Effectiveness of Hydrogen Peroxide in H$_2$S Removal by a Packed High Specific Surface Area Bed Scrubber

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Removal of H$_2$S from waste air streams was investigated in a chemical scrubber packed with new low-cost and high specific surface area media and in the presence of H$_2$O$_2$ in scrubbing liquid. The experimental conditions included superficial gas velocities of v = 500 and v = 840 m h^{-1}, inlet H$_2$S volume fraction in the range of φ = 50 to 250 · 10^{-6}, scrubbing liquid flow rate ranging from Q_L = 1 to 10 L min^{-1} and liquid phase pH of 7 to 12. The results showed H$_2$S removal efficiencies of η = 97.5 % to more than η = 99 % at liquid flow rate of Q_L = 5 L min^{-1} and pH of 10 to 11. Overall, it was determined that the media tested and H$_2$O$_2$ can be used in scrubbers for efficient H$_2$S removal without the possibility of forming any toxic byproducts.
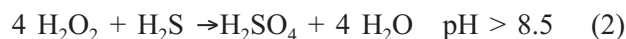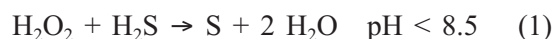
Key words:
Hydrogen sulfide, treatment methods, chemical scrubber, hydrogen peroxide

Introduction

Hydrogen sulfide (H$_2$S) is a toxic, odorous, and corrosive colorless gas that is released to the atmosphere from different industrial processes including petroleum refining, sour gas sweetening, pulp and paper manufacturing, tanning and waste management facilities such as wastewater treatment and composting plants.[1] Chemical scrubbing, physical adsorption, electrochemical treatment, and biofiltration techniques have been used to purify H$_2$S from waste gas streams.[2,3] Chemical scrubbing is among the most popular and successful of these technologies because it is very effective at removing H$_2$S and is flexible with respect to the use of many different scrubbing solutions.[4] The most widely applied oxidant in the scrubbing solutions for the control of odorous compounds has been the various forms of chlorine.[4] However, the use of chlorine has a major drawback of producing chlorinated byproducts such as halomethanes, which are known toxics.[5] To avoid forming these toxic byproducts, research has been focused on finding an efficient surrogate oxidant. Hydrogen peroxide (H$_2$O$_2$), which is the strongest oxidant after O$_3$, has been considered a suitable replacement for chlorine compounds. H$_2$O$_2$ is a very selective and clean oxidant that does not produce toxic and corrosive by-

products.[6] In addition, it is relatively safe to handle and use.

According to eqs. (1) and (2), and depending on the pH of the liquid phase, H$_2$O$_2$ oxidizes H$_2$S to molecular sulfur or sulfate.[2]

$$H_2O_2 + H_2S \rightarrow S + 2\ H_2O \quad pH < 8.5 \quad (1)$$

$$4\ H_2O_2 + H_2S \rightarrow H_2SO_4 + 4\ H_2O \quad pH > 8.5 \quad (2)$$

The aim of this research was to investigate the effectiveness of H$_2$O$_2$ as a surrogate oxidant to chlorine in a packed-bed chemical scrubber reactor packed with low-cost and high specific surface area media for H$_2$S removal.

Materials and methods

Experimental setup and operation procedure

Fig. 1 shows a schematic diagram of the overall experimental setup. A bench scale packed-bed scrubber was constructed from Plexiglas and had a diameter of D = 13.5 cm and a total height of H = 120 cm. The packing materials were low-cost high specific surface area corrugated plastic tube parts. The total bed height and volume of scrubber were D = 70 cm and V = 10 L, respectively. The porosity of the bed was 92 %. The scrubber bed medium had a specific surface area of S = 625 m^2 m^{-3} which was

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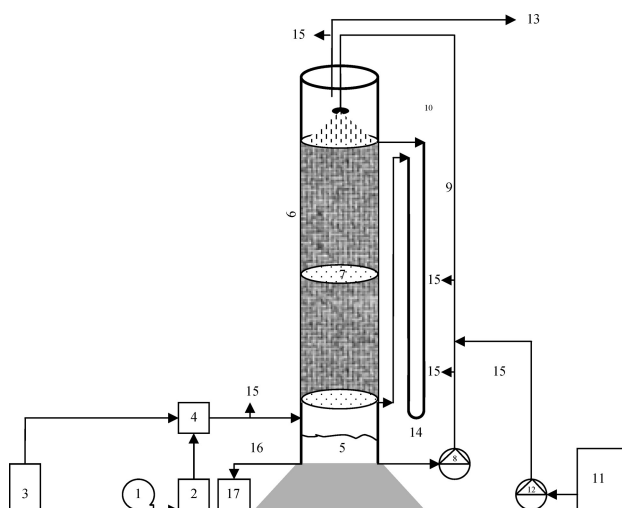
1 – compressor, 2 – GAC column, 3 – H₂S cylinder, 4 – mixer, 5 – recator sump, 6 – scrubber bed, 7 – perforated plate, 8 – recycle liquid pump, 9 – recycle liquid line, 10 – nozzle, 11 – oxidant solution container, 12 – recycle liquid pump, 13 – outlet air line, 14 – monometer, 15 – sampling port, 16 – waste liquid line, 17 – waste liquid container

F i g . 1 – *Schematic drawing of the investigated packed bed scrubber*

much more than that of the media commonly used in scrubbers. Special characteristics of the applied media were low density, low cost, high specific surface area, and corrosion resistance.

The scrubber operated in a counter- current pattern with the polluted air and scrubbing liquid flowing up and downward, respectively. Air was supplied by an air compressor, which was first passed through a GAC column to eliminate the oil and other impurities. The inlet air flow rate to the scrubber was controlled and monitored by a flow meter and the provided valves. Pressure drop across the scrubber bed was determined by a water manometer. A perforated plate, placed in the middle of the bed, helped reduce the channeling of the fluids through the bed.

Contaminated air stream with the desired fraction of H₂S was created by blending the compressed clean air with a concentrated H₂S stream from a custom-made H₂S generator. The generation of H₂S has been described elsewhere.[7] The H₂S-laden gas stream was then passed through the scrubber where H₂S was absorbed in the scrubbing liquid flowing downward and finally oxidized by H₂O₂. The removal of H₂S in the scrubber was monitored by measuring the fractions of H₂S in the inlet and outlet streams.

The section under the bed served as a liquid sump to hold the scrubbing liquid for recirculation. This liquid was recirculated from the sump by a centrifuge pump and sprayed on the top of the bed through a nozzle. The scrubbing liquid for each test

consisted of $V = 5$ L fresh tap water, H₂O₂, and NaOH. A dosing pump (Prominert B0415, GFG) was used to add the oxidant (H₂O₂) and pH buffer (NaOH), at a controlled flow rate. H₂O₂ mass concentration in the spent scrubbing liquid was controlled around $\gamma = 50$ mg L⁻¹ to make sure that enough oxidant was available in the liquid phase for reaction with the absorbed H₂S in the bed. Several pH ranging between 7 and 12 were tested during the investigation to find the optimum pH of the scrubbing liquid for the highest H₂S removal.

Gas contact time in the bed, inlet H₂S fraction, and scrubbing liquid flow rate and pH are generally considered the most important operational factors affecting H₂S removal efficiency. Therefore, the effect of these quantities on the removal of H₂S in the presence of H₂O₂ was investigated. The ranges tested for the selected quantities are, superficial gas velocity between $v = 500$ and 840 m h⁻¹, H₂S fraction from $\varphi = 50$ to $250 \cdot 10^{-6}$, scrubbing liquid velocity from $v = 4$ to 40 m h⁻¹ and scrubbing liquid pH from 7 to 12. Under these conditions, gas contact times in the bed were between $t = 5$ and 3 s and spent liquid retention time in the sump was $t = 5$ to 0.5 min. For each experimental condition, triplicate runs were conducted and the performance of the scrubber at removing H₂S was calculated according to the average value of the experimental data.

Analytical methods

In each experiment, H₂S concentration was measured in samples simultaneously taken from the inlet and outlet sampling ports of the scrubber. H₂S was sampled by aspirating a measured volume of the air through an alkaline suspension of cadmium hydroxide.[8] Sampling set up consisted of two impingers, an air flow meter, an air vacuum pump, tubing, and valves. $V = 50$ mL of alkali absorption solution was pipetted into each impinger. To protect the solution from light effect, the impingers were wrapped up entirely in aluminum foil. Sampling air flow rate was $Q_L = 1$ L min⁻¹ and sampling time was in the range of $t = 5$ to 30 min depending on the H₂S concentration. After sampling, the impinger solutions were analyzed using spectrophotometer (Lambda 25, Perkin Elmer) at the wavelength of $\lambda = 670$ nm.

Samples of the liquid phase were taken from the scrubbing liquid recirculation line to measure H₂O₂, total sulfide, and pH. Liquid pH was determined using a pH meter (E 520, Metrohm Herisau) and sulfide concentration in the spent scrubbing solution was measured by the methylene blue method.[9] H₂O₂ concentration was performed based on the colorimetric titration using potassium permanganate.[10] The amount of H₂O₂ demand per unit

H_2S oxidized was calculated from the H_2S loading, the percent removal of H_2S in the scrubber, and the experiment time.

Results and discussion

The effects of superficial gas velocity, H_2S inlet fraction, scrubbing liquid flow rate, and pH on H_2S removal were investigated in different runs involving H_2O_2 as oxidant in the packed-bed scrubber. As a result, a range of operational conditions was established in which the highest H_2S removal efficiency in the presence of H_2O_2 in the scrubbing liquid was achieved.

Effect of scrubbing liquid pH on H₂S removal

The effect of pH on the H_2S removal efficiency of the scrubber was studied over a range of 7 to 12 and at superficial gas velocities of $v = 500$ and 840 m h^{-1} and H_2S inlet fractions of $\varphi = 50$ and $250 \cdot 10^{-6}$ each. According to eq. (2), the oxidation of H_2S by H_2O_2 in alkaline pH produces sulfuric acid. So, to regulate and control the pH of the liquid phase at a specific value, NaOH solution was injected into the liquid recirculation line. Fig. 2 presents the results of H_2S removal efficiencies vs. pH at the inlet H_2S fraction of $\varphi = 50 \cdot 10^{-6}$. With the pH of the scrubbing solution increasing from 7 to 10, the removal of H_2S increased from about 20 % and 30 % to more than 99 % at the air velocities of $v = 500$ m h^{-1} and 840 m h^{-1}, respectively. With further increase of the pH, the H_2S removal efficiency was unchanged.

Similar experiments were also carried out at high H_2S inlet fraction. Fig. 3 shows the effect of scrubbing liquid pH on H_2S removal efficiency at the inlet fraction of $\varphi = 250 \cdot 10^{-6}$ for the
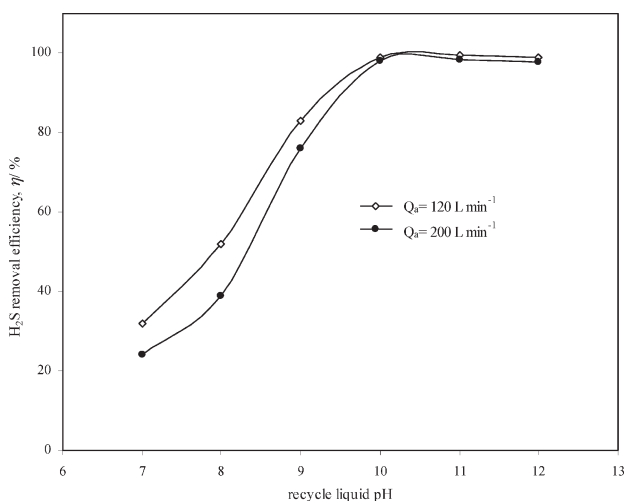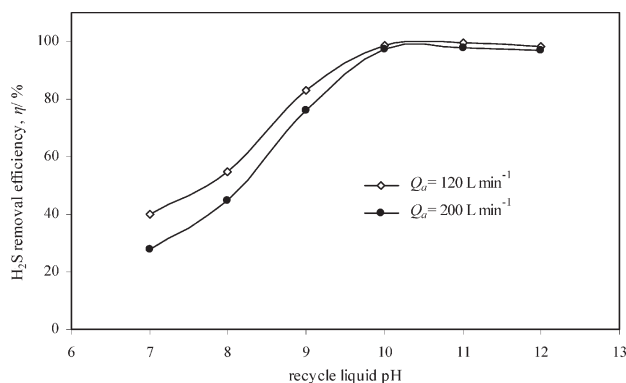
F i g . 3 – *H₂S removal efficiency vs. liquid phase pH at inlet fraction of $\varphi = 250 \cdot 10^{-6}$*

above-mentioned gas velocities. It can be seen that the increase of pH from 7 to 10 resulted in increasing the removal efficiency from $\eta = 38$ % to more than $\eta = 99$ %, and from $\eta = 27$ % to more than $\eta = 99$ % at the superficial gas velocities of $v = 500$ and 840 m h^{-1}, respectively. As with the inlet fraction of $\varphi = 50 \cdot 10^{-6}$ (Fig. 2), when the inlet fraction was $\varphi = 250 \cdot 10^{-6}$, the scrubber performance at both gas velocities was constant at pH greater than 10. Therefore, it is obvious that there is a minimum scrubbing liquid pH below which the H_2S removal efficiency is highly pH-dependent. This behavior can be related to the changes occurring in the percentage of H_2S ionic form in a liquid as function of its pH. The percentage of HS$^-$ increases from around 50 at pH 7 to more than 99.9 in pH 10 which results in the enhancement of the H_2S solubility and so mass transfer between the gas and the liquid phases.

Fig. 3 also indicates that the removal efficiency of H_2S at pH 7 at superficial gas velocity of $v = 840$ m h^{-1} is 11 % lower than that at $v = 500$ m h^{-1}. Comparing Fig. 2 and 3 reveals that inlet H_2S fraction does not affect the removal efficiency at superficial gas velocity of $v = 500$ m h^{-1}, which is corresponding to $t = 5$ s contact time in the scrubber bed. However, the removal efficiency dropped from $\eta = 40$ % to 28 % at the superficial gas velocity of $v = 840$ m h^{-1} when concentration was increased to $\varphi = 250 \cdot 10^{-6}$. This can be due to the decreasing contact time in the bed.

From the results of this part of the study it can be inferred that the pH of the scrubbing liquid plays a vital role in H_2S removal by scrubbers and that the removal efficiency of more than 99 % can be reached at high pH of at least 10. Charron *et al.*[11] have reported H_2S removal efficiency of around $\eta = 97$ % at pH of more than 9 for the scrubbing solution in a chemical scrubber in which H_2O_2 was used as oxidant.[11] Given the results obtained in this research and those from the literature, it can be con-

F i g . 2 – *H₂S removal efficiency vs. pH at inlet fraction of $\varphi = 50 \cdot 10^{-6}$*

cluded that the optimum liquid pH in the scrubber treating H$_2$S in the presence of H$_2$O$_2$ as oxidant is in range of 10 to 11. Therefore, the subsequent experimental runs were carried out with adjusting the pH of scrubbing solution in this optimum range.

Effect of scrubbing liquid flow rate on H$_2$S removal

The selection of the scrubbing liquid conditions is critical in designing an efficient scrubber. In addition to pH, the flow rate is another key parameter for scrubbing liquid, because absorption is directly proportional to the amount of liquid exposed to the gas stream. In this regard, the effect of flow rate of the scrubbing liquid containing H$_2$O$_2$, in range of Q_L = 1 to 10 L min^{-1} at the optimum pH was studied. These flow rates correspond to liquid velocities of v = 4 to 20 m h^{-1} in the scrubber. This step of the study was carried out at two different superficial gas velocities of v = 500 and 840 m h^{-1} and the inlet H$_2$S fractions of φ = 50 and 250 · 10^{-6} for each velocity. Fig. 4 shows the removal efficiency of H$_2$S at two gas velocities of v = 500 and 840 m h^{-1} with φ = 50 · 10^{-6} H$_2$S in the inlet air. The H$_2$S percent removal increased proportionally with the increase of the scrubbing liquid velocity from v = 4 to 20 m h^{-1} in both gas velocities tested. H$_2$S removal efficiency increased from η = 72 % to more than 99 % and from 63 % to more than 99 % at gas velocities of v = 500 and 840 m h^{-1}, respectively. Liquid velocities of greater than v= 20 m h^{-1} did not affect the performance of the scrubber for both superficial gas velocities. These experiments were repeated for the inlet H$_2$S fraction of φ = 250 · 10^{-6} to determine the combined effects of liquid flow rate and fraction on the H$_2$S removal efficiency of the scrubber.

The results shown in Fig. 5 reveal that the H$_2$S removal efficiency had the same trend vs. liquid ve-
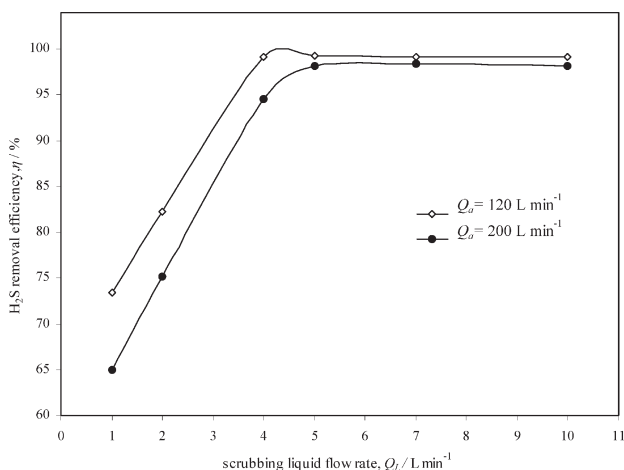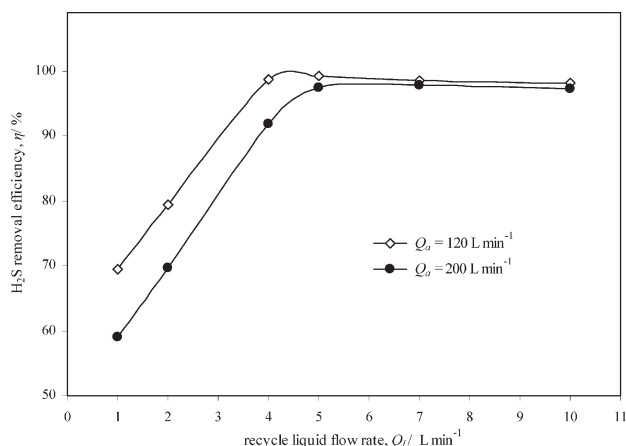

F i g . 5 – *Removal efficiency vs. liquid flow rate at H$_2$S inlet fraction of φ = 250 · 10^{-6}*

locity. That is, the percent removal increased from η = 69 % to around η = 99 % at gas velocity of v = 500 m h^{-1} and from η = 59 % to about η = 99 % at gas velocity of v = 840 m h^{-1}, while scrubbing liquid velocity was increased from v = 4 to 20 m h^{-1}. Therefore, the results indicate that the change in the liquid flow rate had direct effect on the scrubber performance; suggesting that mass transfer resistance in the liquid phase is considerable under these conditions. Wetted surface and thickness of the liquid film on the scrubber packing can be adjusted by manipulating the liquid flow rate to achieve an optimum condition in a scrubber. Nonetheless, H$_2$S removal efficiency for liquid velocities lower than v = 20 m h^{-1} was around η = 10 % lower at gas velocity of v = 840 m h^{-1} than that at v = 500 m h^{-1}. Above v = 20 m h^{-1} liquid linear velocity did not affect the H$_2$S removal efficiency in the scrubber. It is possible that at liquid velocities above v = 20 m h^{-1}, which is the minimum value to achieve high and consistent removal efficiency, the gas to liquid mass transfer limitation due to wetting media ratio has been overcome. According to these findings, efficient scrubbing of H$_2$S, with H$_2$O$_2$ as oxidant, was achieved with minimum scrubbing liquid velocity of v = 20 m h^{-1}.

Some other researchers have also investigated the effect of liquid flow rate on scrubber performance for H$_2$S removal. Charron *et al.*[11] found no real trend between the liquid to gas ratio in the range of 2.3 to 6.2, with respect to the removal efficiency of H$_2$S in a chemical scrubber using H$_2$O$_2$ as the oxidant.[11] Chen *et al.*[12] studied the effect of liquid to gas ratio in the range of 1.25 to 3.75 in a scrubber with NaOCl in liquid phase as oxidant. They concluded that the efficiency of H$_2$S removal was almost constant for the liquid to gas ratios studied.[12]

F i g . 4 – *H$_2$S removal efficiency vs. liquid flow rate at inlet fraction of φ = 50 · 10^{-6}*

Effect of air flow rate and inlet fraction on H$_2$S removal

From the engineering viewpoint, the air flow rate and pollutant concentration, as two main characteristics of waste air streams that are directly linked to pollutant contact time and loading, play critical roles on the reactor performance and thus, reactor sizing and design. On the other hand, H$_2$S removal in an oxidative scrubber is a two-step process where H$_2$S is first absorbed and then oxidized in the liquid phase containing H$_2$O$_2$. So, the air velocity through the bed and the inlet concentration are expected to affect the H$_2$S mass transfer from the gas to the liquid phase, thereby influencing the scrubber performance. In this regard, the effect of superficial gas velocity (air flow rate) and inlet concentration on scrubber performance were investigated by applying two velocities of $v = 500$ and 840 m h^{-1} under optimum conditions of scrubbing liquid and variable inlet H$_2$S fractions ranging from $\varphi = 50 \cdot 10^{-6}$ to $\varphi = 250 \cdot 10^{-6}$.

As shown in Fig. 6, H$_2$S removal efficiency was above $\eta = 99$ % for all the inlet fractions at superficial gas velocity of $v = 500$ m h^{-1}, corresponding to $t = 5$ s contact time in the scrubbing bed. The results indicate that the H$_2$S removal efficiency in the scrubber operating at $t = 5$ s contact time was not affected by the inlet fraction in the range of $\varphi = 50 \cdot 10^{-6}$ to $\varphi = 250 \cdot 10^{-6}$. This high performance was likely due to the use of media with high specific surface area, optimized scrubbing liquid condition, and relatively long retention time of gas in the scrubber bed.

Statistical analysis of the results presented in Fig. 6 reveals that with a confidence limit of 95 %, superficial gas velocity (contact time) and inlet fraction had no significant effect on performance of the scrubber under the operational condit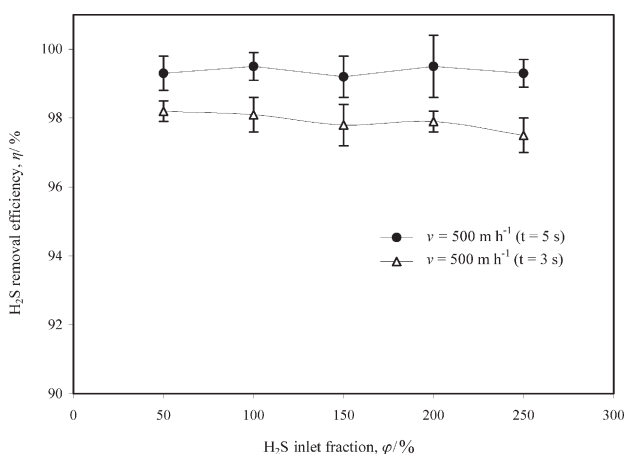ions investigated. Hence, it can be concluded that the scrubber with the tested media can be used for efficient treatment of gas streams containing H$_2$S, achieving a high performance. In addition, increases in H$_2$S removal efficiency with increasing the superficial air velocity and inlet fraction can be interpreted in such a way that mass transfer from gas to the liquid phase is likely an important rate limiting step in the process. Chen *et al.*[12] investigated the effect of gas mass flow rate on H$_2$S removal efficiency at inlet fraction around $\varphi = 200 \cdot 10^{-6}$ in a scrubber using NaOCl as the oxidant. That study showed that the removal efficiency dropped from $\eta = 99.2$ % to 95.1 % when gas mass flux increased from $3.859 \cdot 10^3$ to $1.157 \cdot 10^4$ kg m^{-2} h^{-1}. Charron *et al.*[11] also reported the removal efficiencies in range of $\eta = 89$ % to $\eta = 99$ % in a scrubber using H$_2$O$_2$ at air flow rate of $Q_a = 300$ m^3 h^{-1} and other given conditions.[11] Compared to these reports, the developed scrubber in this study performed better and showed greater efficiency.

The results of sulfide measurement in the spent scrubbing liquid samples taken from recirculation line indicated that sulfide concentration was very low (i.e., undetectable) over the range of experimental runs at the optimum conditions. This observation indicates that all the absorbed H$_2$S was converted to the end product, which is sulfate. Therefore, it can be inferred that liquid retention time of 1 min in the scrubber sump is high enough to oxidize the H$_2$S absorbed. Complete oxidation of H$_2$S in the spent scrubbing liquid before recirculation will overcome the problem of being stripped H$_2$S absorbed in the recycle liquid to the outlet, otherwise removal efficiency will decrease.

Contribution of dissolved oxygen in oxidation and consumption of H$_2$O$_2$

Oxygen is an oxidant with the redox potential of +0.28.[13] As the air passes through the column, oxygen is dissolved into the scrubbing liquid. Hence, the dissolved oxygen (DO) may oxidize the sulfide in the liquid phase. To determine the contribution of DO in sulfide oxidation, a set of batch experiments was performed without H$_2$O$_2$ in the liquid phase that was saturated with oxygen. The result indicated that DO could only remove less than 5 % of the sulfide after $t = 60$ min reaction time in alkaline pH. Since, the contact time of the contaminated air in the scrubbers is much lower than this time; one can conclude that the DO has no significant contribution in sulfide oxidation in this experimental condition.

The consumption of H$_2$O$_2$ during the H$_2$S elimination was measured for the optimum operational conditions, i.e., air flow rate of $Q_a = 200$ L min^{-1}, liquid flow rate of $Q_L = 5$ L min^{-1}; pH 10 for the

F i g . 6 – *Removal efficiency vs. H$_2$S inlet fraction at two different superficial air velocities*

scrubbing liquid, and inlet H$_2$S fraction of φ = 100 · 10^{-6}. The measurements data showed that 4.9 mole H$_2$O$_2$ was consumed per mole of oxidized H$_2$S. Despite being greater than the stoichiometric value (eq. (2)), this is close to what is reported in the literature by Couvert *et al.*[14]

Conclusion

An experimental study was conducted on the effectiveness of H$_2$O$_2$ as an oxidant for the removal of H$_2$S in a chemical scrubber with a new packing medium. The results have demonstrated that the H$_2$O$_2$ in the packed bed scrubber successfully treated the air containing H$_2$S in range of φ = 50 to 250 · 10^{-6} at bed contact time of t = 3 s, with removal efficiencies between η = 97.5 % and more than η = 99 %. To achieve this high performance in the scrubber, minimum liquid flow rate and pH were Q_L = 5 L min^{-1} and 10, respectively. The most important advantages of this chemical scrubber are high removal efficiency, no production of toxic by-products, and efficient low cost media. H$_2$O$_2$ is an oxidant as effective as NaOCl, with the advantage of being much safer and more environmentally friendly for application in scrubbers for H$_2$S removal. In addition, corrugated tube parts are very efficient media to increase contact surface of the gas and liquid phases where packed into scrubbers.

List of symbols

D – diameter, cm

H – height, cm

Q_a – volume air flow rate, L min^{-1}

Q_L – volume liquid flow rate, L min^{-1}

S – specific surface area, m^2 m^{-3}

t – time, s

v – superficial gas velocity, m h^{-1}

V – volume, L

η – efficiency, %

λ – wavelength, nm

φ – volume fraction, 10^{-6}

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