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Use of peroxymonosulfate in wet scrubbing process for efficient odor control

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ABSTRACT

Peroxymonosulfate (PMS) was utilized as an oxidant for methyl mercaptan odor ($CH_3SH_{(G)}$, ~80 ppm/v) removal in wet scrubbing process, and the proposed reaction mechanism was investigated in detail. Under alkaline condition (pH ~ 12) with PMS, the removal of $CH_3SH_{(G)}$ maintained high levels of >95%. The reaction was so quick that no methyl mercaptan ion (CH_3S^-) in aqueous solution was detected before the depletion of PMS. PMS not only reacted with CH_3S^-, which was dissociated from the dissolved $CH_3SH_{(aq)}$ in alkaline solution, but also directly oxidized the dissolved $CH_3SH_{(aq)}$. It was found that 3 mol of PMS would be necessary to oxidize 1 mol of CH_3SH. The major product of the oxidation of CH_3SH was methanesulfonic acid ($CH_3SO_3^-$). Additionally, the stability of PMS, by adding sodium silicate (Na_2SiO_3), was very well maintained even under strong alkaline conditions (less than 5% decomposition). In conclusion, PMS was extremely suitable for $CH_3SH_{(G)}$ removal in wet scrubbing process with the existence of Na_2SiO_3, especially under alkaline condition (pH ~ 12).

1. Introduction

Industrial plants, which are generally located near living areas as societies developed, should be responsible for odor emissions [1]. Odors are harmful for human health because of the potential toxicity, irritation, carcinogenicity, and corrosivity of the odor molecules [2,3]. Control of the emissions of odors has become a major issue in prevention of air pollution. Technologies for odor control can be divided into dry process and wet treatment. Dry processes, including adsorption [4–9], thermal oxidation [10], plasma [11], and UV [12,13], are usually environment-unfriendly because gas products are uncontrollable in the gaseous state [14]. Wet treatment technologies [15], including absorption [16,17], photocatalysis [18], and biological process [19–21], are relatively environment-friendly because of the products dissolving into solution [22]. Among them, chemical scrubbing in packed towers remains one of the most widely used and effective processes for odor control [16,23–25]. Methyl mercaptan ($CH_3SH_{(G)}$) is a type of sulfur-containing compound of odors with a very low olfactory threshold of around 0.021 ppm/v (parts per million by volume) [26] and it has toxic and corrosive characters. It is well known that $CH_3SH_{(aq)}$ can quickly dissociate as CH_3S^- in alkaline solution [27]. The absorption of $CH_3SH_{(G)}$ can be described as reactions (1) and (2) [23].

$$\text{At the interface:}\quad CH_3SH_{(G)} \leftrightarrow CH_3SH_{(aq)} \qquad (1)$$

$$\text{In the liquid phase:}\quad CH_3SH_{(aq)} + OH^- \leftrightarrow CH_3S^- + H_2O \quad pK_a = 9.7 \;\; [27] \qquad (2)$$

The methyl mercaptan ion (CH_3S^-) can be oxidized by some oxidizing reagents including hydrogen peroxide (H_2O_2), sodium hypochlorite (NaClO), calcium hypochlorite ($Ca(ClO)_2$), ozone (O_3), and potassium permanganate ($KMnO_4$) [28]. NaClO was commonly used as oxidant owing to its effectiveness. Unfortunately, it is generally known that NaClO is likely to form chlorinated by-products which are harmful for human health [29] and to produce another very pungent odor, hypochloric acid. H_2O_2 is a promising oxidant because of avoiding the formation of harmful by-products. H_2O_2 is, in fact, well-known to be unstable in basic aqueous solution and to change into oxygen and water [16]. The biggest drawback of H_2O_2 is the low efficiency of CH_3SH removal (45% of removal was obtained with H_2O_2 against 97% with NaClO) [29].

The alternatives of H_2O_2 are emerging oxidants used in water treatment [30–33]. Peroxymonosulfate (PMS) has an O–O bond

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which is similar in structure with H_2O_2. One hydrogen atom in H_2O_2 is replaced by SO_3 to generate HSO_5^-. PMS has the advantage of strong oxidation with standard oxidation–reduction potential (E^0) of +1.82 V/NHE, which is higher than that of H_2O_2 (E^0 = +1.766 V/NHE) [34].

To the best of our knowledge, there is a lack of research about the wet scrubbing process with PMS for odor treatment. Therefore, this study takes an interest in the use of PMS as the oxidant in scrubbing towers. The aims of this study were to investigate the efficiency of using PMS for the $CH_3SH_{(G)}$ removal versus pH and the initial PMS concentration in wet scrubbing process, and to explore the reaction pathways of $CH_3SH_{(G)}$ removal, which might be responsible for the efficiency of $CH_3SH_{(G)}$ removal. The stability of PMS in alkaline solution, which may influence its practical application, was also investigated with and without special stabilizer. The products of wet scrubbing process with PMS were identified by ion chromatography (IC), and a possible reaction ratio of PMS consumption to $CH_3SH_{(G)}$ removal was proposed in the final part of the study. This study was expected to provide helpful information on expanding the wet scrubbing process with PMS for practical odor treatment.

2. Experiment

2.1. Materials

Peroxymonosulfate (PMS, $2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$ available as oxone, containing 42% $KHSO_5$), was purchased from Shanghai Ansin Chemical Company, China. Sodium hydroxide (NaOH, 98%), potassium iodide (KI, 99.0%), sodium thiosulfate ($Na_2S_2O_3$, 99.0%), boronic acid (H_3BO_3, 99.5%) were purchased from Shanghai Chemical Reagent Company, China. Methyl mercaptan ($CH_3SH_{(G)}$) from Dalian Date Gas, which was chosen as the odorous gas source with a concentration of 3000 ppm/v (parts per million by volume), was diluted to the experimental value with zero clean air. Ellman reagent ($C_{14}H_8N_2O_8S_2$, 99%) and (CH_3SNa, 95%) were purchased from Amrecso, USA and Sigma, USA respectively. Chemicals were all used without purification. Distilled water was used to prepare experimental solutions.

2.2. Experimental procedure

The pilot unit designed for the study is shown in Fig. 1. The major components of the set-up were a scrubbing tower, a liquid circulation loop, mass flow meters and methyl mercaptan sensors. $CH_3SH_{(G)}$ gas was continuously pumped into the scrubbing tower from the bottom (the original concentration of ~80 ppm/v except as specially pointed out, the gas flow rate of 1.5 L min^{-1}) and the residual gas would be discharged at the top of the reactor. The alkaline solution was sprayed from the top of the scrubbing tower and maintained circulation (the liquid flow rate of 120 mL min^{-1}). This could ensure good contact between CH_3SH gas and alkaline solution for absorption. At specific time intervals, 2–3 mL of sample was withdrawn and analyzed. $CH_3SH_{(G)}$ removal was defined as the percentages of $CH_3SH_{(G)}$ absorption by wet scrubbing process in $CH_3SH_{(G)}$ input.

Other experiments, that PMS oxidized CH_3S^- at pH 12, were conducted directly adding sodium methyl mercaptan (CH_3SNa) into the aqueous solution without ventilation during experiments. The decomposition of PMS was also investigated in the pilot unit without ventilation at different pH. Every experiment was carried out three times and the obtained results were similar, with variance not greater than 5%. The data referred to in this paper were the mean values.

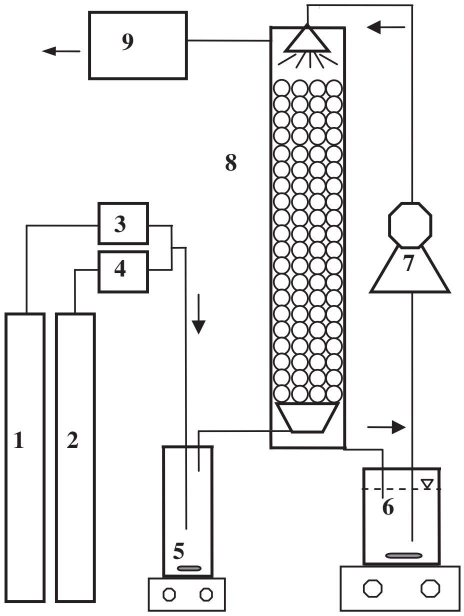

Fig. 1. Pilot unit: 1 – $CH_3SH_{(G)}$ gas cylinder, 2 – air cylinder, 3 – nitrogen flow meter, 4 – air flow meter, 5 – gas buffer bottle, 6 – liquid buffer bottle, 7 – peristaltic pump, 8 – scrubbing tower (plastic pellet packed), 9 – $CH_3SH_{(G)}$ sensor.

2.3. Analytical methods

The concentration of outlet $CH_3SH_{(G)}$ was directly recorded by methyl mercaptan sensors (Zhuochuan WD.103-Q2000, China) with the monitoring range of 0–100 ppm/v (±3%). The CH_3S^- concentration dissolved in the solution was determined by the Ellman method [35]. The major products of the wet scrubbing process with PMS were analyzed by ion chromatography (IC) on ICS-3000 instrument with an IC column (IonPac AS11HC 2 × 250 mm). The mobile phase is KOH (gradient elution). Column temperature is 30 °C. Injection volume is 25 μL. Retention times for SO_4^{2-} and $CH_3SO_3^-$ are 24 min and 11 min separately. The concentration of PMS was analyzed by an iodometric titration method [36]. The pH of the solution was measured by using a pHSJ-4A model digital pH meter.

3. Results and discussion

3.1. Absorption and oxidation of CH_3SH by PMS in alkaline solution

PMS is a strong oxidizer [37,38], and in theory could be used for $CH_3SH_{(G)}$ gas removal by wet chemical absorption. In order to determine its ability of removing $CH_3SH_{(G)}$ in wet scrubbing process, the experiment was performed with PMS concentration of 1.0 g L^{-1} at pH 12. The experimental results are presented in Fig. 2. Experimental data for the absorption of $CH_3SH_{(G)}$ into alkaline solution in the absence of PMS was also depicted for the reference purpose. $CH_3SH_{(aq)}$ can dissociate as CH_3S^- in alkaline solution according to the reactions (1) and (2) [23]. Without PMS, the alkaline solution can absorb $CH_3SH_{(G)}$ and the concentration of CH_3S^- increased with the continuously absorption before saturation. The $CH_3SH_{(G)}$ removal declined with reaction time with CH_3S^- gradually reaching a state of saturation, which has been accepted by researchers [39–41]. As seen in Fig. 2, it was clear that in the presence of PMS the $CH_3SH_{(G)}$ removal aggrandized significantly. With PMS, CH_3S^- cannot be detected in the alkaline solution before the inflection point of CH_3S^- concentration. At about 100 min, when PMS had run out by detecting, there was a corresponding and conspicuous inflection point of CH_3S^- concentration