REMOVAL OF HYDROGEN SULFIDE IN SYNTHESIZED AIR BY CHEMICAL ABSORPTION IN A PACKED COLUMN

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ABSTRACT

In this study, hydrogen sulfide (H_2S) removal rate by different alkali and oxidative absorbing solutions (i.e., NaOH, $Ca(OH)_2$, NaOCl, $Ca(OCl)_2$, and water) was compared using a packed absorption column. The results showed that NaOH solution was the suitable absorbent based on its removal efficiency, mass transfer coefficient, and overall enhancement factor. NaOH solution was then selected for further experiments and the effects of operation parameters including initial pH of solution, liquid flow rate, and the height of the packed column were determined. For the initial gas concentration of 75 mg/m^3 and the gas flow of 22.4 m^3/h, the absorption by NaOH solution at the initial pH of 10.5, flow rate of 1 L/min, and packed height of 1.4 m resulted in the removal rate of 90.1% and H_2S concentration in the effluent lower than the allowable value (i.e. 7.5 mg/m^3, as given in QCVN 19: 2009/BTNMT). The overall enhancement factor of 20.74 obtained from this study would be a good reference for designing the treatment system in practical applications.

Keywords: H_2S, chemical absorption, gas scrubber, air pollution control.

1. INTRODUCTION

H_2S is foul-smelling, corrosive and toxic agent causing much harm to the environment and society. Air streams containing H_2S can be generated from natural gas treatment, hydrogen purification, refinery tail gas treatment, ammonia synthesis, methanol gas synthesis [1], and biogas [2]. H_2S concentration from different sources varied strongly, e.g. 30-200 ppm in coal seam of Fenghuangshan coal mines [3], 10 ppm from coal-bed methane, 920 ppm from Tunisia sour-well, or 33000 ppm from Alberta Sour well [4]. In biogas, H_2S was found at 2 ppm [5] or between 4-500 ppm [6]. At concentrations of 5 ppm or higher, H_2S causes effects on human health such as nausea, headache, insomnia [7]. Particularly, with a concentration from 1000 ppm to 2000 ppm, H_2S is almost immediately deadly for the victim [3]. Besides, if the concentration of H_2S in the soil is too high, H_2S will occupy the place of oxygen (O_2). This phenomenon affects the respiration of plant roots and decreases nutrient uptake. In industrial systems, H_2S causes corrosion of machinery, equipment, pipes because of its acidity. Due to

its risks and hazards, treatment of H_2S in the gas is necessary before releasing into the atmosphere.

Many methods of H_2S treatment such as absorption, adsorption, and biotechnology have been studied in recent years. Depending on the pollution characteristics, each method has its own advantages and disadvantages. While adsorption is superior to removing H_2S from the biogas and biological methods predominate in the treating of bad smell with low concentrations of air pollutants, the absorption method is known as the most common way of removing H_2S in industrial application. Absorption as a traditional method has a long history of research and development, and plays an important role in the exhaust gas treatment technology of many factories. Absorption consists of physical absorption and chemical absorption and an emerging membrane contactor for absorption of H_2S [8, 9], in which chemical absorption is more effective than physical absorption in the case of no requirement of solvent regeneration and solute recovery. Several studies have been focused on the absorption of H_2S using organic solution for recovery purpose [10-17]. On the other hand, other authors preferred alkali solution for removal of H_2S [18-21]. Using of chlorine solution such as NaOCl and Cl_2 was proven to help oxidizing H_2S and therefore enhance the absorption efficiency [18, 20]. However, there has no any work compared the absorption removal efficiency by different alkali and chlorine solutions.

On the other hand, absorption calculation and absorber design are complicated and mostly based on mass transfer theory, meaning that rate of absorption is usually determined by the rates of diffusion in both the gas and liquid phases. The gas transfer in physical absorption with water is calculated using Henry's law, which provides the equilibrium of pollutants between gas and liquid (water) phases. The Henry's law constant can be found or calculated from experiments from the literature, which is summarized by Sander [22]. For chemical absorption, both mass transfer (i.e., in gas and liquid phases) and intrinsic reaction rate (i.e. chemical reaction of pollutant and reagent in liquid phase) affect the absorption rate. Practically, most of the chemical absorption process is calculated based on experimental data or physical absorption with enhancement factor obtained from experiment [25]. The fact is that the information of equilibrium between gas and liquid phases for the pollutants is hard to find in the literature, except for the removal of SO_2 by calcium-based reagents (e.g. $CaCO_3$ and $Ca(OH)_2$). The calculation in designing chemical absorption process for removal of H_2S in polluted gas still faces many difficulties and requires experiments in order to obtain the suitable design parameters.

Therefore, this study aims to compare the H_2S absorption ability of water, NaOH, $Ca(OH)_2$, NaOCl, $Ca(OCl)_2$ solutions from air stream. Effect of operating conditions including initial pH of solution, liquid flow rate, the height of the packed column, and the recycling of absorption solution was investigated to ensure the removal of H_2S with minimum efficiency of 90% as well as H_2S concentration in the effluent which comply with the Vietnam National Technical Regulation on Industrial Emission of Inorganic Substances and Dusts (QCVN 19: 2009/BTNMT).

2. MATERIALS AND METHODS

The absorbents used in this study were sodium hydroxide (NaOH), calcium hydroxide ($Ca(OH)_2$), sodium hypochlorite (NaOCl), calcium hypochlorite ($Ca(OCl)_2$) at the concentration of 0.01% (w/w). They were bought from Viet Hoang Long Co., Ltd. Packed material was K2 (Kaldnes) which was provided by Nam Trung Viet Technology Environment Co., Ltd. Image of this material and its characteristics were given Fig. 1 and Table 1, respectively.

Fig. 1. The packed material (Kaldnes K2)

Table 1. Kaldnes packing material's characteristics

Material	PVC plastic
Size	25 × 25 mm
Specific surface area	306.22 m^2/m^3
Void volume	0.8125 m^3/m^3
Surface tension	0.0379 kg/s^2
Working temperature	20-80 ^oC

The absorption experiment was conducted using a model as shown in Fig. 2. A certain proportion of inlet-airflow was chosen by the mixing the H_2S gas and the clean air. Hydrogen sulfide gas is generated by the reaction between sodium sulfide (Na_2S) and sulfuric acid (H_2SO_4) 5%. The clean air was supplied into the system by the fan. To compare the removal efficiency by different absorbent solutions, H_2S was prepared at initial concentrations varied from 65-91 mg/m^3. In general experiment, 22.4 m^3/h of H_2S-contained airflow at 75 mgH_2S/m^3 was pumped from the bottom of fix-bed absorption column with the diameter of 0.89 m and the packed height of 1.6 m. The absorbent solution at 0.8 L/min was showered at the top of this column by a metering pump. H_2S then removed from the gas phase to the liquid phase. The concentration of this gas was determined by the methylene blue method and iodine titration [23]. The samples were taken within each 2 minutes [23, 24]. To determine the optimum operating condition, the effect of initial pH (10-11), liquid flow rate (0.6-1.2 L/min), packed column (1.3-1.6 m), and recycling absorption solution on removal efficiency were investigated.

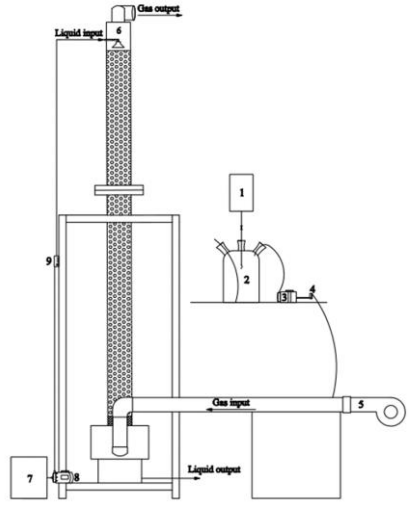

Fig. 2. Experimental set-up for chemical absorption of H_2S in air: (1) sulfuric acid solution tank, (2) H_2S generator, (3) air pump, (4) air flow meter, (5) centrifugal fan, (6) packed column, (7) absorbing solution tank, (8) liquid pump, (9) liquid flow meter.

The mass transfer coefficient and enhancement factors were then calculated based on experimental data. Details on formula and calculation step can be seen from the book of McCabe *et al.* [25]. The enhancement factor in the liquid phase (ϕ, dimensionless) and overall enhancement factor for gas absorption (E, dimensionless) were obtained from following equations:

$$\phi = k_{L\ chemical}/k_{Lwater} \quad (1)$$

Where k_L is individual mass transfer coefficient for liquid phase based on concentration difference, kmol/($m^2 \times s \times$ unit mole fraction)

$$E = K_{G\ chemical}/K_{G\ water} \quad (2)$$

Where K_G is overall mass-transfer coefficient for gas phase, kmol/($m^2 \times s \times$ unit mole fraction).

3. RESULTS AND DISCUSSION

3.1. Effect of absorbent solution

This experiment was carried out with various absorbents including solutions of NaOH, $Ca(OH)_2$, NaOCl, $Ca(OCl)_2$, and distilled water. The operational parameters were set up at gas flowrate of 22.4 m^3/h and absorption flowrate of 0.8 L/min. The removal efficiency and overall enhancement factor of the absorbing solutions are presented in Fig. 3 and Table 2, respectively. As can be seen from Fig. 3a, NaOH and $Ca(OH)_2$ showed quite coincidence lines of the removal efficiencies which were higher in comparison with the efficiencies achieved from other absorption solutions. At initial H_2S concentration of 75 mg/m^3, the absorption efficiency reached 93.58%, 93.18%, 87.79%, 84.86% and 21.20% by NaOH, $Ca(OH)_2$, NaOCl, $Ca(OCl)_2$ and distilled water, respectively (Fig. 3b). The highest and lowest absorption efficiencies were obtained from the NaOH solution and distilled water, respectively. NaOCl and $Ca(OCl)_2$ solutions gave relatively high efficiencies but the resulted H_2S effluents did not meet the standard. Compared to the physical absorption by water, the chemical absorption by NaOH, $Ca(OH)_2$, NaOCl and $Ca(OCl)_2$ were superior. Since H_2S gas is poorly soluble in water at room temperature, water is not a suitable absorbent solution in this case. Thought both NaOH and $Ca(OH)_2$ provided the comparable removal rates, we selected NaOH as suitable absorbent instead of $Ca(OH)_2$ because of the less solubility of $Ca(OH)_2$ itself as well as the generation of CaS and $CaCO_3$ sludge which may cause difficulties for cleaning the system, recycling or discharging of absorption solution after the treatment, and pipeline and packed column stuck for long duration of operation. Also, the preparing of $Ca(OH)_2$ suspension requires more equipment (e.g. equipment for converting lime from the dry to wet stage to produce a slurry and then for diluting to milk of lime before feeding into the treatment process), as well as more labor intensive than that of NaOH solution. Therefore, NaOH is more suitable for small-scale air pollution control system, where the capital cost should be low but operational cost is not a big problem as in large-scale system.

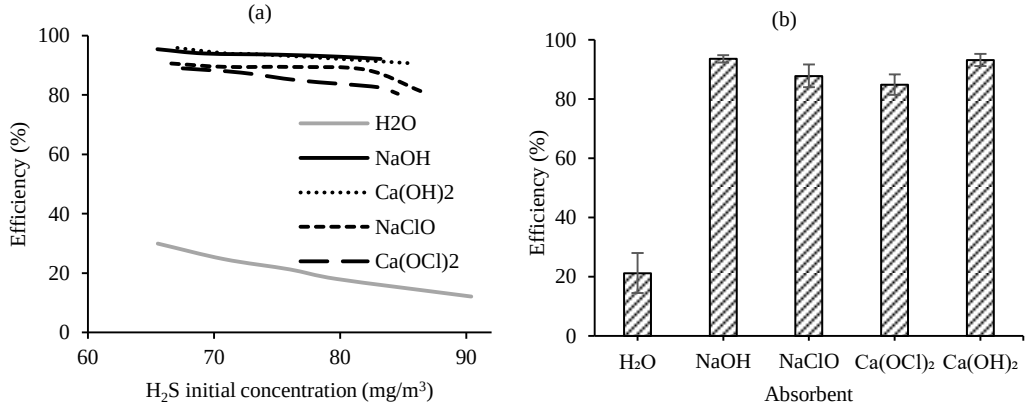

Fig. 3. H_2S absorption efficiency of H_2O, NaOH, $Ca(OH)_2$, NaClO, and $Ca(OCl)_2$
(a) at different H_2S initial concentrations and (b) at H_2S initial concentration of 75 mg/m^3 (n = 5)

Table 2. Mass transfer coefficient and overall enhancement factor for various absorbing solutions

Solution	K_G	E
Water	7.11×10^{-5}	1
NaOH	1.48×10^{-3}	20.74
$Ca(OCl)_2$	0.97×10^{-3}	19.45
$Ca(OH)_2$	1.38×10^{-3}	15.16
NaClO	1.08×10^{-3}	13.67

3.2. Effect of initial pH of absorption solution

NaOH was chosen for these experiments to determine the optimal pH. The initial pH values were adjusted from 10.0 to 11.0. As can be seen from Fig. 4, the higher initial pH value resulted in the better absorption efficiency due to more OH^- ion availability for H^+ (from H_2S) absorption reaction. Particularly, the efficiency is over 90% at the pH value of 10.5 which was then selected for the next experiment.

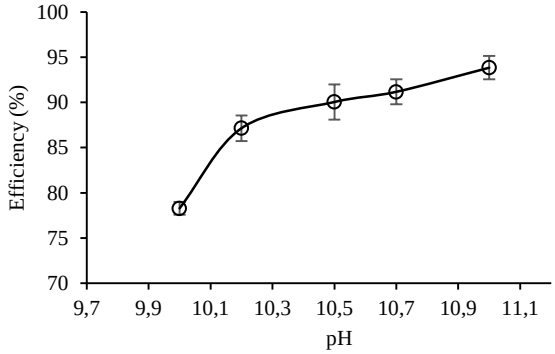

Fig. 4. Effect of initial pH on H_2S removal efficiency (n = 3) (NaOH)

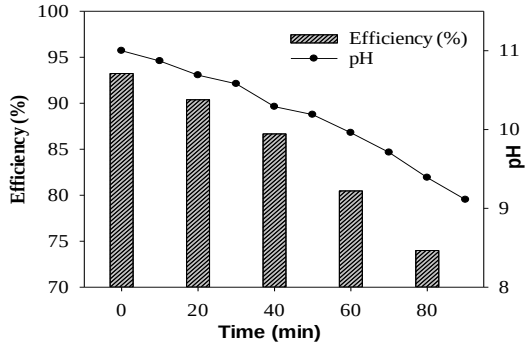

Fig. 5. Change of H_2S removal rate and pH from recycling NaOH solution

To evaluate the effect of recycling absorption solution on pH solution and removal rate, NaOH solution was then prepared at pH 11 and showered in to the top of packed column at flow rate of 0.8 L/min. The solution was collected at the bottom of the column and then recycled again back to the top of the column. pH of the solution and H_2S removal rate were measured after each 10 and 20 min of operation, respectively. As can be seen from Fig. 5, pH of the solution was reduced gradually after recycling of absorption solution because of the increasing of accumulated H^+ amount (from H_2S) by time in the solution. Consequently, H_2S removal rate was also reduced from 93.24 to 73.98%, which is consistent with the above result as the change of initial pH of solution being proportional to the change of H_2S removal rate. One more reason for the reduction of removal rate would be accounted for the increase in S^{2-} (from H_2S) in the recycled NaOH solution which may lead the solution getting near the equilibrium state of NaOH and H_2S reaction.

3.3. Effect of liquid flow rate

Liquid flow rate is an important parameter that affects the efficiency of the packed column. These experiments were carried out with NaOH solution at pH 10.5 and the liquid flow rate was varied from 0.6 to 1.2 L/min. As can be seen from Fig. 6, when the liquid flow rate increased from 0.6 to 1.0 L/min, the wetted surface area of packing increased, which

resulted in the increase of absorption efficiency. However, further increasing of liquid flow rate to 1.2 L/min reduced the efficiency. This could be explained by the excess of liquid causing the uneven distribution of liquid, since we observed that more liquid hold up at the wall of the absorption column compared to the case of lower flow rates. Hence, the flow rate of 1.0 L/min was selected as the optimum value.

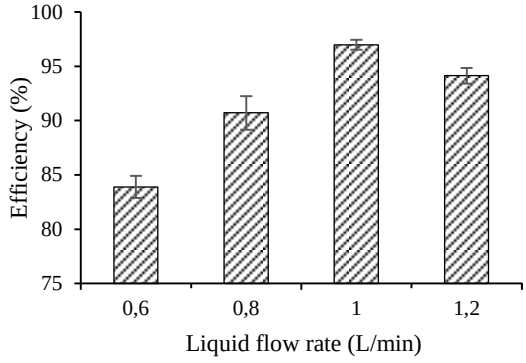

Fig. 6. The change of removal efficiency by liquid flow rate (n = 3)

3.4. Effect of packed column height

The experiments were carried out with the packed column height varied from 1.3-1.6 m, using NaOH solution at pH 10.5 and liquid flow rate of 1.0 L/min. Experiment results show that increasing the packed height led to the increase of removal efficiency (Fig. 7), due to the increasing contact time between liquid and gas stream. At the height of 1.6 m, the removal efficiency was highest at 97%, which is comparable with the result from [26] by using iron(III) chelate, [27] by an iron-chelated solution catalyzed (Fe/EDTA) (i.e. ~ 96%), [28] by Monoethanolamine (i.e. 98%). To achieve the removal efficiency of 90%, the height required was 1.4 m. The mass transfer coefficient was calculated and the enhancement factor (in Eq. 1) in the liquid phase was found to be 367.

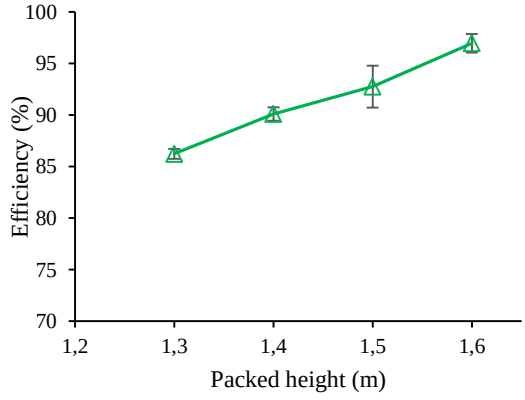

Fig. 7. Effect of packing height on the absorption efficiency (n = 6)

4. CONCLUSIONS

The removal of H_2S by absorption was investigated using water and different alkali and oxidative adsorbing solutions. Results showed that NaOH solution is the most suitable solution for H_2S removal, with the removal efficiency up to 97%. For initial gas concentration of 75 mg/m^3 and the gas flow of 22.4 m^3/h, achieving 90% of H_2S removal efficiency and

H_2S concentration in the effluent met the National Technical Regulation required the absorption process using NaOH at initial solution pH of 10.5, liquid flow rate of 1.0 L/min, and packed column height of 1.4 m. The mass transfer coefficient and enhancement factor calculated in this study can be a good reference for designing the H_2S treatment system. Future works should focus on the recirculation of absorbed solution as well as the use of new and effective packing materials.

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TÓM TẮT

XỬ LÝ H_2S TRONG KHÍ THẢI TỰ TỔNG HỢP BẰNG HẤP THỤ HÓA HỌC TRONG THÁP ĐỆM

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Nghiên cứu này lần đầu tiên so sánh hiệu quả xử lý H_2S bằng phương pháp hấp thụ trong cột đệm sử dụng dung dịch hấp thụ mang tính kiềm (NaOH, $Ca(OH)_2$), oxy hóa (NaOCl, $Ca(OCl)_2$), và nước. Dựa trên kết quả về hiệu quả xử lý, hệ số truyền khối và hệ số tăng cường hấp thụ hóa học tổng quát, NaOH là dung dịch hấp thụ phù hợp nhất để xử lý H_2S so với các dung dịch hấp thụ khác. Do đó, dung dịch NaOH đã được lựa chọn là chất hấp thụ để nghiên cứu tìm điều kiện vận hành tối ưu của pH, lưu lượng dung dịch hấp thụ, và chiều cao cột hấp thụ. Với nồng độ khí ô nhiễm ban đầu 75 mg/m^3, lưu lượng khí đầu vào 22,4 m^3/giờ, và chiều cao lớp vật liệu đệm là 1,4 m, dung dịch NaOH ở pH 10,5 với lưu lượng 1,0 L/phút cho hiệu quả xử lý H_2S đạt 90,1% và nồng độ H_2S trong khí đầu ra đạt tiêu chuẩn cho phép về khí thải công nghiệp (7,5 mg/m^3 trong QCVN 19: 2009/BTNMT). Kết quả thu được của hệ số tăng cường hấp thụ hóa học tổng quát (20,74) từ nghiên cứu này có thể sử dụng cho việc tính toán thiết kế các hệ thống xử lý H_2S ứng dụng trong thực tế.

Từ khóa: H_2S, hấp thụ hóa học, rửa khí, kiểm soát ô nhiễm không khí.