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Research Article

Preparation of activated red mud and its application for removal of hydrogen sulfide in air

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ABSTRACT

Red mud is a highly alkaline solid waste from the Bayer process for aluminum production. Red mud reservoirs are usually considered as a potential environmental risk. The treatment of red mud is costly due to the lack of an effective and economical treatment technology. On the other hand, the main components of red mud are Fe_2O_3, Al_2O_3, SiO_2, and Na_2O, which could be employed as a promising precursor for the preparation of various nanomaterials. In this study, we prepared activated red mud by thermal and acid treatment method and applied it for adsorption of H_2S in air. The red mud was activated under different temperatures (i.e., 200, 400, 600, and 800 ^oC for 4 h), types of acid (i.e., H_2SO_4 and HCl), and acid concentrations (i.e., 0.5, 1.5, and 2.5 M). The produced materials were then applied for H_2S removal in air with concentration of 90 – 110 mg/m^3 using a fix-bed adsorption column test. Results showed that red mud activated at 800 ^oC and with 1.5 M H_2SO_4 solution had the highest adsorption capacity of 29.38 mg/g with an average removal efficiency of 80.2%. The effects of gas flow rate and initial H_2S concentration were also investigated, and the highest removal capacity was achieved at an inlet concentration of 100 mg/m^3 and flow rate of 1 L/min. Both Langmuir and Freundlich adsorption isotherms were employed for modelling the H_2S adsorption by this material and the experimental result was more fitted with the Langmuir isotherm. The thermal desorption and recyclability test were also conducted for evaluating the practical application of activated red mud material and 200 ^oC was the suggested desorption temperature with 81.7% adsorption capacity recovery.

Key words: red mud, hydrogen sulfide, adsorption, air pollution control

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INTRODUCTION

Hydrogen sulfide (H_2S) is a toxic and colorless gas with a very unpleasant odor that originated from both nature and human activities. It greatly affects the air quality and also causes the corrosion of equipment and pipes[1]. H_2S is a common pollution gas in industry, biogas, coal storage, and in the processes that release odor such as sewage systems, wastewater treatment, and solid waste composting[2]. Air pollution due to H_2S gas is a problem that has been mentioned in lots of documents and research works[3]. For H_2S treatment, many methods were studied and applied such as absorption, oxidation, and biofiltration[4]. Among them, adsorption is considered as a simple but effective method. Therefore, finding a new, effective, and inexpensive adsorbent for H_2S removal is of interest.

On the other hand, red mud is a highly alkaline solid waste with pH from 10 – 12 from the Bayer process for aluminum production[5,6], which requires a large amount of NaOH[7]. It comprises very fine-grained particles with a size of < 10 μm and a specific surface area of about 10 - 30 m^2/g[8]. The main components of red mud are Fe_2O_3, Al_2O_3, SiO_2, and Na_2O. Many studies showed that red mud has a good adsorption capacity, particularly when activated by acid, heat, or combining activation with other metal oxides[9–13]. Currently, the research of using red mud to adsorb H_2S emission is still limited[14]. Therefore, in this study, we aimed to collect red mud from Tan Rai bauxite plant and then activate it by acid and thermal treatment for H_2S adsorption. Besides, other factors were also investigated such as flow rate and input concentration as well as the absorption and reuse of the adsorbent.

MATERIALS AND METHODS

According to the study of Minh[15], the pH of raw red mud from Tan Rai bauxite plant was very high at pH 11.5. Their X-ray diffraction analysis showed that the phase composition of raw red mud is mainly gibbsite (Gi) γ-Al(OH)$_3$, goethite (Go) α-FeOOH, and hematite (He) α-Fe_2O_3[15]. The elemental composition of red mud includes Fe, Al, O, Na, C, Si, Ca, Ti,

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and S with a weight percentage of 18.00, 6.85, 55.21, 7.62, 8.37, 2.42, 0.21, 1.00, and 0.32 %, respectively.

The collected dry red mud was firstly ground and sieved to the size of 0.097 - 0.450 mm. The material was then calcined at different temperatures of 200, 400, 600, and 800 ^oC for 4 h. Calcined red mud was subsequently activated with H_2SO_4 or HCl solutions at different concentrations of 0.5, 1.5, and 2.5 M according to a process published in the literature[16,17]. The produced materials were denoted as RMXC-Y (activated by HCl) and RMXS-Y (activated by H_2SO_4) where X represents the calcined temperature (e.g., X = 4 for 400 ^oC) and Y is the concentration of acid. In this study, commercial activated carbon (AC) with a size of 0.097 - 0.45 mm was also prepared and employed as reference material.

The schematic for the H_2S adsorption test is illustrated in Figure 1. H_2S gas is generated by slowly adding of H_2SO_4 solution to a reactor containing Na_2S solution. The generated gas with a flow rate of 0.05 - 0.20 L/min was then mixed with clean air to reach the desire H_2S concentration before passing through the adsorption column with an internal diameter of 16 mm made of acrylic material. A glass wool ball was employed to support an adsorbent layer of 15 - 25 mm height. The superficial airflow velocity in the column was calculated to be about 0.2 m/s and the flow was controlled in the range of 1.0 - 3.0 L/min depending on the experiments. H_2S gas in the inlet and outlet was sampled and analyzed according to TCN 676 – 2006 (hydrogen sulfide determination process in the air at cattle farm of Ministry of Agriculture and Rural Development, Viet Nam), which are referenced from Methods of air sampling and analysis[18]. The sampling device included two impingers connected sequentially to sample H_2S gas for analysis and concentration determination. Most of the experiments were conducted three times, and the average values and errors are presented in the results.

RESULTS AND DISCUSSION

Adsorption test

The adsorption tests were conducted with 29 different materials, including activated carbon, thermal activated red mud, and acid activated red mud. The H_2S concentration was in range of 90 – 110 mg/m^3 and 3 g of adsorbent was used. The results are presented in Figure 2.

As seen in Figure 2, the adsorption capacity of most adsorbents derived from red mud was higher than that of AC except for RM2, RM2C-0.5, and RM4 materials. It is also obvious that the adsorption capacity of the thermally treated materials is proportional to their activation temperature. Under high temperature, there was a phase transformation of red mud component (e.g., goethite to hematite) and the join of aluminum into the material lattice to form Al-hematite[15], which acts as internal adsorption sites. In addition, since water is removed from the material at the high temperatures, the pore system is enhanced, and the material surface area could be improved.

For acid-activated red mud, it is reported that the specific surface area of material increases while the particle size tends to decrease with the acid concentration[15]. Therefore, the adsorption capacity also increases with the increases of acid concentration in a certain range but then decreases due to the material structure disruption under high acidic treatment condition. Besides, H_2SO_4 was proved to be more effective than HCl for activating of red mud in terms of H_2S adsorption, possibly due to the higher volatility of HCl than H_2SO_4. Among all materials, RM8S-1.5 had the highest H_2S adsorption capacity of 29.38 mg/g, which was about 1.4 times better than that reported by Sahu *et al.*[14].

Isotherm study

RM8S-1.5 material was then chosen for isotherm study with input H_2S concentration from 40 to 120 mg/m^3. As seen in Figure 3, the adsorption capacity increases when input H_2S concentration increases from 40 to 100 mg/m^3 but then decreased with a further increase of input concentrations from 100 to 120 mg/m^3.

Langmuir and Freundlich adsorption isotherm models were established to determine the parameters of H_2S adsorption by RM8S-1.5. As summarized in Table 1, the adsorption of H_2S on RM8S-1.5 is more fitted with Langmuir (R^2 = 0.906) than with the Freundlich isotherm adsorption model (R^2 = 0.781). This implied that the adsorption of H_2S on RM8S-1.5 not only physical adsorption by electrostatic attraction but also chemical interaction of H_2S and oxides of iron and aluminum formed after calcined at a high temperature of 800 ^oC. The maximum adsorption capacity was calculated to be 36.68 mg/g.

To evaluate if an adsorption process is fitted with the single-layer adsorption model described by Langmuir equation, it is required to be evaluated through equilibrium parameter R_L[17], as expressed in Equation (1). Results from Table 2 with $R_L < 1$ confirmed the suitability of the Langmuir isotherm model for H_2S adsorption by RM8S-1.5 in this input concentration range.

$$R_L = \frac{1}{1+K_L C_O} \quad (1)$$

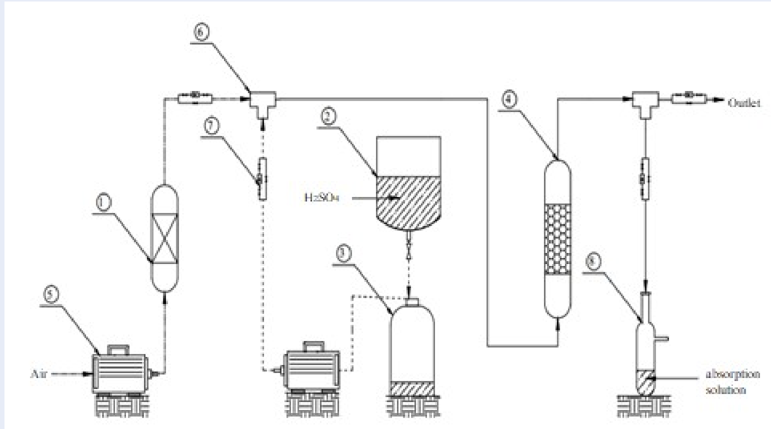

Figure 1: Schematicfor H_2S adsorption test Diagram of research model: (1) preliminarytreatment, (2) H_2SO_4 tank, (3) Na_2S tank, (4) adsorption column, (5) air pump, (6) tee, (7) flowmeter, (8) impinger

Table 1: Parameters of frendlich and langmuir isotherms

Freundlich isotherm		
n	Kf $(mg/g)/(mg/m^3)^{1/n}$	R^2
0.392	4.427	0.782
Langmuir isotherm		
a_{max}(mg/g)	KL(m^3/mg)	R^2
36.68	0.0270	0.906

Table 2: Value of R_L with different concentrations

C_o	45.13	63.78	85.74	105.71	126.16
R_L	0.45	0.37	0.30	0.26	0.23

Where K_L is the mass transfer coefficient according to the Langmuir equation and C_o is input concentration.

Influence of input flow rate

This experiment was carried out with the flow rate in a range of 1.0 - 3.0 L/min and an input concentration of 100 - 110 mg/m^3. Obviously, the adsorption capacity continuously decreased from 30.49 mg/g to 16.58 mg/g with an increase of flow rate from 1.0 to 3.0 L/min (Figure 4). This is because of the decrease of contact time between H_2S and adsorbent with the increase of gas flow rate, which leads to the low H_2S adsorption on the surface of RM8S-1.5 material.

Regeneration of adsorbent

The recycle test was also conducted to investigate the effect of the desorption process on the sorption capacity of RM8S-1.5 material. The desorption process was carried out by drying saturated RM8S-1.5 samples at 200 and 400 ^oC for 20 min. After desorption, the material was cooled and then reused for adsorption. As presented in Figure 5, the capacity of the regenerated materials was lower than the original one although still at high levels. The adsorption capacity of material regenerated at 400 ^oC was higher than that at 200 ^oC. However, the difference was not much since capacity increased only from 24.0 to 26.9 mg/g as compared to double temperature with higher energy consumption.

CONCLUSION

Adsorbents from red mud were successfully synthesized and applied for H_2S adsorption. Results showed that adsorption capacity increased with the increase of calcination temperature and H_2SO_4 was better than HCl for red mud activation. The highest adsorption capacity of 30.49 mg/g was achieved at input concentration of 100 mg/m^3 and flow rate of 1 L/min using red mud calcined at 800 ^oC and activated with 1.5

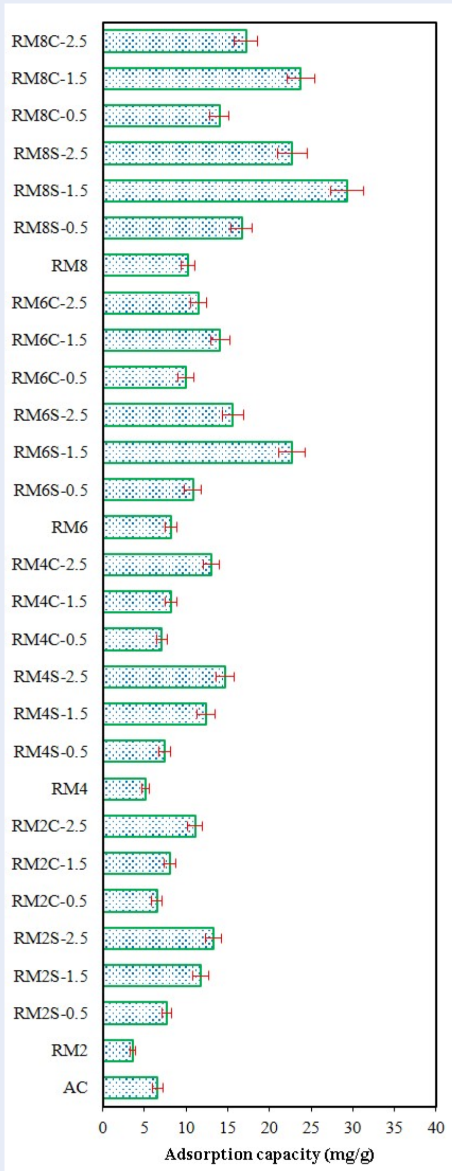

Figure 2: H_2S adsorption capacity of different materials

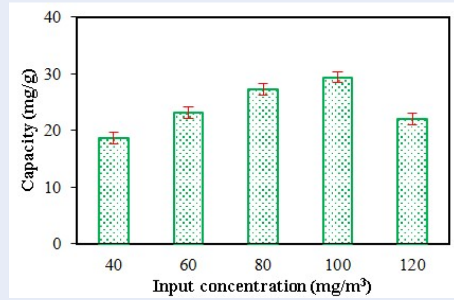

Figure 3: Adsorption capacity of RM8S-1.5 at different input concentrations

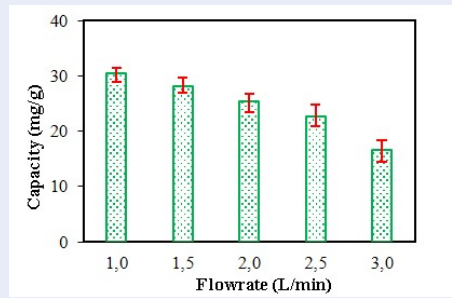

Figure 4: Adsorption capacity of RM8S-1.5 with different gas flow rates

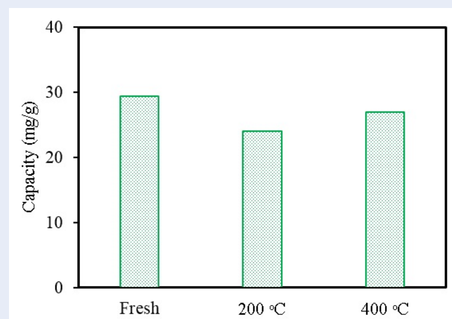

Figure 5: H_2S adsorptionresult of RM8S-1.5 material after desorption at different temperatures

M H_2SO_4 solution. The adsorption process follows Langmuir (R^2 = 0.906) rather than the Freundlich adsorption model. Moreover, the material can be regenerated by thermal treatment at 200 ^oC with 81.7% capacity. These results suggest a potential use of activated red mud for H_2S and maybe other gases treatment.

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ABBREVIATION

AC: activated carbon
RM: red mud
RMX: red mud activated at X00 ^oC
RMXC-Y: red mud activated at X00 ^oC and by HCl with concentration of Y (M)
RMXS-Y: red mud activated at X00 ^oC and by H_2SO_4 with concentration of Y (M)

CONFLICT OF INTEREST

There is no conflict of interest regarding this manuscript.

AUTHOR CONTRIBUTION

Lam Pham Thanh Hien helped with funding, planed the experiment, and prepared the draft manuscript.
Le Truong Anh Huy, Pham Dan Thanh, Le Nguyen Dang Khoa, Bui Khanh Le, Le Thi Kieu Thi, Vo Thi Thanh Thuy did the experiment, collected, and composed data.
Nguyen Nhat Huy outlined the research, prepared the figures, and completed the manuscript.

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Bài Nghiên cứu

Nghiên cứu chế tạo vật liệu bùn đỏ hoạt hóa ứng dụng hấp phụ H_2S trong khí thải

Lâm Phạm Thanh Hiền[1,2], Lê Trường Anh Huy[1,2], Phạm Đan Thanh[1,2], Lê Nguyễn Đăng Khoa[1,2], Bùi Khánh Lê[1,2], Lê Thị Kiều Thi[1,2], Võ Thị Thanh Thùy[1,2], Nguyễn Nhật Huy[1,2,*]

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TÓM TẮT

Bùn đỏ là một loại chất thải rắn có tính kiềm cao phát sinh từ quá trình sản xuất nhôm từ quy trình Bayer. Các hồ chứa bùn đỏ thường được xem là rủi ro môi trường tiềm tàng. Việc xử lý bùn đỏ khá tốn kém do chưa có một công nghệ hiệu quả và kinh tế. Mặt khác, thành phần chính của bùn đỏ bao gồm Fe_2O_3, Al_2O_3, SiO_2, và Na_2O có thể sử dụng như những tiền chất để chế tạo các loại vật liệu nanao. Nghiên cứu này được thực hiện nhằm đánh giá khả năng hoạt hóa bùn đỏ và ứng dụng để xử lý chất ô nhiễm H_2S trong khí thải. Bùn đỏ được hoạt hóa ở các nhiệt độ khác nhau, với các loại axít khác nhau và ở các nồng độ khác nhau. Bùn đỏ hoạt hóa sau đó được sử dụng để hấp phụ khí thải H_2S trong không khí với nồng độ từ 90 đến 110 mg/m^3 sử dụng cột hấp phụ tầng tĩnh. Kết quả cho thấy bùn đỏ hoạt hóa ở 800 ºC sử dụng axít H_2SO_4 ở nồng độ 1,5 M cho hiệu quả xử lý H_2S cao nhất. Hiệu suất hấp phụ trung bình ở mức 80,2 % và dung lượng hấp phụ đạt đến 29,38 mgH_2S/g bùn đỏ hoạt hóa. Ảnh hưởng của lưu lượng dòng khí và nồng độ đầu vào lên quá trình hấp phụ cũng được khảo sát và kết quả chỉ ra rằng hiệu suất hấp phụ cao nhất ở nồng độ H_2S đầu vào 100 mg/m^3 và lưu lượng 1 L/phút. Mô hình hấp phụ đẳng nhiệt Langmuir và Freundlich đã được áp dụng để mô tả quá trình hấp phụ và kết quả thực nghiệm cho thấy quá trình hấp phụ H_2S sử dụng bùn đỏ hoạt hóa phù hợp hơn với mô hình Langmuir. Thí nghiệm giải hấp và độ bền vật liệu cũng đã được thực hiện để đánh giá khả năng ứng dụng thực tế của vật liệu bùn đỏ hoạt hóa và nhiệt độ giải hấp được đề xuất ở 200 ^{o}C tương ứng với khả năng hấp phụ đạt 81.7% dung lượng hấp phụ ban đầu.

Từ khoá: Bùn đỏ, hydro sulfua, hấp phụ, xử lý khí thải

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