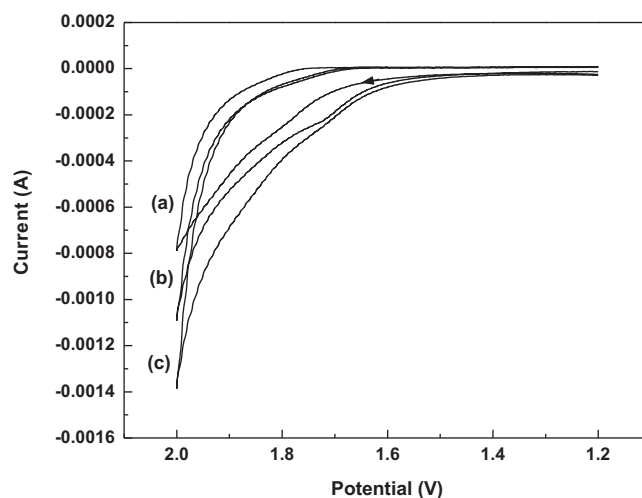


Fig. 7. CV responses of CH_3SH and H_2S under different conditions in 6 M HNO_3 solution: (a) Ag(I) only; (b) $\text{Ag(I)} + \text{H}_2\text{S}$; (c) $\text{Ag(I)} + \text{H}_2\text{S} + \text{CH}_3\text{SH}$. Working electrode: Pt; scan rate: 100 mV s^{-1} ; Ag(I) concentration: 0.005 M, H_2S and CH_3SH concentrations: 200 ppm.

The superior performance of the low concentration Ag(II)/Ag(I) based MEO process for the 100% removal of $\text{CH}_3\text{SH}/\text{H}_2\text{S}$ can be realized by comparison with the published results [19,25,30]. The Ce(IV)/Ce(III) based MEO system has been studied by our group [19], but only for H_2S ; however, Couvert et al. [25] used H_2O_2 for the chemical oxidation of CH_3SH . Although Ce(IV)/Ce(III) showed >94% removal efficiency, it required high concentrations of Ce(III) (0.1 M); whereas, H_2O_2 showed 90% CH_3SH removal. However, to the best of our knowledge, no studies have been performed on the simultaneous removal of H_2S and CH_3SH using a MEO process. The high removal efficiencies by the Ag(II)/Ag(I) system for CH_3SH and H_2S (100%) can be attributed to its higher oxidizing capability, resulting from its more favorable redox potential, $E^0 = 1.98 \text{ V (NHE)}$, compared to 1.62 V for Ce(IV)/Ce(III) and 0.95 V and 1.27 V for the ClO_2 system; the formation of intermediates simply enhanced the oxidation efficiency [30].

4. Conclusions

A mediated electrocatalytic wet scrubbing process, a combination of the electrocatalysis and scrubbing techniques, was developed for the simultaneous removal of odorous gases. Our experimental results confirmed that this process was able to effectively remove both CH_3SH and H_2S from a synthetic odorous gas mixture. The removal efficiencies of CH_3SH and H_2S in the presence of 18.8×10^{-4} M Ag(II) were 100%, which were better than in 6 M HNO_3 (65%) solution alone; thus, confirming the strength and influence of the Ag(II) mediator in the destruction reactions. The experimental results demonstrated that both low gas and high liquid flow rates were suitable for the removal of CH_3SH . Irrespective of the flow rate and concentration, the 100% removal efficiency of H_2S demonstrates that charge transfer dominated the reaction pathway between Ag(II) and H_2S . The simultaneous removal of CH_3SH and H_2S were well maintained, at high levels of nearly 100%, with a Ag(II) loading of 18.8×10^{-4} M. The CV result suggested that contrary to CH_3SH destruction alone, the destruction pathway for the mixture of CH_3SH and H_2S followed a mediated electrochemical oxidation. In fact, unlike the other methods developed for the removal of odorous gases, the MEO was more economical and safer, since it operates at room temperature and atmospheric pressure, and utilizes conventional transition metal oxide electrodes more commonly used in industrial applications. This developed process is

now being tested at our municipal food processing site in Suncheon city.

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