

Removal of CH₃SH with in-situ generated ferrate(VI) in a wet-scrubbing reactor

Ling Ding,^{a*} Tong-Xu Liu^b and Xiang-Zhong Li^a



Abstract

BACKGROUND: A wet scrubbing process with in-situ electro-generation of ferrate(VI) has been developed for removing odour from foul gas in wastewater treatment plants. In this process, methyl mercaptan (CH₃SH) in synthetic gas is removed through absorption and oxidation by contacting the gaseous stream with aqueous NaOH electrolyte that offers in-situ generation of ferrate(VI).

RESULTS: The process parameters including electrolyte concentration, applied current density, initial CH₃SH concentration, gas flow rate and gaseous CH₃SH compositions were investigated to determine the best operating conditions and design parameters for a scale-up design. Under all the experimental conditions, gaseous CH₃SH was completely removed by the wet scrubbing process at room temperature and atmospheric pressure. The process proved to be quite effective for dissolved CH₃S⁻ degradation under the optimum experimental condition at the NaOH concentration of 6 mol L⁻¹, current density of 2.22 mA cm⁻² and CH₃SH loading below 30 g m⁻³ h⁻¹. A very short contact time of 0.06 s between the gas and the liquid phases was achieved in this in-situ ferrate(VI) generation reactor.

CONCLUSIONS: This process is effective for CH₃SH control, and holds great promise for industrial applications due to its high efficiency, simplicity and stability.

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Supporting information may be found in the online version of this article.

Keywords: wet scrubbing oxidation; in-situ generated ferrate; CH₃SH removal

INTRODUCTION

Regulators and government bodies receive more and more complaints concerning odour problems nowadays.¹ Wastewater treatment plants (WWTPs), usually located near residential areas, are responsible for unpleasant odour emissions, since odorous gases are produced in the course of wastewater treatment.^{2,3} Typically, the species responsible for odours in WWTPs have been identified to be reduced sulphur, nitrogen, fatty organic acids, aldehydes or ketones compounds. Among them, methyl mercaptan (CH₃SH) is a representative member of the sulphur species with a very low odour threshold of around 0.4 ppb/v.⁴ The daily average concentrations of CH₃SH directly from the wastewater treatment processes were measured in the range 3–14 mg m⁻³ from the beginning of spring to the end of summer.⁵ Thus, odour treatment in WWTPs has become essential.

In order to control these odorous gases, two types of techniques are implemented with the aim of high treatment efficiency, low running cost, easy operation, small footprint and simple equipment, including: (1) a number of dry processes such as activated carbon adsorption,^{4,6,7} thermal oxidation,⁸ and newly developed non-thermal oxidation processes called 'cold oxidation techniques' such as plasma,^{9–11} UV,^{12,13} and microwave techniques;¹⁴ and (2) a number of wet processes such as water absorption (chemical scrubbers)^{15–18} and biological processes (biofilters or bioscrubbers).^{19–22} Comparatively, the scrubbing technique has proven to be one of the most effective and reliable

processes for odour treatment in wastewater treatment plants, since the high water content (moisture) in these odorous gases can eliminate the efficiency of most dry processes greatly.

In a wet chemical scrubber, the odorants can be quickly absorbed by liquid media such as water and then oxidized by oxidizing reagents including chlorine, sodium hypochlorite, hydrogen peroxide and ozone.^{23–26} Therefore, the contact time and pH of the scrubbing solution are two key parameters for odorants removal in this process. For example, in a compact scrubber with aqueous NaClO/NaOH washing solution, H₂S with initial concentration of 10 ppm/v can achieve 99.5% removal at a residence time of 0.02 s, while CH₃SH removal with initial concentration of 4 ppm/v was only 78%.²⁷ In the photocatalytic wet scrubbing process, CH₃SH absorption by the solution is a rate-determining step at pH < 11.5.²⁸ The pK_a of CH₃SH is equal to 9.7. The crucial step is that the pH of the scrubbing solution

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is not basic enough to dissociate CH_3SH to ionized species and then enhance its mass transfer rate from gas phase to liquid phase (by moving the gas–liquid equilibrium).²⁹ To enhance gas–liquid mass transfer, three improvements can be achieved: solution with higher pH, longer contact time and higher oxidation potential of chemical. Indeed, conventional scrubbing processes require high investment and capital costs for the construction of high and wide towers for sufficient gas–liquid contact and distribution.

Up to now, different concepts of electrochemical gas purification have increased the interest in electrochemical abatement strategies. For example, removal of NO_x , SO_2 , H_2S by an electrochemically generated redox mediator system were investigated.^{30–32} Similarly, ferrate(VI) can be synthesized electrochemically by oxidation of an iron anode.³³ Liquid ferrate prepared by an on-line electrochemical technique has proved to be feasible for odour control.³⁴ Electrochemical techniques offer several advantages including no requirement for the continuous dosing of large amounts of chemical reagents and then no consideration for the transport and storage of hazardous and unstable chemicals.

In this study, a wet scrubbing-oxidation process has been developed for removing CH_3SH from synthetic odour gas through absorption and oxidation by contacting the gaseous stream with aqueous NaOH electrolyte that offers in-situ generation of ferrate(VI). In order to optimize the operating conditions, the efficiency of CH_3SH removal was characterized in a laboratory-scale unit in this study. Experimental investigations were conducted for removal of CH_3SH from synthetic odorous gas by in-situ electro-generation of ferrate(VI) in an absorption/oxidation scrubbing system. The influencing factors of NaOH electrolyte concentration, applied current density, CH_3SH loading and CH_3SH compositions, were investigated.

EXPERIMENTAL METHODS

Materials

Methyl mercaptan gas from a certified gas cylinder, which has a traceable concentration of 2000 ppm/v balanced in nitrogen supplied by BOC Gases, was used as an odour source. NaOH, Na_2HPO_4 and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ chemicals of analytical grade were obtained from Sigma-Aldrich Chemical Co. and used without further purification. Deionized distilled water was used for the preparation of all aqueous solutions.

Equipment and experimental procedures

The experimental set-up is shown in Fig. 1(a). CH_3SH gas and air from cylinders were simultaneously pumped into a surge flask, where they were mixed well with the required concentrations. Two mass flow controllers were used to adjust the CH_3SH concentrations in the synthesized odorous gas. As the first methyl mercaptan sensor was at the inlet of the absorption/oxidation reactor, any oxidation between CH_3SH and oxygen in the mixing gas before reaching the reactor was not counted. The second sensor S2 was used to in-line monitor the outlet CH_3SH concentration. However, in all the experiments, the CH_3SH with even maximum concentration 2.88 mmol L^{-1} in the liquid phase reacted with a large excess of NaOH ($3\text{--}14 \text{ mol L}^{-1}$), resulting in zero CH_3SH at the outlet S2.

A cylindrical reactor containing aqueous NaOH electrolyte was used as a wet scrubbing-oxidation reactor, in which an iron anode and a stainless steel cathode were positioned at its centre. The

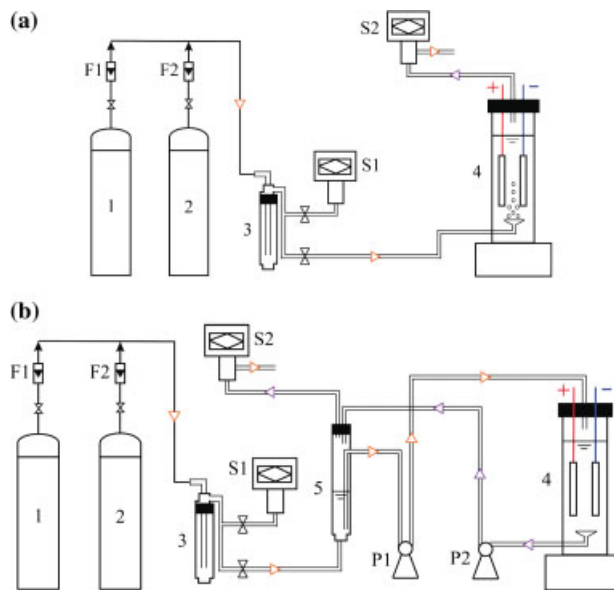


Figure 1. (a) Experimental setup of gaseous CH_3SH removal in the in-situ ferrate(VI) generation reactor: (1) CH_3SH gas cylinder; (2) air cylinder; (3) surge flask; (4) wet scrubbing reactor; F1–F2 mass flow controller; S1–S2 CH_3SH sensor. (b) Experimental setup of the gaseous CH_3SH removal in the in-situ ferrate(VI) generation reactor: (1) CH_3SH gas cylinder; (2) air cylinder; (3) surge flask; (4) oxidation reactor; (5) absorption scrubber; F1–F2. Mass flow controller; S1–S2. CH_3SH sensor; P1–P2. Peristaltic pump.

electrolysis process with a constant current density in the NaOH solution was well controlled by a potentiostat/galvanostat power supply (ZF-9 DC, Zhengfang Electronics Company, China).

It should be noticed that in practical applications of odour gas treatment, while CH_3SH can be quickly absorbed by aqueous NaOH solution, the CO_2 contained in foul gas will also be dissolved and consume NaOH as an extra operating cost. It is better to separate the two steps of absorption and oxidation. Hence, a two-unit reactor system was designed as shown in Fig. 1(b), with a small absorption scrubber for wet scrubbing only with a very short contact time of less than one second to avoid dissolution of CO_2 , and a cylindrical reactor for oxidation, the same as that in Fig. 1(a). No residual odour detected by S2 was released from outlet gas even in such a small absorption scrubber. The experiments for gaseous CH_3SH treatment were carried out in a wet scrubbing–oxidation reaction system equipped with two electrodes and filled with aqueous NaOH solution for simultaneous ferrate(VI) generation and CH_3SH degradation. The synthetic CH_3SH gas was prepared by mixing CH_3SH gas with air, nitrogen, and oxygen from gas cylinders at different ratios using mass flow controllers and continuously pumped into aqueous NaOH solution through an air diffuser from the bottom, and the solution was magnetically stirred to ensure good contact between the dispersed gas bubbles and the solution.

Analytical methods

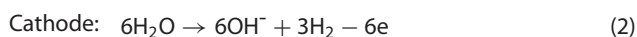
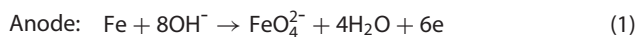
In this study, the ferrate(VI) concentration in aqueous solution was determined by a UV/Vis spectrophotometer (Libra S35, Biochrom) according to the molar absorptivity of $1150 \text{ M}^{-1} \text{ cm}^{-1}$ at $\lambda = 510 \text{ nm}$.³⁵ While gaseous CH_3SH concentrations at the inlet and outlet were monitored by two CH_3SH sensors (Detcon DM-100- CH_3SH) in the range $0.1\text{--}100 \text{ ppm/v}$ ($\pm 2\%$), the CH_3S^- concentration in aqueous solution before and after the reactions were determined by the Ellman's reagent method with details described by Riener *et al.*,³⁶ in which the sample solution was first

buffered at pH ~8.0 and then the light absorbance at 412 nm was measured using the spectrophotometer after incubation for 15 min.

RESULTS AND DISCUSSION

Theoretical aspects

The basic principle of ferrate(VI) synthesis in aqueous alkaline solution by electrolysis is shown by Equations (1)–(3).³⁷

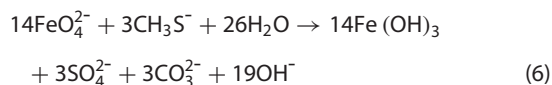
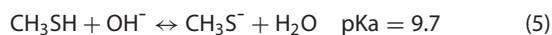


CH₃SH absorption/oxidation in aqueous alkaline solution can be described by the following reactions:^{27,38}

At the gas–liquid interface:



In the liquid phase:



From Equation (5) it can be seen that mass transfer was promoted through the dissociation of CH₃SH into CH₃S[−], resulting in an increase of the CH₃SH apparent solubility and in a mass transfer acceleration between the gas and the liquid phases. Then, CH₃S[−] was oxidized into its by-products by the in-situ generated ferrate(VI), Equation (6). Both of these mechanisms reduce the CH₃SH accumulation in the liquid phase, and thus, improve its gaseous removal.

To investigate the feasibility of continuous CH₃SH removal from odorous gases, several sets of experiments were conducted in the wet scrubbing–oxidation reactors with in-situ generation of ferrate(VI) as a standalone odour treatment process at room temperature. The experiments to study the effects of NaOH concentration, current density and CH₃SH loading were carried out in the system shown in Fig. 1(a), while the experiments to study the effects of CH₃SH gas compositions were conducted in the system shown in Fig. 1(b).

Effect of NaOH concentration

The first set of experiments was performed to determine the optimum NaOH concentration for CH₃SH removal. The synthetic CH₃SH gas with an inlet concentration of 43 ppm/v was continuously fed into the reactor at 600 mL min^{−1} and then the absorbed CH₃S[−] in aqueous NaOH solution was immediately oxidized by ferrate(VI) freshly and continuously produced from the iron anode at a current density of 2.22 mA cm^{−2}, and CH₃SH concentrations in the gas phase and liquid phase were monitored. In addition, a set of control experiments without applying electricity was also conducted to monitor CH₃SH absorption only.

In all experiments, it was found that CH₃SH concentrations in the outlet gas were well below the detection limit of the CH₃SH sensor (<1 ppm/v), which means the removal of CH₃SH from the gas phase was almost complete. Furthermore, in the

Table 1. Saturation concentrations of CH₃SH at different NaOH concentrations

NaOH (mol L ^{−1})	1	3	6
CH ₃ S [−] (mmol L ^{−1})	472	1275	2250

control experiments without ferrate(VI) generation, the amount of absorbed CH₃S[−] in all NaOH solutions (3–14 mol L^{−1}) was almost equivalent to its dose from the gaseous phase, which means that the CH₃SH absorption by NaOH solution was rapid and complete in such a simple bubbling reactor system. In order to operate this reactor continuously, it is important to determine the saturated concentrations of CH₃SH in the aqueous solutions with different NaOH concentrations. Therefore, experiments on the absorption of gaseous CH₃SH by aqueous NaOH solution with different NaOH concentrations were carried out and the experimental results are shown in Table 1. Owing to the high saturation concentration of CH₃SH in NaOH solution, CH₃SNa chemical was pre-dissolved in NaOH solution and then gaseous CH₃SH was pumped into the NaOH solution until CH₃S[−] concentration did not change. The saturation concentration of CH₃SH at 6 mol L^{−1} NaOH solution was found to be 2250 mmol L^{−1}, which was five orders of magnitude of aqueous CH₃S[−] concentration remaining in the NaOH solutions with in-situ generation of ferrate(VI). This result indicates that the driving force for CH₃SH absorption by NaOH solution is very strong. Moreover, the saturation concentrations of CH₃SH from 1 mol L^{−1} to 6 mol L^{−1} NaOH increased linearly. Considering the chemical absorption mechanism, the saturation concentrations of CH₃SH would further increase with increased NaOH concentrations. Therefore, it is believed that the overall process of CH₃SH removal is not limited by absorption rate from gaseous phase into the liquid phase at all.

The experiments were conducted for 150 min, in which electricity was not applied during the first 30 min as pre-treatment to build up the concentration of dissolved CH₃S[−] in the solution, and then electricity was continuously applied for a further 120 min. After electrical current was applied, the dissolved CH₃S[−] concentration first dropped significantly due to CH₃S[−] degradation by freshly generated ferrate(VI), and then gradually recovered to eventually approach a balanced level, when the degradation rate was equivalent to the absorption rate. The concentration of dissolved CH₃S[−] in aqueous solution was monitored and the experimental results are shown in Fig. 2. The dissolved CH₃S[−] concentration at 120 min vs. NaOH concentration in all experiments declined significantly compared with that in the control experiments. In particular, the experiments in 5–8 mol L^{−1} NaOH solutions showed a shock fall of CH₃S[−] concentration due to the faster rate of CH₃S[−] reduction by ferrate(VI) than the CH₃S[−] intake rate.

Other experiments in NaOH solutions either below 5 mol L^{−1} or above 8 mol L^{−1} showed higher concentrations of dissolved CH₃S[−], indicating that the reaction rates of CH₃S[−] reduction by ferrate(VI) in these solutions were not as fast as that in 5–8 mol L^{−1} NaOH solutions. Ferrate(VI) was generated from the iron anode in the NaOH electrolyte. As indicated by Equation (3), increasing the NaOH concentration results in an increase in ferrate(VI) generation. However, the ferrate(VI) oxidation potential decreases when the concentration of OH[−] ions increases. Therefore, an optimum condition for CH₃S[−] removal should be achieved with a good balance between the above two factors. Under our experimental

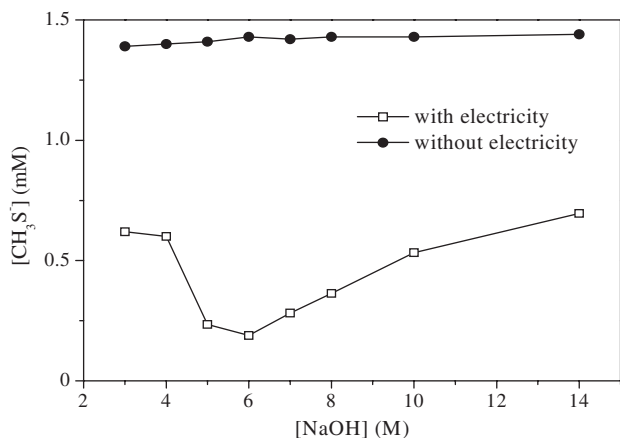


Figure 2. Aqueous CH_3S^- concentration in different NaOH solutions after 120 min reaction in the in-situ ferrate(VI) generation reactor (current density = 2.22 mA cm^{-2} ; $[\text{CH}_3\text{SH}]_{\text{inlet-gas}} \sim 43 \text{ ppm/v}$; gas flow rate = 600 mL min^{-1}).

conditions, an optimum NaOH concentration was found to be at around 6 mol L^{-1} .

Effect of current density

Experiments on the effect of current density were conducted in 6 mol L^{-1} NaOH solution with initial CH_3SH concentration of 43 ppm/v and a gas flow rate of 600 mL min^{-1} for 180 min, in which electricity was not applied during the first 30 min as pre-treatment to build up the concentration of dissolved CH_3S^- in the solution and then electricity was continuously applied for further 150 min. The variation of the aqueous CH_3S^- concentration at different current densities is shown in Fig. 3. After electricity was switched on, the dissolved CH_3S^- concentration in all experiments declined with reaction time significantly compared with that in the control experiment. In particular, the CH_3S^- concentration at the current density of 4.44 mA cm^{-2} almost approached zero due to the rapid generation of ferrate(VI) at high current density. The insert shows the relationship between CH_3S^- concentration at 150 min and the applied current density from 0.56 to 4.44 mA cm^{-2} . The aqueous CH_3S^- concentration at 150 min decreased rapidly with increased current density from 0.56 to 2.22 mA cm^{-2} and then gradually declined beyond 2.22 mA cm^{-2} , which indicates that the CH_3S^- was rapidly reduced even with a very low current density, but further increasing the current density did not increase its reaction rate very much.

From an energy consumption point of view, the specific energy consumption per mole of degraded CH_3S^- (SEC) by ferrate(VI) at various NaOH concentrations with a constant current intensity of 30 mA was calculated in terms of kWh/M using Equation (7) below:

$$\text{SEC} = \frac{\int I \times U dt}{M} \quad (7)$$

Fig. 4 shows the effect of current density on specific energy consumption and on the performance of CH_3S^- removal. It is seen that an increase in current density from 0.56 to 4.44 mA cm^{-2} led to a linear increase in SEC from 0.047 to 0.172 kWh/M . When the current density was increased from 0.56 to 2.22 mA cm^{-2} , the CH_3S^- removal efficiency dramatically increased from 41.2% to 84.2% . However, when the current density was further increased from 2.22 to 4.44 mA cm^{-2} , the efficiency of CH_3S^- removal increased

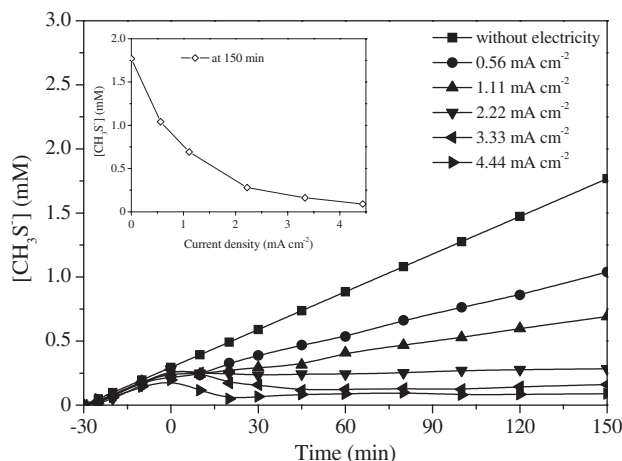


Figure 3. Effect of current density on gaseous CH_3SH removal in the in-situ ferrate(VI) generation reactor (NaOH concentration = 6 mol L^{-1} ; $[\text{CH}_3\text{SH}]_{\text{inlet-gas}} = 43 \text{ ppm/v}$; gas flow rate = 600 mL min^{-1}). Insert: variation of aqueous CH_3S^- concentration at 150 min vs. current density.

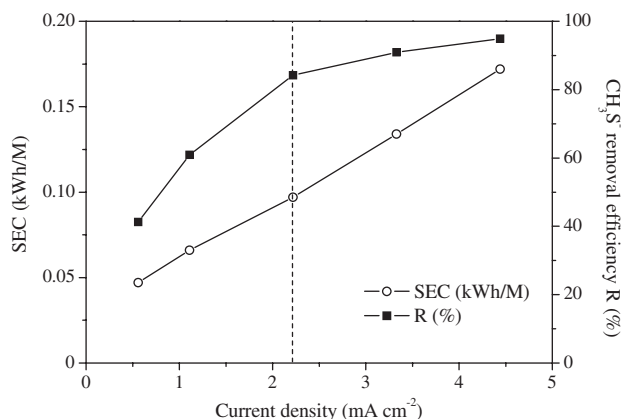


Figure 4. Effect of current density on specific energy consumption of gaseous CH_3SH removal and CH_3S^- removal efficiency at 150 min in the in-situ ferrate(VI) generation reactor (NaOH concentration = 6 mol L^{-1} ; $[\text{CH}_3\text{SH}]_{\text{inlet-gas}} = 43 \text{ ppm/v}$; gas flow rate = 600 mL min^{-1}).

slightly from 84.2% to 94.9% . Therefore, a suitable current density is 2.22 mA cm^{-2} , which can achieve not only high CH_3S^- removal, but also low energy consumption, with both technical and economic benefits.

In the course of the in-situ ferrate(VI) reaction process, ferrate(VI) concentration was also monitored and the experimental results are shown in Fig. 5(a). It was found by using the UV-vis spectrophotometer at 510 nm that ferrate(VI) concentration in the presence of CH_3S^- at current density 0.56 and 1.11 mA cm^{-2} was below the detection limit. The ferrate(VI) concentration with CH_3S^- present levelled off at around 0.004 and 0.07 mmol L^{-1} at current densities of 2.22 and 3.33 mA cm^{-2} , respectively, while the ferrate(VI) concentration quickly increased after 45 min at a current density of 4.44 mA cm^{-2} . To compare the variation of ferrate(VI) concentration in the presence or absence of CH_3S^- , control experiments of electrochemical ferrate(VI) generation were also conducted. From Fig. 5(b) it can be seen that ferrate(VI) concentration in the absence of CH_3S^- linearly increased with a relatively steep slope as the current density was increased from 1.11 to 4.44 mA cm^{-2} . Fig. 5(b) also shows the relationship between $\text{CH}_3\text{S}^-/\text{ferrate(VI)}$ concentration and current density. It was found

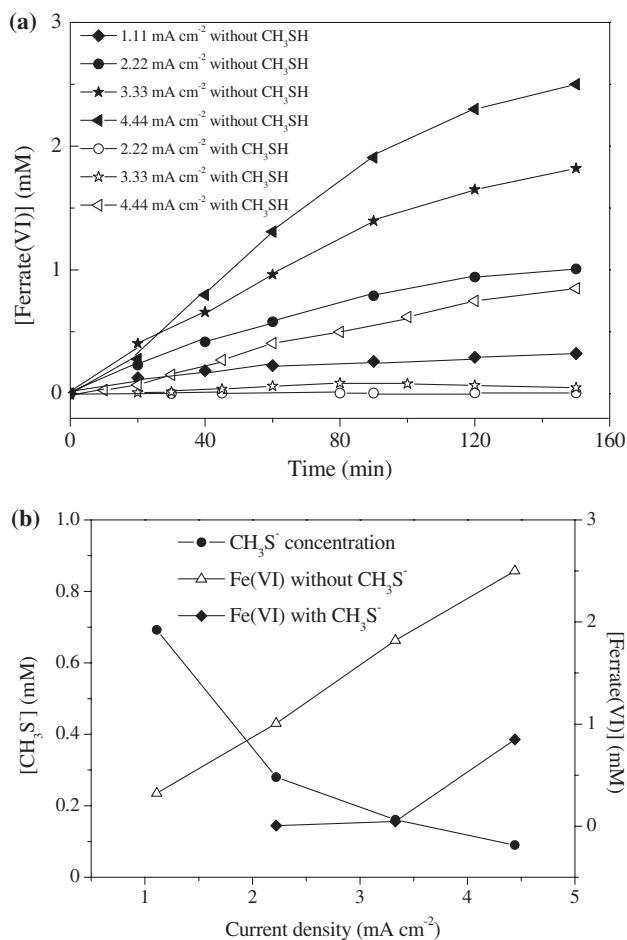


Figure 5. (a) Effect of current density on ferrate(VI) concentration in the in-situ ferrate(VI) generation reactor (NaOH concentration = 6 mol L⁻¹; [CH₃SH]_{inlet-gas} = 43 ppm/v; gas flow rate = 600 mL min⁻¹). (b) Variation of ferrate(VI) concentration with or without CH₃S⁻ and aqueous CH₃S⁻ concentration at 150 min vs. current density.

that once nearly all the aqueous CH₃S⁻ had been degraded at the current density 4.44 mA cm⁻², ferrate(VI) concentration rapidly increased.

Effect of CH₃SH loading

To study the effect of CH₃SH loading on CH₃SH removal in the in-situ ferrate(VI) reaction process, experiments were conducted in 6 mol L⁻¹ NaOH solution at 2.22 mA cm⁻² but with different CH₃SH loadings. The first set of experiments was performed with a fixed gas flow rate of 600 mL min⁻¹ but variable CH₃SH concentrations in the inlet gas, whereas the second set of experiments was performed with a fixed CH₃SH concentration of ~44 ppm/v, but variable gas flow rates. During the experiments, the CH₃SH concentrations in the gas and liquid phases were both monitored to evaluate the CH₃SH removal performance.

The experimental results are shown in Figs. S1 and S2 (Supporting Information) and further summarized in Fig. 6. It can be seen that when CH₃SH loading was below 30 g m⁻³ h⁻¹, the rate of CH₃S⁻ degradation in aqueous solution was exactly the same as the rate of its intake. When the CH₃SH loading was further increased, the rate of CH₃S⁻ degradation gradually levelled off. Furthermore, the gaseous CH₃SH concentrations in the outlet determined by CH₃SH sensor were still zero at CH₃SH loading up

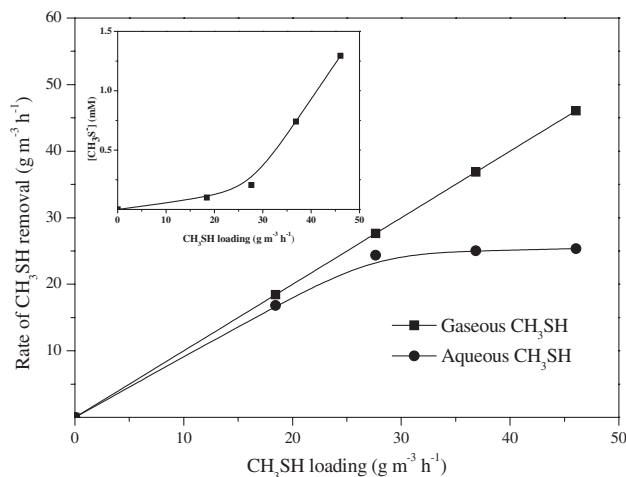


Figure 6. Dependence on CH₃SH loading ([CH₃SH]_{inlet-gas} Q/V) of the overall CH₃SH removal at 150 min (NaOH concentration = 6 mol L⁻¹; [CH₃SH]_{inlet-gas} = 43 ppm/v; gas flow rate = 0.4 ~ 1.0 L min⁻¹). Inset: Variation of aqueous CH₃S⁻ concentration at 150 min vs. CH₃SH loading rate.

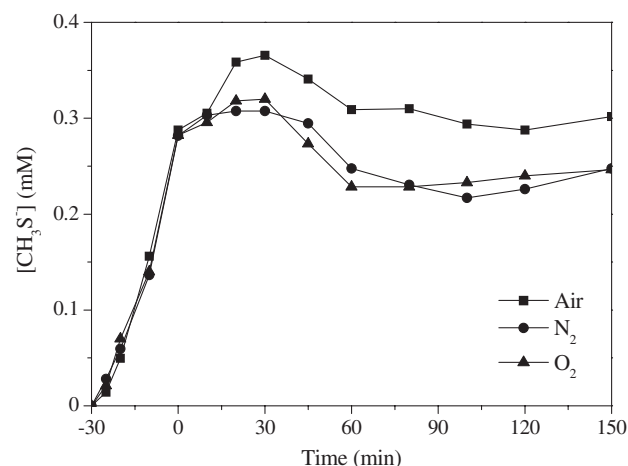


Figure 7. Effect of CH₃SH compositions on gaseous CH₃SH removal in the in-situ ferrate(VI) generation reactor (NaOH concentration = 6 mol L⁻¹; [CH₃SH]_{inlet-gas} = 43 ppm/v; gas flow rate = 600 mL min⁻¹)

to 46 g m⁻³ h⁻¹, which indicates that the rate of gaseous CH₃SH removal equals the stoichiometric rate of CH₃SH input up to 46 g m⁻³ h⁻¹. From Table S2, the maximum amount of CH₃SH in the NaOH solution was 2.88 mmol L⁻¹, which rapidly reacted with 6 mol L⁻¹ NaOH since CH₃SH with NaOH was a 1 to 1 reaction.

Effect of CH₃SH gas compositions

The influence of the gas components O₂, N₂ and air, on CH₃SH removal in the in-situ ferrate(VI) generation reactor was investigated at the current density of 2.22 mA cm⁻², initial CH₃SH concentration of 43 ppm/v and gas flow rate of 600 mL min⁻¹. Variation of the remaining CH₃S⁻ concentration with gas composition as a function of time is shown in Fig. 7.

It was interesting to find that the aqueous CH₃S⁻ concentrations were almost the same when the synthetic CH₃SH gas was prepared with N₂ and O₂ gas, although the aqueous CH₃S⁻ concentration was slightly higher when the synthetic CH₃SH gas was prepared with air under the same experimental conditions. The CH₃SH removal

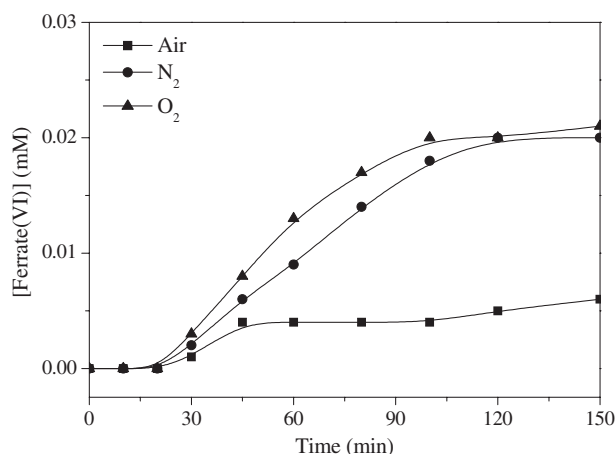


Figure 8. Effect of CH_3SH compositions on ferrate(VI) concentration in the in-situ ferrate(VI) generation reactor (NaOH concentration = 6 mol L^{-1} ; $[\text{CH}_3\text{SH}]_{\text{inlet-gas}} = 43 \text{ ppm/v}$; gas flow rate = 600 mL min^{-1}).

in the gas phase was still complete among the three experiments, which indicated that the higher aqueous CH_3S^- concentration when mixing with air may result from the lower reaction between CH_3S^- and ferrate(VI). As the same amount of CH_3S^- is dissolved in the liquid solution under the three conditions, the possible reason may be less ferrate(VI) generated in NaOH electrolyte when CH_3SH gas was prepared with air. This was proved by the results of ferrate(VI) concentration simultaneously measured under the same experimental conditions and shown in Fig. 8. Ferrate(VI) concentration was only $0.006 \text{ mmol L}^{-1}$ at 150 min when CH_3SH gas was prepared with air, while ferrate(VI) concentration was up to $0.020 \text{ mmol L}^{-1}$ and $0.021 \text{ mmol L}^{-1}$ when CH_3SH gases were separately prepared with N_2 gas and O_2 gas. It was also interesting to find that ferrate(VI) concentration using O_2 gas was slightly higher than when using N_2 gas. This result may be attributed to the formation of O_2^- ions from the reaction of dissolved O_2 with OH^- ions ($3\text{O}_2 + 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 4\text{O}_2^-$),³⁹ which benefits ferrate(VI) conversion from intermediate iron-oxo species (FeO_2^- and FeO_2^{2-}).⁴⁰ However, this slight improvement in ferrate(VI) generation did not influence the efficiency of CH_3S^- removal.

Since CO_2 from air was simultaneously introduced into the NaOH solution. The contact time of the gas and the liquid phase in our reactor as shown in Fig. 1(a) was 12 s, which is sufficient to complete CO_2 absorption and its reaction with NaOH.²³ Thus, sodium carbonate was accumulated in the reacting solution. It was reported that the presence of sodium carbonate might decrease the rate of ferrate(VI) generation by inhibition of the active dissolution sites at the electrode surface.⁴¹ Moreover, the presence of CO_2 actually led to extra NaOH electrolyte consumption. From the point of practical application of this new process, the presence of CO_2 in foul gas will not only decrease the process efficiency but also increase the operating cost. However, if we reduce the contact time between foul gas and NaOH solution down to a very low level, the effect of CO_2 on NaOH consumption can be reduced to a minimum. Therefore, the experimental setup of the in-situ ferrate(VI) generation reactor as shown in Fig. 1(b) for gaseous CH_3SH removal was developed by using an absorption scrubber with a very small volume of scrubbing solution before the oxidizing reactor. Thus the contact time between the gas and the liquid phase was reduced from 12 to 0.06 s only, which was the lowest contact time of the system.

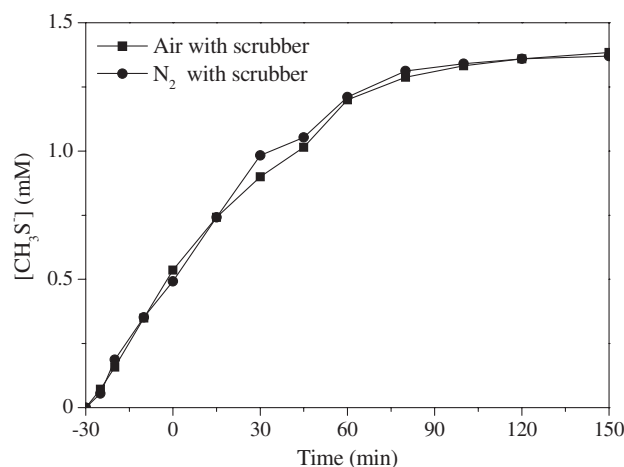


Figure 9. Effect of CH_3SH compositions on gaseous CH_3SH removal in the in-situ ferrate(VI) generation reactor (NaOH concentration = 6 mol L^{-1} ; $[\text{CH}_3\text{SH}]_{\text{inlet-gas}} = 13 \text{ ppm/v}$; gas flow rate = 5000 mL min^{-1}).

In this experimental set-up, the aqueous NaOH solution was continuously circulated between the absorption scrubber and the oxidation reactor. No residual odour was released from the outlet gas even with such a small volume of scrubbing solution at a high gas velocity of 5 L min^{-1} . From Fig. 9, it is seen that the experimental set-up developed resolved the CO_2 absorption problem successfully. The added absorption scrubber enabled a very short gas–liquid phase residence time, which can effectively limit the effective CO_2 mass transfer from gas to liquid to avoid CO_2 absorption and extra consumption of NaOH solution.

CONCLUSION

An electrochemical process with in-situ generation of ferrate(VI) developed in this study demonstrated a good combination of absorption and oxidation scrubbing techniques for gaseous odour treatment. Experimental results showed that gaseous CH_3SH was completely removed by this wet scrubbing–oxidation process at room temperature and atmospheric pressure. The optimum experimental conditions were established as NaOH electrolyte 6 mol L^{-1} , electrical current density 2.22 mA cm^{-2} , and CH_3SH loading below $30 \text{ g m}^{-3} \text{ h}^{-1}$. The contact time between the gas and liquid phase was shortened to 0.06 s in this in-situ ferrate(VI) generation reactor system. As a new effective strategy of CH_3SH control, this work has great academic significance and also application value.

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Supporting Information

Supporting information may be found in the online version of this article.

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