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Removal of H_2S using a new Ce(IV) redox mediator by a mediated electrochemical oxidation process

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Abstract

BACKGROUND: Hydrogen sulfide (H_2S) from industrial activities and anaerobic manure decomposition in commercial livestock animal operations is an offensive malodorous and toxic gas even in small concentrations, causing serious discomfort and health and social problems. The objective of this study was to employ for the first time a novel, attractive, low cost, environmentally benign mediated electrochemical oxidation (MEO) process with Ce(IV) as the redox catalyst for H_2S gas removal from an H_2S–air feed mixture.

RESULTS: The influence of liquid flow rate (Q_L) from 2–4 L min^{-1}, gas flow rate (Q_G) from 30–70 L min^{-1}, H_2S concentration in the H_2S–air feed mixture from 5–15 ppm, and Ce(III) pre-mediator concentration in the electrochemical cell from 0.1–1 mol L^{-1} on H_2S removal efficiency were investigated. Both liquid and gas flow rates influenced the removal efficiencies, but in opposite directions. Nearly 98% H_2S removal was achieved when the concentration of Ce(IV) mediator ion in the flowing scrubbing liquid reached 0.08 mol L^{-1}.

CONCLUSIONS: The new MEO method proved promising for H_2S removal, achieving high removal efficiency. Integration of the electrochemical cell with the scrubber set-up ensured continuous regeneration of the mediator and its repeated reuse for H_2S removal, avoiding use of additional chemicals. Since the process works at room temperature and atmospheric pressure utilizing conventional transition metal oxide electrodes more commonly used in industrial applications, it is also safe and economical.

Keywords: deodorization; H_2S removal; mediated electrochemical oxidation process; Ce(IV)/Ce(III) redox system; wet scrubbing

INTRODUCTION

The development of processes for the removal of hydrogen sulfide from the atmosphere has been stimulated by the increasing importance of the control of pollution by hydrogen sulfide.[1–3] H_2S gas is not only malodorous, but also toxic, and even in small amounts it can be fatal to both animals and human beings.[4] It also has detrimental effects on many industrial catalysts;[5] it is a major source of acid rain when oxidized to sulfur oxide on combustion,[6] and it is also highly corrosive both in gaseous form and in solution. H_2S is produced from many industrial activities including the paper industry, petrochemical plants and natural gas refineries. The anaerobic decomposition of sulfur-containing organic and inorganic matter as in wastewater treatment plants is yet another source for H_2S emission. Bacterial growth during storage, agitation and spreading of manure in animal or pig farms releases large quantities of odorous sulfur compounds (H_2S, methyl mercaptan, dimethyl sulfide and dimethyl disulfide) with H_2S showing the highest concentration and emission rate;[7] H_2S contributes substantially to the total odour, since its odour threshold limit is very low ranging from 0.0005–0.3 ppm.[8] Note that the toxicity threshold of this compound is about 10 ppm.[9] Thus, strict environment regulations are continually being strengthened throughout the world to lessen the odour problem, and several H_2S removal methods have been developed for this purpose.

The conventional methods for H_2S removal include fixed-bed solid adsorption,[10] precipitation,[11] liquid biofiltration,[12] alkali aqueous solution absorption,[13] amine aqueous solution absorption,[14] liquid redox processes using soluble oxidants or solid catalysts,[15] a method based on ceria-mixed oxide composites as high temperature desulfurization sorbents,[16] etc., with each method having specific advantages and associated disadvantages. Among the numerous methods developed for H_2S removal, the liquid redox method has been studied extensively in recent times using several soluble oxidants, namely NaOCl,[9,17] H_2O_2,[18] Cl_2,[19] O_3,[20] etc., in wet scrubbing columns, because liquid scrubbing is economically attractive when the volume of odorous gas to be treated is greater than 5000 m^3 h^{-1} compared with other methods which are suitable for treating the removal of low concentrations of H_2S.[21] Liquid scrubbing of gases involves bringing the odorous gas stream into intimate contact with the scrubbing liquid. A liquid scrubber needs to be well designed to ensure adequate contact between the gas and liquid phases. However, the general

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problem encountered in the wet scrubbing systems utilizing various chemicals is that they are consumed in the stiochiometric amount of gases removed, necessitating the use of large amounts of expensive chemicals, which also further add to environmental pollution.

The above problem is circumvented by using electrochemical methods,[22–25] since a clean reagent ‘electron’ is used in redox processes. Winnick and his coworkers[26,27] reported an electrochemical process for H_2S gas removal from natural gas. The prototype cell consisted of an electrochemical membrane separator, impregnated with a molten electrolyte, in between the anode and the cathode with a stream of H_2S-containing process gas passing the two electrodes at 650 °C. The electrochemical removal process involved reduction of H_2S at the cathode to H_2 and sulfide ion (Equation (1)), migration of S^{2-} ion through the electrolyte for its oxidation at the anode to elemental sulfur (Equation (2)).

$$H_2S + e^- \longrightarrow H_2 + S^{2-} \quad (1)$$

$$S^{2-} \longrightarrow 1/2\, S_2 + 2\, e^- \quad (2)$$

The reaction kinetics at both the cathode and anode were rapid enough (0.1 A cm^{-2}) to be negligible for rate-limiting, and the removal rate of H_2S was found to be limited either by gaseous diffusion from the fuel stream to the cathode–electrolyte interface or by liquid diffusion of sulfur ions through the electrolytic membrane, depending on operating conditions and cell design. However, as the process was operated at high temperatures, materials of stringent specification were required. For example, eutectic mixtures of sulfides or carbonates of alkali metals as electrolyte, porous MgO or lithiated AlO_2 ceramic membrane or yttria-stabilized zirconia as separator, porous graphite or porous Ni or lithiated $Y_{0.9}Ca_{0.1}FeO_3$ or CoS_2 as cathode, and porous graphite or porous Ni or lithiated NiO as anode were used.

On the other hand, laboratory scale studies by Kelsall *et al*.[28] revealed that HS^- on electro-oxidation on a gold electrode at pH = 9.3 formed a multilayer of sulfur and soluble oxidation products at 25 °C; however, the elemental sulfur on reduction gave polysulfide ions ($S_n{}^{2-}$ ($n = 2$–5)), rather than HS^-. Ateya *et al*.[29] studied the electrochemical removal of hydrogen sulfide from polluted brines at room temperature using porous carbon felt flow-through electrodes. Formation of elemental sulfur on oxidation was observed, and the reaction rate and the removal efficiency increased with sulfide concentration, potential, temperature and electrolyte flow rate.

In this work, a novel process for H_2S gas removal combining the benefits of liquid scrubbing with the advantages of an electrochemical method has been demonstrated using the mediated electrochemical oxidation (MEO) process with Ce(IV) in 3 mol L^{-1} HNO_3 as the redox catalyst. The MEO process has been identified as one of the most promising future technologies by the United Nations Environmental Programme (UNEP) for the ambient temperature destruction of toxic pollutants and waste streams.[30] This technology uses the absorption of the pollutant species from the gas phase into a liquid electrolyte, where a metal ion in a high oxidation state is utilized as a mediator to oxidize the dissolved component, and the oxidized form of the mediator is continuously electro-generated in a divided/undivided cell in a closed cycle.[31–33] Integration of the electrochemical cell with a scrubber column ensures that the reagent used to capture H_2S can be regenerated and reused, thereby avoiding the problem of using fresh oxidant for removal. Although several metal ion based redox systems (Ag(II)/Ag(I), Ce(IV)/Ce(III), Co(III)/Co(II), Mn(IV)/Mn(III)) are available for use as mediators in MEO systems, the Ce(IV)/Ce(III) redox couple was chosen in the present studies for H_2S removal, because this redox system was found to be highly effective in the electrochemical treatment of waste biological materials[34] as well as in the removal of NO_x and SO_2 from waste gases.[35,36] Interestingly, the Ce(IV)/Ce(III) redox system was used successfully for the destruction of organic pollutants in aqueous media, and it was found to possess excellent catalytic activity towards organic oxidation.[37–42] Consequently, the aim of the present work was to study the oxidative removal of H_2S by Ce(IV) oxidant in a scrubber under different experimental conditions to establish the performance of the Ce(IV)/Ce(III) based MEO process for removal of gaseous odour.

MATERIALS AND METHODS

Materials

Cerium(III) nitrate ($Ce(NO_3)_3.6H_2O$, 99.9%) from TERIO Corporation, China, nitric acid (HNO_3, 60%) from Sam Chun Chemicals, Korea, and ferrous sulfate ($FeSO_4.7H_2O$) from Junsei Chemical Co., Ltd, Japan were used as received without further purification. 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 made using water purified by reverse osmosis (Human Power III plus, Korea). H_2S cylinder gas (2% H_2S with 9% N2) supplied by P.S. Chem. Co., Ltd, Korea, and moisture-free air from air compressor supplied by Kyungwon Co., Korea were used.

Apparatus and process

The experimental set-up used for H_2S removal consisted of two main components: an electrochemical cell reactor and a wet scrubber column. A schematic diagram is shown in Fig. 1. The electrochemical cell, used for Ce(IV) electro-generation, was 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 help of two Vitron rubber gaskets (thickness = 2 mm). The electrode assembly set-up was tightly clamped to Ti end plates 5 mm thick with the help of a series of Teflon plates (thickness = 5 mm) and rubber gaskets. Two such cells arranged in series were used in the present work. Provisions were made for separate channels by which the anolyte and catholyte solutions flowed across the respective electrodes. A 2.0 L solution of cerium (III) nitrate in 3 mol L^{-1} nitric acid and a 1.0 L of 2.0 mol L^{-1} sulfuric acid, stored in separate anolyte and catholyte glass tanks, were continuously circulated through the anode and cathode compartments of the electrochemical cell at 2 L min^{-1} constant flow rate using a magnetic pump (Pan World Co., Ltd, Taiwan). The electrolysis for generation of the Ce(IV) redox mediators was conducted galvanostatically by applying a constant current of 10 A from a locally made constant current source (Korea Switching Instrument). The effective surface area of each electrode exposed to the solution was 224 cm^2.

The H_2S removal system was composed of H_2S and an air supply, scrubbing liquid tank, the scrubber column, a data logger and gas analysis systems. The glass scrubber column (ID = 10 cm, height = 160 cm) was filled with 25.4 mm diameter Tri-pak packing. The H_2S–air mixture, obtained by controlled the mixing of air and H_2S using mass flow controllers (MFC), was introduced at the bottom of the scrubber at a constant gas flow rate, and the

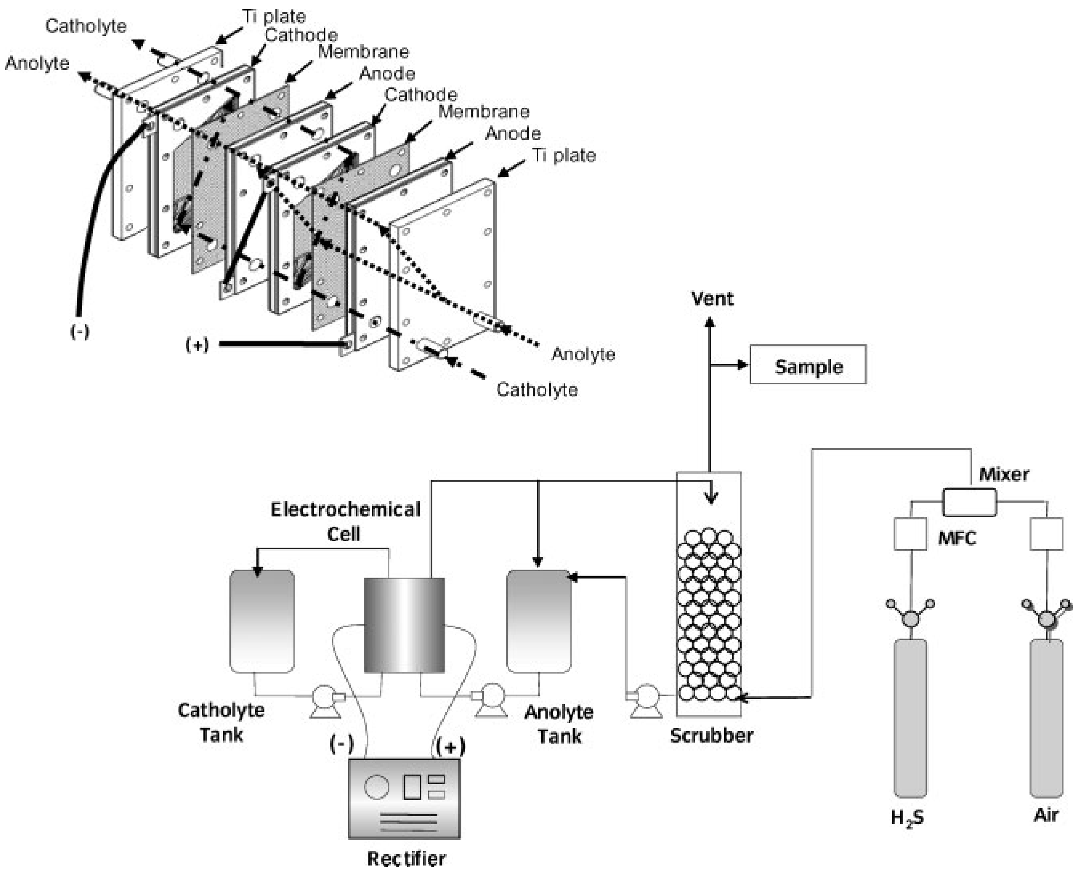

Figure 1. Schematic view of experimental set-up and details of electrochemical cell design used in this study for continuous removal of H_2S from H_2S–air mixture by Ce(IV)/Ce(III)-based mediated electrochemical oxidation process.

scrubbing solution (3 mol L^{-1} HNO_3 with Ce(IV)) was introduced at the top of the scrubber in a counter-current flow pattern at a constant liquid flow rate. The outlet scrubbing solution containing the reduced form of cerium (Ce(III)) was passed through the electrochemical cell for Ce(IV) generation, and was further re-circulated.

Analytical methods

The outlet H_2S gas concentration was measured at regular time intervals by 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 in an aluminum-layered Tedlar sample bag (Top Trading Eng Co., Korea) which was connected through a Teflon valve to a low volume air sampler (Pulse Pump, AeroVironment Inc., USA) with a flow rate of 1.5–2.0 L min^{-1}. After sampling, the bags were immediately analyzed. The operating conditions of the thermal desorption unity and the GC/PFD are given in Table 1. Before each of the successive measurements, pure air from sampling bags was passed through the STD and GC units under the same operating conditions, as used during H_2S measurement, to drain-off the adsorbed traces of H_2S from the tubing and column.

Before start of the removal experiments, the electrochemical cell was first run until the Ce(III) to Ce(IV) oxidation conversion attained 80%, followed by measuring Ce(IV) in the anolyte by titrating it potentiometrically with Fe(II). Only then was the scrubbing solution allowed into the scrubber.

Table 1. Operating conditions of sequential thermal desorber (STD) and GC/FPD

STD	Sampling time	30 mL min^{-1} ×10 min
	Cold Trap temperature	Low : −10 °C, High : 250 °C
	Hold time	2 min
	Outlet split	10 mL min^{-1} (10 : 1 split ratio)
	Flow path temperature	200 °C
GC/FPD	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

The removal efficiencies were calculated from the inlet and outlet H_2S concentrations. All the H_2S removal measurements were carried out at 20 ± 1 °C.

RESULTS AND DISCUSSION

The reproducibility in the H_2S measurements with the STD/GC instrument was tested by measuring five times with 10 ppm samples and the coefficient of variation was 7.66%.

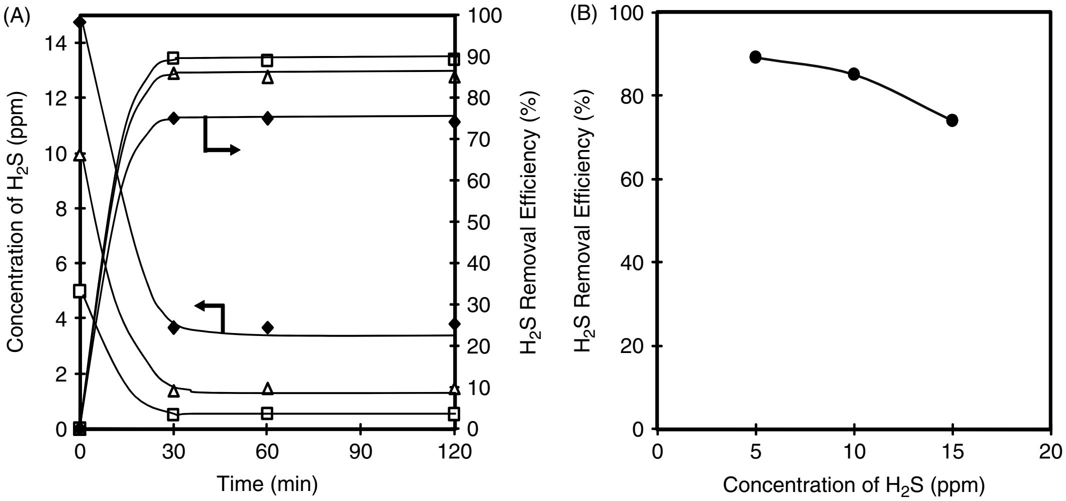

Figure 2. (A) H_2S concentration and its removal efficiency as a function of time for various initial feed concentrations of H_2S (ppm): (□) 5; (△) 10; (♦) 15. (B) Dependence of H_2S removal efficiency at 120 min on initial H_2S feed concentration (experimental conditions: $Q_G = 70$ L min^{-1}; $Q_L = 4$ L min^{-1}; $[\mathrm{Ce(IV)}]_{\mathrm{initil}} = 0.08$ mol L^{-1} in 3 mol L^{-1} HNO_3 and [Ce(III)] + [Ce(IV)] = 0.1 mol L^{-1}).

Effect of H_2S concentration on H_2S removal efficiency

The effect of initial feed H_2S concentration was studied from 5–15 ppm at a given gas flow rate of 70 L min^{-1} with the scrubbing liquid of 0.5 mol L^{-1} Ce(III) (80% of it as Ce(IV), see Materials and methods) in 3 mol L^{-1} HNO_3 at a liquid flow rate of 4 L min^{-1}. Figure 2(A) shows the H_2S concentration profile and its removal efficiency with respect to treatment time for the different feed concentrations. It was observed for each concentration that the concentration decreased with time and attained a constant value within 30 min, and remained the same thereafter for an extended time as long as 120 min. The steady state concentration was higher for higher feed concentration. In terms of the removal efficiency, one can see that it increased sharply within 30 min before reaching a uniform value. The final removal efficiency was found to decrease with increase in H_2S concentration in the range 5–15 ppm, as shown in Fig. 2(B). While 5 ppm H_2S showed an 89% destruction efficiency, this was reduced to 74% for 15 ppm initial concentration.

Regarding the MEO mechanism, the following reactions could be envisaged for the efficient removal of H_2S by the scrubbing liquid (Ce(IV) mediator catalyst ions in 3 mol L^{-1} HNO_3) in the scrubber.

In the electrochemical cell, the electrochemical generation of Ce(IV) from Ce(III) oxidation occurred at the anode:

$$\mathrm{Ce(III)} \longrightarrow \mathrm{Ce(IV)} + e^- \qquad (3)$$

The cathodic reaction was the reduction of H^+ ions:

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (4)$$

The anodically generated Ce(IV) mediator ions fed into the scrubber could bring about the H_2S removal as a combination of several of the following processes.

The absorption of H_2S gas into the liquid phase could be represented as an equilibrium at the gas–liquid interface as follows:

$$H_2S_{(G)} \Leftrightarrow H_2S_{(L)} \qquad (5)$$

H_2S is a week dibasic acid with dissociation constants $pK_{a1} = 7.04$ and $pK_{a2} = 11.96$ at 18 °C,[43] and in the liquid phase it dissociates according to the following equations:

$$H_2S \Leftrightarrow H^+ + HS^- \quad pK_{a1} = 7.04 \qquad (6)$$

$$HS^- \Leftrightarrow H^+ + S^{2-} \quad pK_{a2} = 11.96 \qquad (7)$$

The scrubbing medium being highly acidic, in the present MEO system (3 mol L^{-1} HNO_3) the dissolved H_2S gas in solution would be present entirely in the molecular form. The corresponding oxidation reaction that could occur in the bulk solution under this solution condition is:

$$H_2S + 8\,\mathrm{Ce(IV)} + 4H_2O \longrightarrow SO_4{}^{2-} + 8\,\mathrm{Ce(III)} + 10\,H^+ \qquad (8)$$

Therefore the above reaction scheme: solubility of H_2S into the solution (Equation (5)), followed by its oxidation (Equation (8)) in the liquid phase was responsible for its efficient removal. Although the solubility of H_2S in the liquid phase is moderate, since the Henry's constant for H_2S is 856 Pa m^3 mol^{-1} (compared with 2630 Pa m^3 mol^{-1}[19] for the freely soluble CO_2), the fast irreversible oxidation reaction (Equation (8)), would favour the solubility of H_2S by moving the equilibrium (Equation (5)), to the right towards the solublized species.

Effect of scrubbing liquid flow rate on H_2S destruction efficiency

Figure 3 shows the changes in H_2S removal as a function of experiment time for different flow rates of the scrubbing liquid *ca* 0.1 mol L^{-1} Ce(III) + Ce(IV) in 3 mol L^{-1} HNO_3 solution. These data were collected for liquid flow rates varied from 2–4 L min^{-1} at a constant gas flow rate of 50 L min^{-1}, and H_2S concentration of 10 ppm.

One can see here that again the H_2S removal efficiency increased with time and tended to reach a steady state after 30 min. It was observed that the higher the liquid velocity the better the hydrogen sulfide removal; as shown in Fig. 3 (inset), the 75% removal efficiency at low liquid flow rate 2 L min^{-1} increased to 90% when the flow rate was increased to 4 L min^{-1}. Two kinds of benefit could be associated with the improvement at higher flow rates; one factor was the availability of more of the fresh mediator

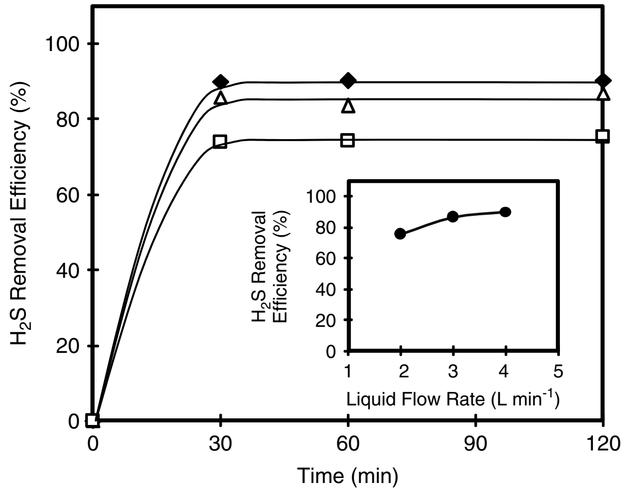

Figure 3. H_2S removal efficiency as a function of time for various liquid flow rates (L min^{-1}): (□) 2; (△) 3; (◆) 4. Inset: dependence of H_2S removal efficiency at 120 min on liquid flow rate (experimental conditions: Q_G = 50 L min^{-1}; H_2S concentration = 10 ppm; $[Ce(IV)]_{initil}$ = 0.08 mol L^{-1} in 3 mol L^{-1} HNO_3 and [Ce(III)] + [Ce(IV)] = 0.1 mol L^{-1}).

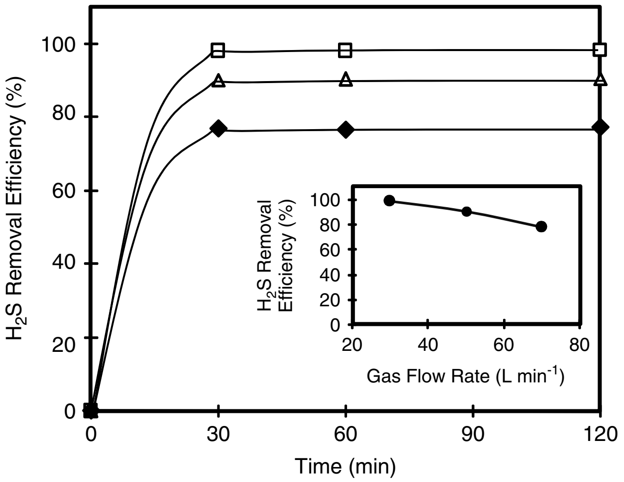

Figure 4. H_2S removal efficiency as a function of time for various gas flow rates (L min^{-1}): (□) 30; (△) 50; (◆) 70. Inset: dependence of H_2S removal efficiency at 120 min on gas flow rate (experimental conditions: Q_L = 4 L min^{-1}; H_2S concentration = 10 ppm; $[Ce(IV)]_{initil}$ = 0.08 mol L^{-1} in 3 mol L^{-1} HNO_3 and [Ce(III)] + [Ce(IV)] = 0.1 mol L^{-1}).

catalyst ion, Ce(IV), with a consequent enhanced H_2S oxidation and its removal. An increase in the mass transfer parameters, namely, interfacial area and mass transfer coefficient, at higher liquid flow rate leading to high efficiency is the other possibility. However, exact measurements of the mass transfer parameters are needed to substantiate such a proposal.

Effect of gas flow rate on H_2S destruction efficiency

In a series of measurements, removal of 10 ppm H_2S by 0.1 mol L^{-1} Ce(III) + Ce(IV) in 3 mol L^{-1} HNO_3 solution was studied at a liquid flow rate of 4 L min^{-1}, varying the gas flow rate from 30–70 L min^{-1}. The results are summarized in Fig. 4. There was uniform behaviour at the different gas flow rates, with the H_2S removal efficiency increasing sharply in the initial stage, reaching a steady state at around 30 min, and remaining constant thereafter. However, in this case the final removal efficiency was highest (*ca* 98%) at the lowest flow rate studied (30 L min^{-1}), and decreased with increasing gas flow rate (77% at the highest flow rate 70 L min^{-1}), as shown in Fig. 4 (inset). Note that in the above case the supply of oxidant Ce(IV) was maintained constant. The decrease in the H_2S removal at higher gas flow rate was expected, since at high gas flow rate the Ce(IV) concentration decreases as there is more H_2S to oxidize.

It is of significance to note that Turpin *et al.*[9] reported a similar decrease of H_2S removal efficiency with superficial gas velocity (U_G) in the presence of sodium hypochlorite oxidant; however, this behavior was considered by the authors as unexpected in view of the increased liquid-side volumetric mass transfer coefficient (k_La) with increasing U_G. Considering (i) the importance of the chemical reaction (H_2S abatement was realized by chemical reactions after H_2S had transferred from the gas to the liquid phase), and hence the residence time in the column of the gas, (ii) negligible gas-side resistance, and (iii) the graphically observed empirical relation between k_La, U_G and the superficial liquid velocity (U_L), it was shown that the removal efficiency was proportional to $U_G{}^{-0.12}$, suggesting that H_2S removal efficiency would decrease with gas flow rate. It is tempting to interpret the present results in terms of a similar mechanism, since both studies used fluids (liquid and gas) circulated counter-currently in the column. However, judging from the fact that the compact scrubber column used by Turpin *et al.* was of a spray type, whereas in the present studies a packed tower was used, complete measurement of the hydrodynamic and mass transfer parameters (pressure drop within the reactor (ΔP), interfacial area (a), k_La, gas-side volumetric mass transfer coefficient (k_Ga)) for the packed bed column is essential as a function of liquid and gas flow rates for a comprehensive understanding of the H_2S removal process in the scrubbing system designed for deodorization. Work is in progress in this direction.

Effect of Ce(IV) concentration on H_2S destruction efficiency

Some trial experiments were performed to determine the influence of Ce(IV) concentration on H_2S removal efficiency in the packed column. For a given liquid flow rate 4 L min^{-1}, the redox ion (Ce(III)) concentration in the electrochemical cell was varied from 0–1 mol L^{-1} in 3 mol L^{-1} nitric acid solution. Figure 5 shows the effect of Ce(IV) concentration on H_2S removal efficiency. For these measurements, the concentration of H_2S was kept to a value of 10 ppm, and gas flow rate at 70 L min^{-1}. There was better removal of H_2S at higher Ce(IV) ion concentration. For example, the steady state removal efficiency was 77% at 0.08 mol L^{-1} Ce(IV) concentration, which increased to 95% at 0.8 mol L^{-1} Ce(IV) concentration (Fig. 5 (inset)), apparently indicating that working with a higher Ce(IV) concentration was more advantageous. It should, however, be noted that a removal efficiency as high as 98% was obtained with low Ce(IV) concentration (0.08 mol L^{-1}) at low gas flow rate of 30 L min^{-1} (Fig. 4), revealing that low Ce(IV) concentrations and low gas flow rates were beneficial for efficient H_2S removal.

It is of significance to notice in Fig. 5 that a neat 3 mol L^{-1} HNO_3 solution devoid of any Ce(IV) also exhibited similar removal behaviour. That is, the efficiency initially increased with time, reaching a maximum at 30 min. However, the maximum efficiency for the HNO_3 alone was low, i.e. around 30%, which subsequently decreased with time. This small but noticeable H_2S removal (30%) by pure HNO_3 may be associated with increased gas solubility in the aqueous nitric acid in the presence of the packing material, which could offer increasing surface area and

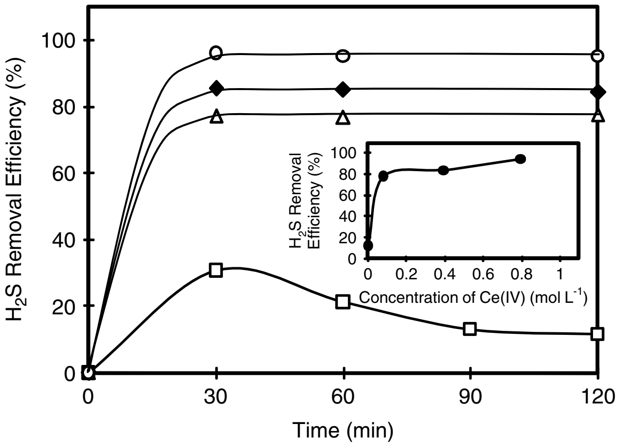

Figure 5. H_2S removal efficiency as a function of time for various Ce(IV) concentrations in 3 mol L^{-1} HNO_3 (mol L^{-1}): (□) 0; (△) 0.08; (◆) 0.4; (○) 0.8. Inset: dependence of H_2S removal efficiency at 120 min on Ce(IV) concentration (experimental conditions: $Q_G = 70$ L min^{-1}; $Q_L = 4$ L min^{-1}; H_2S concentration = 10 ppm).

thus mass transfer to achieve considerable gas absorption into the acid solution. Comparing this behavior of pure nitric acid with the Ce(IV)-containing nitric acid system towards H_2S removal (Fig. 5 (inset)), clearly shows the remarkably efficient and selective performance of the Ce(IV)/Ce(III) based MEO redox system in nitric acid for successfully removing H_2S in the environment at room temperature and pressure.

A comparison of the present MEO process with other electrochemical methods developed for H_2S removal (e.g. using a membrane separator integrated molten electrolyte,[26,27] and using flow-through porous electrodes[29]) clearly indicates the simplicity and superior advantages of the MEO method. The severe problems encountered in handling molten electrolytes, and selection of materials for electrodes and cell housing for use at high temperatures in the method of Winnick *et al.*,[26,27] and selection of specific types of electrodes in the method by Ateya *et al.*[29] are completely avoided in the MEO process, since it works at room temperature and atmospheric pressure utilizing conventional transition metal oxide electrodes more commonly used in industrial applications.

CONCLUDING REMARKS

The following can be concluded from the present work concerning the application of Ce(IV)/Ce(III) based MEO process for the removal of H_2S from an air–H_2S mixture containing H_2S at concentrations 5–15 ppm. (1) The proposed method proved promising for H_2S removal, reaching a high removal efficiency. (2) The present study with different liquid and gas velocities indicated that both altered H_2S removal efficiencies, but in opposite directions. (3) It was shown that, for a given gas flow rate, H_2S removal increased with increasing liquid flow rate, related to the availability of more fresh Ce(IV) mediator catalyst ion, and an increase in the mass transfer parameters. (4) On the other hand, increasing gas flow rate decreased H_2S removal efficiency as a consequence of more H_2S to oxidize. (5) There was a dramatic increase in efficiency with low Ce(IV) concentration (0.08 mol L^{-1}) in the flowing scrubbing liquid, reaching 98% at 30 L min^{-1}. (6) Unlike other electrochemical methods developed for H_2S removal, which work at high temperatures (≈650 °C) or which require special electrodes, the MEO is more economical and safer, since it works at room temperature and atmospheric pressure, utilizing conventional transition metal oxide electrodes more commonly used in industrial applications.

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