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EFFECTIVE IMPROVEMENT OF HYDROGEN SULFIDE ADSORPTION FROM BIOGAS BY MEANS OF WATER TREATMENT SLUDGE AFTER ITS ZINC MODIFICATION

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Abstract

In this study, waste sludge from different water treatment plants in Ho Chi Minh City, Vietnam, was used as adsorbents for H₂S filtration in biogas. The results of the experimental process showed that the sludge calcined at 200 °C then modified with Zn(NO₃)₂·6H₂O could reach an H₂S adsorption capacity of 235.54 mg/g with operating conditions at 1775±169 ppm of H₂S inlet concentration, 5 g of adsorbent, and 1 L/min of flow rate. Under the best conditions, the maximum adsorption capacity estimated by the Langmuir adsorption isotherm model can be up to 333.30 mg/g. Brunauer-Emmett-Teller method, X-ray diffraction, Fourier transform infrared spectroscopy, and scanning electron microscopy and energy-dispersive X-ray spectroscopy were the techniques used to determine material characteristics before and after adsorption. These results prove that sludge from wastewater treatment plants is a potential resource for the production of cheap but effective materials for environmental treatment.

Keywords: biogas; H₂S adsorption; utilizing solid waste; water treatment sludge.

ЕФЕКТИВНЕ ПОКРАЩЕННЯ АДСОРБЦІЇ СІРКОВОДНЮ З БІОГАЗУ ЗА ДОПОМОГОЮ ОСАДУ ВОДОПІДГОТОВКИ ПІСЛЯ ЙОГО МОДИФІКАЦІЇ ЦИНКОМ

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Анотація

У цьому дослідженні відпрацьований мул з різних водоочисних станцій міста Хошимін, В'єтнам, використовувався як адсорбент для фільтрації H₂S в біогазі. Результати експериментального процесу показали, що мул, прожарений при 200 °C, а потім модифікований Zn(NO₃)₂·6H₂O, може досягти адсорбційної здатності H₂S 235.54 мг/г за умов експлуатації при концентрації H₂S на вході 1775±169 ppm, 5 г адсорбенту і швидкості потоку 1 л/хв. За найкращих умов максимальна адсорбційна ємність, розрахована за моделлю ізотерми адсорбції Ленгмюра, може становити до 333.30 мг/г. Для визначення характеристик матеріалу до і після адсорбції використовували метод Брунауера-Еммета-Теллера, рентгенівську дифракцію, інфрачервону спектроскопію з перетворенням Фур'є, а також растрову електронну мікроскопію та енергодисперсійну рентгенівську спектроскопію. Отримані результати доводять, що осад очисних споруд є потенційним ресурсом для виробництва дешевих, але ефективних матеріалів для очищення довкілля.

Ключові слова: біогаз; адсорбція H₂S; утилізація твердих відходів; мул водоочищення.

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Introduction

Biogas is a source of biological energy widely used as an alternative to natural gas in life and industry. The wastes from agricultural activities provide raw materials for the biogas production process, and the generated gas can be used directly in households. On an industrial scale, biogas from anaerobic digestion can be used as a fuel for electricity generators to help reduce production costs and greenhouse gas emissions. However, the heat generated when burning 1 m³ of raw biogas is about 21.5 MJ, which is 1.67 times lower than the heat of 1 m³ of pure CH₄. This is because raw biogas contains impurities other than CH₄ such as CO₂, H₂, O₂, H₂S, and NH₃. In which, H₂S is the main cause of the odor (bad smell of H₂S) and air pollution (SO₂ from the combustion process). The concentration of H₂S in biogas depends on many factors (e.g., anaerobic technology, raw organic material, and capacity of digester), in the range of 50 to 5000 ppm or up to 20000 ppm [1]. In addition, the presence of H₂S also causes pipeline corrosion, thus reducing the lifetime of equipment and structures. Moreover, H₂S is also a toxic gas and has an unpleasant odor that directly affects health and can lead to death when exposed to high concentrations.

On the other hand, the sludge generated from the supply water treatment process (water treatment sludge, WTS) with large discharge into the environment is a big challenge for management and treatment. This discharge is usually higher on days when the treatment plant discharges sludge from the settling tank. With a diverse composition of metal elements (i.e. Fe, Al, Cu, Zn,...)[2-5], WTS can be utilized for many different purposes, especially as H₂S adsorbent [3, 4] or phosphorus adsorption [5]. Iron is an element that often occurs in highly efficient H₂S adsorbents since Fe²⁺ can react directly with H₂S to produce FeS (black) or can act as a catalyst to oxidize sulfide (S²⁻) to elemental sulfur (S⁰) [6]. The utilization of sewage sludge and WTS for H₂S adsorption has been reported in many studies. The alum sludge modified at different temperatures gave different H₂S treatment capacities. In which, the best H₂S filtration capacity belongs to the sludge calcined at 300 °C [3]. The addition of iron significantly improved the treatment capacity of WTS as demonstrated in the study of Polruang, Banjerdikij [4] with an adsorption capacity of 105.22 mgH₂S/g. Ren, Lyczko [7] suggested that the metal mineral composition, microporous structure, and alkaline pH in the waterworks residue promote H₂S

adsorption due to the formation of metal sulfate species. Iron-based catalysts calcined at 500 °C derived from sludge were developed for efficient H₂S oxidation [8]. Optimization with 2 M NaOH further enhanced catalytic activity, attributed to improved surface properties, higher Fe³⁺ content, and increased oxygen vacancies.

In this study, WTS from different supply water plants were collected, modified, and applied for H₂S adsorption. The influences of H₂S concentration and the amount of adsorbent were investigated. In addition, the possibility of material regeneration by heating was also studied. A comparative experiment with commercial adsorbents was also conducted to form the basis for the material development in further studies.

Materials and Methods

Materials

The chemicals used in the experiments are sourced from China and are highly purified. The WTS used in this study was collected from water supply plants in Ho Chi Minh City, Vietnam (i.e., Tan Hiep, Thu Duc, Tan Phu, and BOO Thu Duc). The raw sludge was dried at 105 °C, ground, and sieved to the desired size (0.105–2 mm) as shown in Fig. 1. After that, the WTS was modified with HCl, H₃PO₄, NaHCO₃, Zn(NO₃)₂·6H₂O, and Mg(NO₃)₂·6H₂O. The modification process was based on previous publications [9-11] with some changes to adapt it to the actual conditions. Chemicals and abbreviated names of the modified materials are summarized in Table 1, where WTS can be replaced by TH, TD, TP, and BOO representing sludge from the water treatment plants of Tan Hiep, Thu Duc, Tan Phu, and BOO Thu Duc, respectively. The acid-modified WTS was prepared by mixing 1 g of WTS with 1 mL of acid solution (commercial concentration), which was then stirred for 30 min, filtered and washed with distilled water to pH 7, and finally dried at 105 °C for 24 h. The impregnation of WTS with NaHCO₃ was conducted by mixing 3 g WTS with 33 mL of 1 M NaHCO₃ solution, stirring and aeration for 30 min (2 L/min), then filtering and washing with distilled water to pH 7, and drying at 105 °C for 24 h. Regarding the modification of WTS by metal ions, 10 g WTS was added to 200 mL of 0.25 M salt solution, which was then added with 800 mL of distilled water. Next, the pH was adjusted to 11 by 30 % NH₄OH solution and the solution was ultrasonically treated for 1 h. Subsequently, the material was filtered and washed with distilled water to pH 7 and dried at 105 °C for 12 h. The modified WTS with

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were denoted as Mg/WTS and Zn/WTS, respectively. In addition, Zn/TP materials were also selected to investigate the effect of thermal treatment (e.g., calcined at 200 °C for 6 h). The order of thermal treatment in

material modification is also of interest as we compare two materials of 200 °C-calcined TP sludge + modified with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (200-Zn/TP) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ -modified TP sludge + calcined at 200 °C (Zn/TP-200).



Fig. 1. WTS before modification

Table 1

Abbreviation of modified adsorbents				
Adsorbent*	Ratio adsorbent:chemical	Chemical	Reference	
WTS-HCl	1 g : 1 mL (commercial solution)	HCl	HCl	[9]
WTS-H ₃ PO ₄			H ₃ PO ₄	
WTS-NaHCO ₃	3 g : 33 mL (solution, 1 M)	NaHCO ₃	NaHCO ₃	[10]
Zn/WTS	10 g : 200 mL (solution, 0.25 M)		$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	[11]
Mg/WTS			$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	

*WTS can be replaced by TH, TD, TP, and BOO representing sludge from Tan Hiep, Thu Duc, Tan Phu, and BOO Thu Duc water treatment plants, respectively.

The material properties such as surface area, crystalline structure, surface functional groups, morphology, and elemental composition were determined by the Brunauer-Emmett-Teller method (BET, Nova 4000E, Quantachrome, USA), X-ray diffraction (XRD, D2 Phaser, Bruker), Fourier transform infrared spectroscopy (FTIR, Tensor 27, Bruker), and scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDX, JSM-IT200, JEOL), respectively.

H₂S adsorption experiment

The H₂S adsorption experiment was set up as shown in Fig. 2. The concentrated H₂S stream was

formed by the reaction between $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 10 % H_2SO_4 solution (Flow 1). A stabilizer was arranged to make it easier to control the gas flow concentration. Flow 2 is the air that is pumped to the air tee and mixed with Flow 1. The gas flow rate was controlled by the flowmeter so that the total treatment flow was kept constant during the tests. The adsorbent was placed in a 26 mm diameter mica tube and the gas flows through the adsorbent layer in the top-down direction. Gaseous H₂S was analyzed by absorption spectroscopy at 670 nm according to Vietnam standard (10 TCN 676-2006 – Ministry of Agriculture and Rural Development).

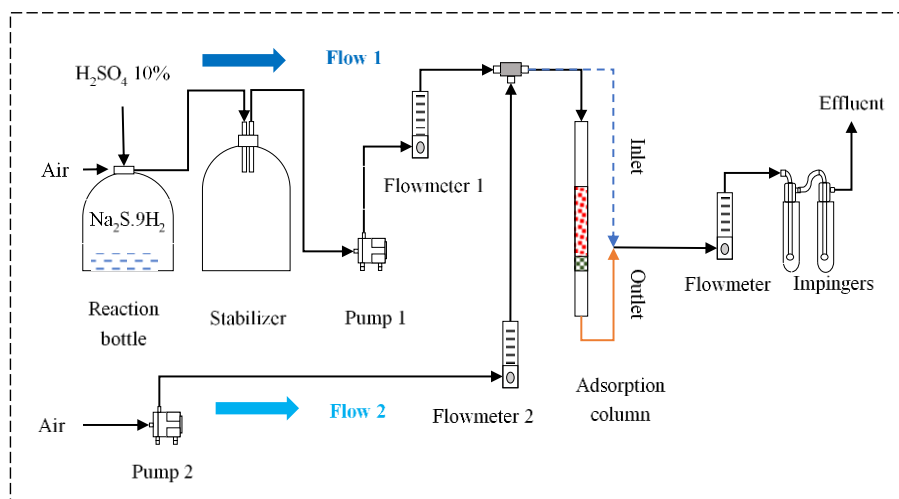


Fig. 2. H₂S adsorption experiment system

The experiments were conducted as shown in Fig. 3, and the H₂S removal efficiency was recorded when changing the adsorbent, adsorbent amount (2.5, 5, 7.5, and 10 g), and initial concentration (1000, 1500, 2000, 2500, and 3000 ppm) with 1 L/min of flowrate. The H₂S removal efficiency (RE, %) was calculated by Equation 1, where C_{in} and C_{out} are the H₂S inlet and outlet concentrations, respectively.

$$RE = \left(1 - \frac{C_{out}}{C_{in}}\right) \times 100 \% \quad (1)$$

Langmuir and Freundlich isotherm models were applied to determine the adsorption parameters for the H₂S adsorption process

(Equations 2 and 3). Where $C = C_{in}$ is the H₂S initial concentration (mg/m³). a and a_{max} are the capacity and its maximum value (mg/g), and K_L , K_F , and n are the adsorption constants ($0 < n < 1$).

$$\frac{C}{a} = \frac{1}{a_{max}} \left(\frac{1}{K_L} + C \right) \quad (2)$$

$$\ln a = \ln K_F + n \times \ln C \quad (3)$$

The reusability of the material was also investigated using a desorption experiment. The material after the first adsorption was desorbed by heating for 2 h at different temperatures (200, 300, and 400 °C) and by blowing air over the material layer for 4 h at a gas flow rate of 2 L/min.

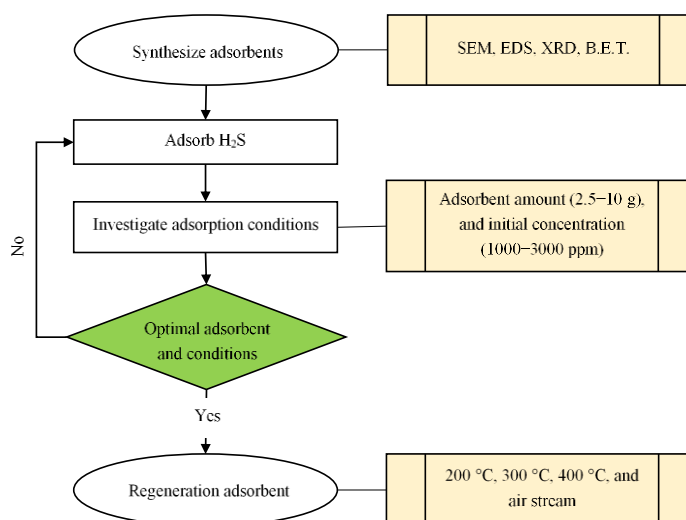


Fig. 3. Research experiment diagram

Results and Discussion

Effect of adsorbent

The adsorbent is a key factor in the adsorption process and the H₂S removal efficiency of different adsorbents was first investigated. As shown in Fig. 4, the adsorption capacity depended on the raw sludge origin and the modification method, in which, the acid modification proved ineffective when the capacity fluctuated in the range of 3.9–10.6 mg/g with WTS-HCl and 9.3–19.4 mg/g with WTS-H₃PO₄. Actually, the use of acid can dissolve the mineral components in the raw sludges, thus helping to strengthen the porous structure of the material and increasing the surface area. However, the acid solution can strongly reduce the adsorption efficiency of the adsorbent by reacting with metal elements to lose the metal adsorption centers and reacting with available alkaline elements to reduce the efficiency of acid gas such as H₂S.

The WTS-NaHCO₃ had a higher H₂S adsorption capacity than WTS-HCl and WTS-H₃PO₄ for the sludge from the Tan Phu Plant and Thu Duc Plant.

Specifically, for the sludge from Tan Phu Plant, the adsorption capacity of TP-NaHCO₃, TP-HCl, and TP-H₃PO₄ were 61.8, 10.6, and 17.7 mg/g, respectively. For the sludge from Thu Duc Plant, the values were 47.8, 6.2, and 9.3 mg/g, respectively. Thus, for these two plants, modification with acid and bicarbonate resulted in adsorption capacities in the order of WTS-NaHCO₃ > WTS-H₃PO₄ > WTS-HCl. Meanwhile, for sludge samples from BOO Plant and Tan Hiep Plant, modification with H₃PO₄ yielded better results than NaHCO₃, but the difference was not significant. The adsorption capacities of BOO/TH-NaHCO₃, BOO/TH-HCl, and BOO/TH-H₃PO₄ were 3.5/4.3, 19.4/9.0, and 3.9/3.5 mg/g, with the order of WTS-H₃PO₄ > WTS-NaHCO₃ > WTS-HCl. This difference may be due to the different elemental compositions (high density) of these sludge types. Tan Phu Plant treats iron-contaminated groundwater while Thu Duc Plant uses iron salt as a coagulant for surface water treatment. Therefore, the iron content available in the sludge from these two plants is quite high,

which can react with NaHCO_3 to create the $\alpha\text{-FeOOH}$ phase that promotes the H_2S adsorption [10].

For sludges impregnated with Mg^{2+} (Mg/WTS) and Zn^{2+} (Zn/WTS), the adsorption efficiency was significantly improved in all sludge samples as compared with materials modified by other methods. This may be because the layered double hydroxide (LDH) structure, which is similar to the mineral hydrotalcite, forms with the co-occurrence of added bivalent metal elements (Mg^{2+} and Zn^{2+}) and available trivalent metal in the sludge (Fe^{3+}) [12; 13]. With their basic surface and large specific surface area, LDH-structured materials are an excellent choice for acid gas adsorption such as H_2S [14]. Mg is reported to be

in the element group that combines more with sulfur in anionic clays, along with Al, Ni, Fe, and Cu [14]; therefore, this enhanced the H_2S adsorption capacity of Mg/WTS. On the other hand, ZnO belongs to the oxide group with good desulfurization ability at high temperatures [14], room temperature [15], and moist condition [16]. According to a report on the physicochemical composition of the WTS from Tan Hiep, Tan Phu, and Thu Duc Plants [2], the iron element content (%w/w) in the sludge sample from the Tan Phu Plant was the highest, followed by Thu Duc sludge, and the lowest is Tan Hiep sludge. This explained the outstanding H_2S adsorption ($2\text{Fe}^{n+} + n\text{H}_2\text{S} \rightarrow \text{Fe}_2\text{S}_x \text{ (black)} + 2n\text{H}^+$).

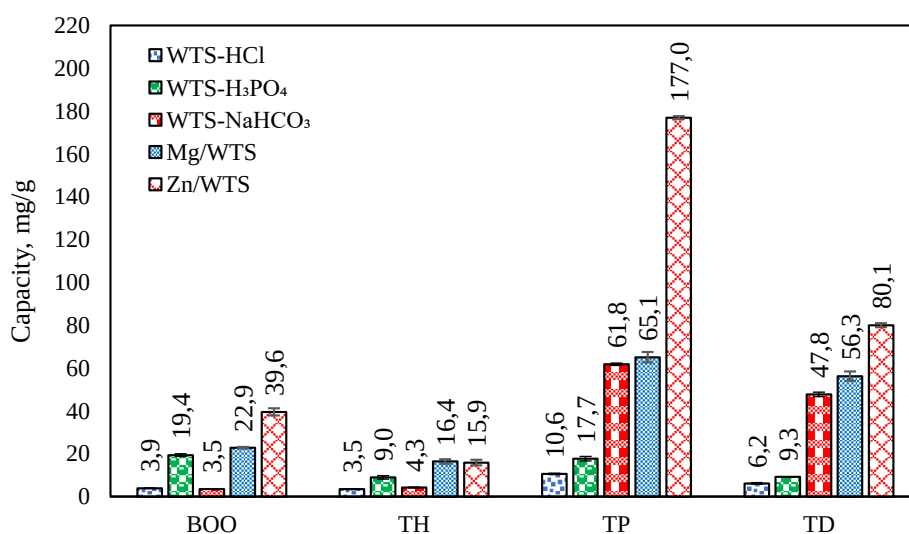


Fig. 4. The H_2S capacity of different adsorbents (operating conditions: 1775 ± 169 ppm of H_2S , 5 g of adsorbent, and flow rate of 1 L/min)

The influence of thermal modification as well as the order of the thermal modification step in the material modification process was also investigated with three adsorbent materials of Zn/TP, 200-Zn/TP, and Zn/TP-200 (Fig. 5). These results showed that the thermal treatment step clearly affects the adsorption process. Specifically, the adsorption capacity increased in the order of $\text{Zn/TP} < \text{Zn/TP-200} < \text{200-Zn/TP}$ with $166.30 < 186.70 < 235.54$ mg/g, respectively. When the material is heated at a high temperature (200°C), volatile components are removed and the pore volume is increased, thereby improving the adsorption ability of the material. The thermal treatment step was performed before the Zn^{2+} -impregnating process to help solidify the sludge structure and convert dissolved cation forms into more stable oxides. This avoids the metals being washed away during the impregnation process and increases the number of adsorption centers on the material surface for H_2S adsorption. This

would be the main reason for the strong enhancement of the H_2S removal efficiency and adsorption capacity of 200-Zn/TP materials.

In order to better understand the process of the H_2S adsorption by materials from the water treatment plant, the raw sludge from Tan Phu Water Treatment Plant, 200-Zn/TP before and after adsorption ($200\text{-Zn/TP}_{\text{ba}}$ and $200\text{-Zn/TP}_{\text{aa}}$) were selected to analyze some material characteristics by SEM, EDX, XRD, FTIR, and BET. The SEM images in Fig. 6 show that the surface of Tan Phu-raw sludge and $200\text{-Zn/TP}_{\text{ba}}$ is relatively different. Tan Phu-raw sludge has a smooth surface and slight roughness, which may be due to the presence of sand particles in the WTS [17]. They are usually larger than the rest of the ingredients (Fig. 6a). In addition, the observed rough surfaces can be attributed to the presence of precipitated heavy metals, such as calcium and iron present in the sludge [18; 19].

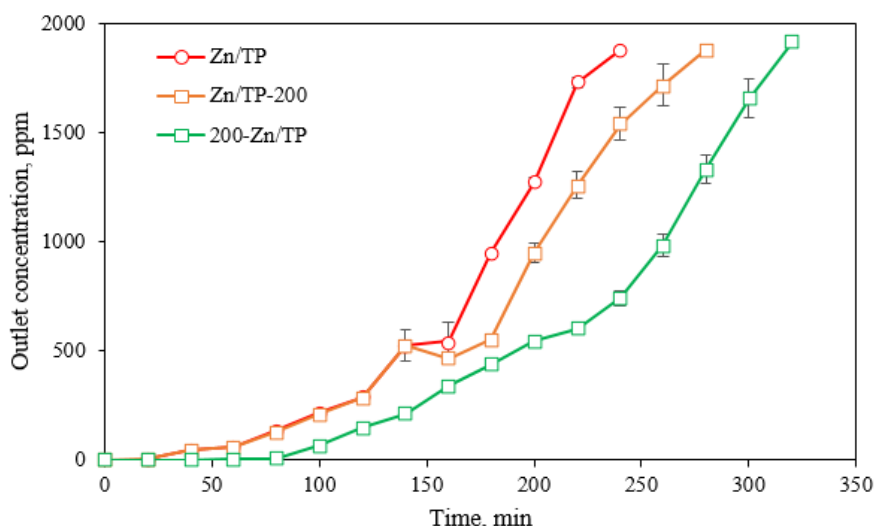


Fig. 5. Breakthrough curve of H_2S adsorption with Zn/TP, Zn/TP-200, and 200-Zn/TP (operating conditions: 1775 ± 169 ppm of H_2S , 5 g of adsorbent, and flow rate of 1 L/min)

These particles are smaller in size as compared to other components in the slurry and have been observed to form clumps and occupy part of the sand surface. Fig. 6b shows that the 200-TP-Zn_{ba} material has a more porous structure than the

coarse sludge, and the smooth or slightly rough surfaces were reduced. After being impregnated with Zn^{2+} in an NH_4OH environment, more precipitates were formed on the surface of the material than in the raw sludge.

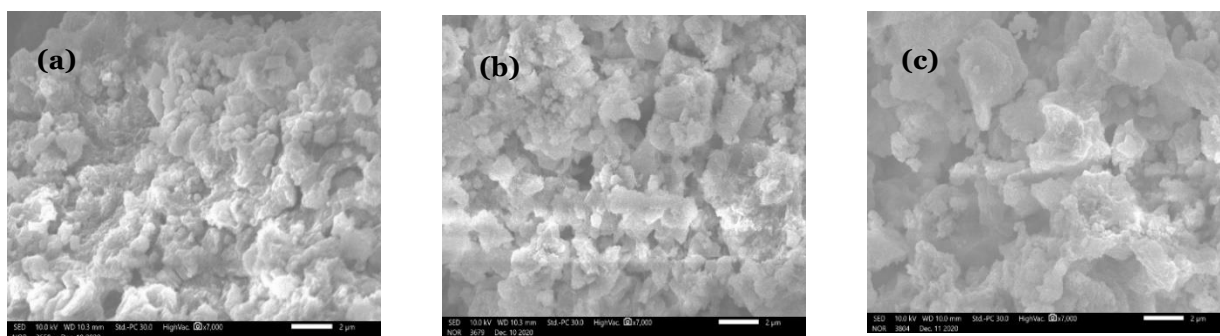


Fig. 6. SEM images of (a) Tan Phu-raw sludge, (b) 200-Zn/TP before adsorption (200-Zn/TP_{ba}), and (c) 200-Zn/TP after adsorption (200-Zn/TP_{aa})

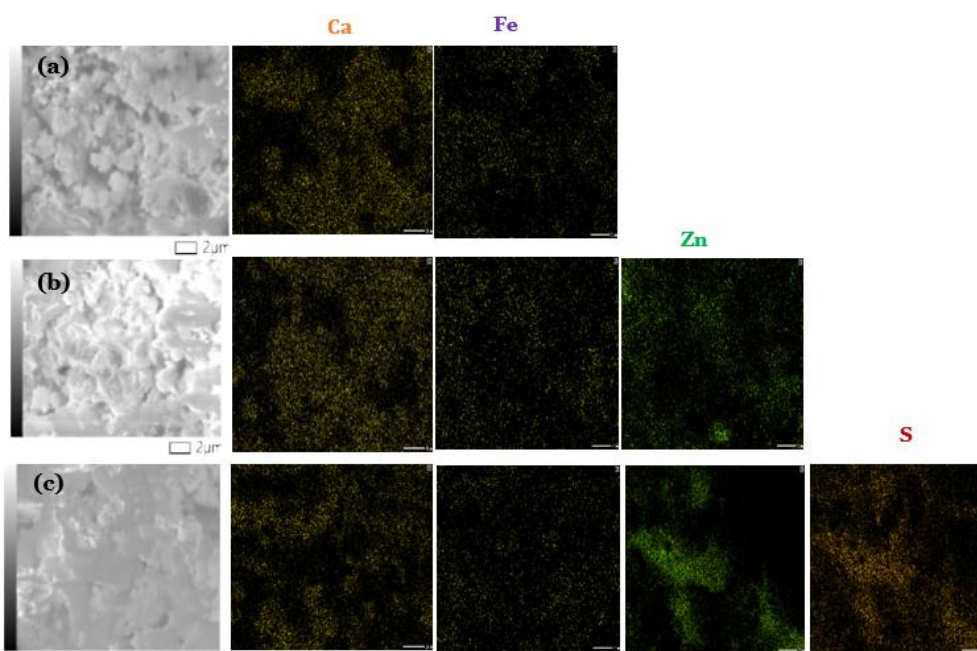


Fig. 7. SEM-EDX Mapping of (a) Tan Phu-raw sludge, (b) 200-Zn/TP before adsorption (200-Zn/TP_{ba}), and (c) 200-Zn/TP after adsorption (200-Zn/TP_{aa})

The SEM-EDX mapping result in Fig. 7b shows the presence of Zn element on the surface of 200-TP-Zn_{ba} material (~5.60 % w/w). This confirmed that the 200-TP-Zn material was successfully prepared. After the adsorption, the H₂S gas molecules adhere to the surface of the adsorbent and insert into the pores, thus making the surface of the 200-TP-Zn_{aa} less rough (Fig. 6c). Sulfur was also found in the 200-TP-Zn_{aa} sample (Fig. 7c) with a ratio of 9.64 % w/w, indicating that H₂S was really retained after passing the adsorbent column. The active Ca element in Tan Phu sludge (Fig. 7) originates from the use of Ca(OH)₂ at this plant as an alkaline element that is beneficial for the adsorption of acidic gases such as H₂S. However, Fig. 7c shows that the positions of S are almost similar to those of Fe and Zn, proving that Fe and Zn are the major active centers of H₂S adsorption in this study.

The crystalline characteristics are shown by XRD results in Fig. 8. Tan Phu-raw sludge and 200-Zn/TP_{ba} samples have similar peaks at 2 θ of 22.10°, 26.67°, 29.33°, 36.10°, 35.56°, 43.17°, 47.40°, 48.40°, and 57.56°, which are characteristics for CaCO₃ (card No. 01-089-1304). After the adsorption process, the XRD spectrum of the Zn-modified sludge calcined at 200 °C appeared more peaks at 11.5°, 14.8°, 25.5°, and 37.4° for FeS (card No. 00-037-0047), 24.6° and 28.7° for Fe₃S₄ (card No. 01-089-1998), 21.9°, 27.7°, 31.5°, and 36.2° for ZnS (card No. 00-036-1450), and 23.2° and 26.6° for CaSO₄ (card No. 00-055-0954). Thus, both SEM-EDX mapping and XRD pattern indicate that Fe and Zn are present in 200-Zn/TP_{ba} with an amorphous form. From the above results, chemical adsorption is predicted to be the main adsorption mechanism with the appearance of FeS, Fe₃S₄, ZnS, and CaSO₄ components in the material after H₂S adsorption.

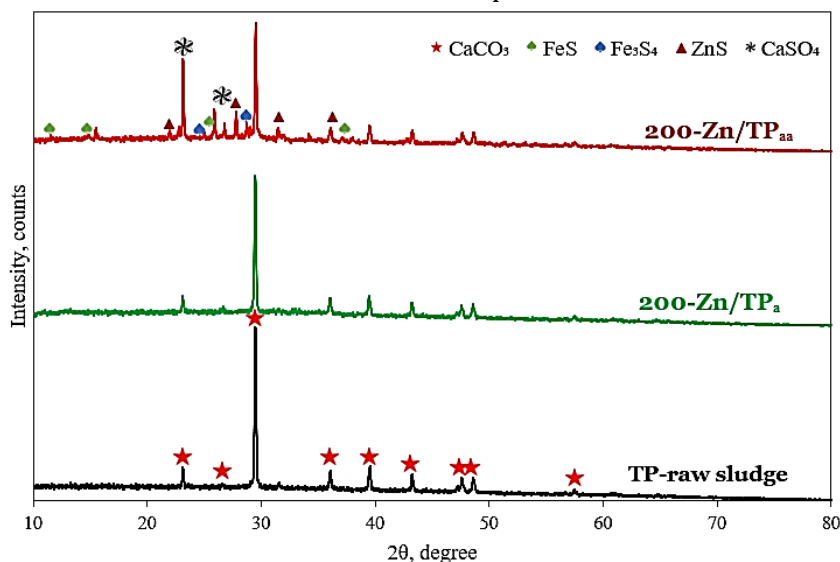


Fig. 8. XRD patterns of Tan Phu-raw sludge, 200-Zn/TP before adsorption (200-Zn/TP_{ba}), and 200-Zn/TP after adsorption (200-Zn/TP_{aa})

The FTIR results of the three samples in Fig. 9 show that the spectrum of the raw sludge has vibration peaks at 3442, 2512, 1427, 1015, 875, and 712 cm⁻¹. The band at 3442 cm⁻¹ is thought to be a prolonged vibration of the hydroxyl groups [20] while the weak bands at 2512 and 1623 cm⁻¹ exhibit O–H bending vibrations of the adsorbed water molecules [21]. The weak peak at 1795 cm⁻¹ corresponds to the C=O bonds from the carbonate group [22]. The wide and deep band at 1427 cm⁻¹ may correspond to the iron oxides present in the sludge [23] or the bond of the C=O group from the carbonate group [22]. The medium and narrow band at 875 and 712 cm⁻¹ corresponds to Ca–O bonds [22] or calcium carbonate [24]. The weak band at 1020 cm⁻¹ may represent a hydroxyl

group bound to Fe, Mg, or Si [23]. The FTIR of the Zn-modified sludge calcined at 200 °C has a peak at 2361 cm⁻¹ and the narrow band at 1020 cm⁻¹ was replaced by a wide band at 1031 cm⁻¹. This may be due to the association of the hydroxyl group with Zn and Fe during the preparation of 200-Zn/TP_{ba} material. After adsorption, the peaks at position 2361 and 1031 cm⁻¹ were completely lost, indicating that the hydroxyl groups associated with Zn and Fe participated in the H₂S reaction to form ZnS and FeS, which is consistent with the XRD results in Fig. 8. In addition, the peaks with weak intensity at 1150, 1005, 659, and 601 cm⁻¹ correspond to SO₄²⁻ group bonding of metal oxides present in the material, mainly Ca [25].

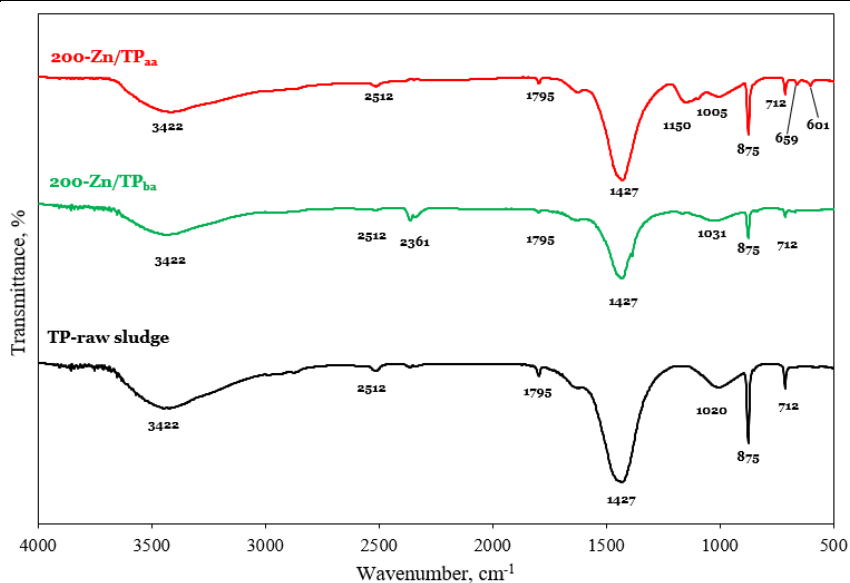


Fig. 9. FTIR spectra of Tan Phu-raw sludge, 200-Zn/TP before adsorption (200-Zn/TP_{ba}), and 200-Zn/TP after adsorption (200-Zn/TP_{aa})

N₂ adsorption and desorption were carried out at $-196\text{ }^{\circ}\text{C}$ with 200-Zn/TP, the adsorption and desorption curves in Fig. 10 show that the material has a type IV adsorption isotherm. The amount of adsorption is low in the region of relatively low pressure ($P/P_0 < 0.01$) while the adsorption and desorption isotherms have a steep slope in the region of high relative pressure ($P/P_0 \sim 0.9\text{--}1.0$). This could be explained by the fact that the pores in the material are mainly mesopores [26; 27] similar to the pore size distribution. From the appearance of the type A hysteresis loop, it can be

inferred that the 200-Zn/TP has some tubular pores. The BET surface of the 200-TP/Zn sludge is $89.51\text{ m}^2/\text{g}$, much lower than that of other H₂S adsorbents such as OMSs (MCM-41, $1141\text{ m}^2/\text{g}$ [28]), activated carbon (BAX, $1000\text{ m}^2/\text{g}$ [29]). Also, the pore size distribution in Fig. 10 shows that the material structure contains pores with sizes distributed from 3 to 100 nm, with a total pore volume of $0.2044\text{ cm}^3/\text{g}$. However, most of pores are the mesopores with diameters mainly from 3.0 to 14.6 nm which coincides with the adsorption and desorption isotherms.

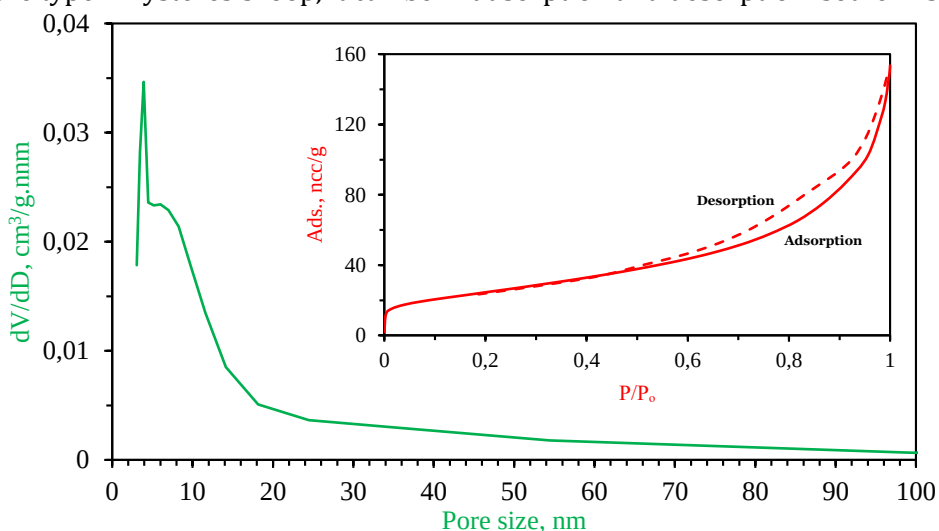


Fig. 10. The adsorption and desorption isotherms and pore size distribution of 200-Zn/TP

Effect of empty bed contact time on efficiency

Empty bed contact time (EBCT) is an important parameter characterizing the relationship between the volume of the adsorbent layer and gas flow rate. In this study, the effect of EBCT on the adsorption process was investigated with the change of adsorbent amount (2.5–10 g) when the

treatment gas flow was fixed at 1 L/min and the initial H₂S concentration was controlled at $\sim 2410 \pm 169\text{ ppm}$.

The breakthrough curves in Fig. 11 show that by increasing EBCT from 0.32 s to 1.32 s, the effective adsorption time (denoted as t_b , determined at the time when $C_{\text{out}} \sim 0$) increased

from 20 min to 460 min. This is completely consistent with the theory of adsorption in the contact time between the gas phase and the solid phase. As EBCT is enhanced, the mass transfer process is better and more H_2S is retained in the material layer. This helps the airflow to be thoroughly treated for a longer time. Although increasing EBCT is beneficial for the adsorption process, this value will be limited in practice by the device pressure loss. In addition, to ensure the uniformly distributed gas flow, the uniformity of the adsorbent along with the size parameter of the material layer are also important factors in

determining which EBCT value is appreciated. In this experiment, only the uniformity of the adsorbent was controlled (0.105–2 mm) while the remaining factors were assumed to have a negligible influence on the lab-scale system. The adsorption capacity of the materials with different EBCTs was also calculated. Accordingly, when using 2.5 g of 200-Zn/TP sludge, the adsorption capacity reached 199.9 $\text{mgH}_2\text{S/g}$ and then this value increased to 1.45 times when using 10 g of adsorbent, reaching 289.1 $\text{mgH}_2\text{S/g}$, which is consistent with those reported in the literature [30] and our previous study [19].

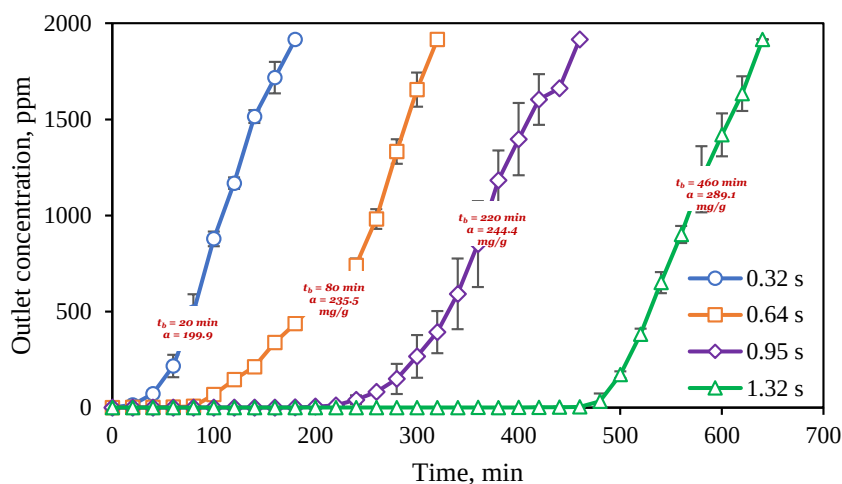


Fig. 11. Breakthrough curve of H_2S adsorption at different EBCT, t_b - the effective adsorption time and a - the H_2S adsorption capacity (operating conditions: 1733 ± 169 ppm of H_2S , 2.5–10 g of 200-Zn/TP, and 1 L/min of flow rate)

Effect of H_2S initial concentration

H_2S adsorption tests were conducted at different initial concentrations in the range of 1000–3000 ppm, with 10 g of 200-Zn/TP sludge and a flow rate of 1 L/min. The H_2S adsorption capacity in Fig. 12 shows that when the initial concentration increased from 1000 to 2500 ppm, the capacity also increased from 261.4 to 309.9 $\text{mgH}_2\text{S/g}$. However, if the H_2S concentration continued to increase, the obtained capacity tended to decrease. For the mass transfer, when the contaminant concentration increases, the kinetics of the process is also improved, thereby increasing the adsorption efficiency. In addition, the tendency of multilayer adsorption can also be a reason for more efficient treatment. However, if the concentration of pollutants is too high, the adsorbent surface can quickly become saturated, and H_2S cannot penetrate deeply into the pore system of the material, thus reducing the adsorption efficiency as well as the adsorption capacity. This result was similar to the study of Choo, Lau [31] when H_2S was adsorbed by K_2CO_3 -impregnated activated carbon.

According to the experiment at different H_2S initial concentrations, Langmuir and Freundlich isotherms were applied to calculate characteristic parameters for the H_2S adsorption process (Fig. 13). The results show that the H_2S adsorption with 200-Zn/TP sludge in the range of 1000–3000 ppm H_2S (~ 1390 – 4170 $\text{mgH}_2\text{S/m}^3$) described by Langmuir isotherm ($R^2 = 0.9926$) was more suitable than Freundlich isotherm ($R^2 = 0.8583$). This result is consistent with some of our previous studies on H_2S adsorption by red mud [32] and alum sludge of water treatment plants [33]. At the same time, a study using oil-sludge-based adsorbents for H_2S removal in oilfield gases also showed that the Langmuir isotherm fits better than the Freundlich isotherm [34]. The coefficient of conformity assessment of the Langmuir isotherm (R_L) was calculated to check the experiment results following Equation 4, where K_L is the Langmuir constant in Equation 2 and C_{in} is the H_2S initial concentration (mg/m^3). All R_L values in the investigated concentration were in the range of 0–1, indicating that the H_2S adsorption with 200-Zn/TP described by Langmuir isotherm is completely consistent [35].

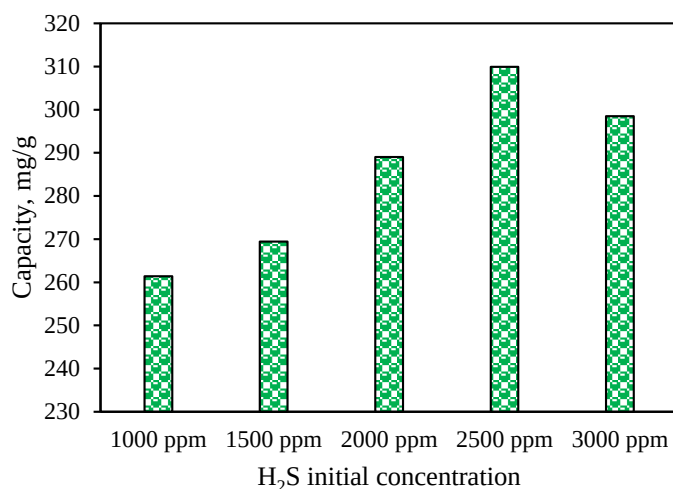


Fig. 12. Effect of initial concentration on adsorption capacity (operating conditions: 1000–3000 ppm of H₂S, 10 g of 200-Zn/TP, and 1 L/min of flow rate)

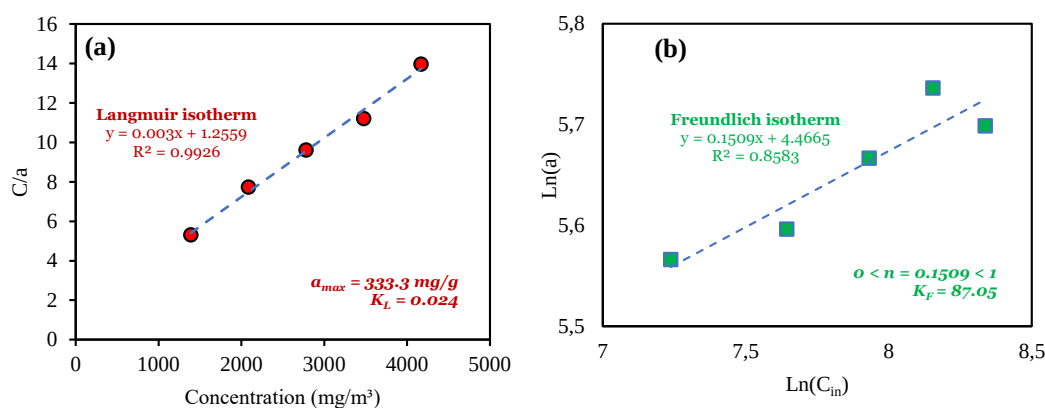


Fig. 13. Langmuir isotherm (a) and Freundlich isotherm (b) of H₂S adsorption with 200-Zn/TP

Since this experimental process is more consistent with Langmuir isotherm, it can be predicted that monolayer adsorption is more dominant, the adsorption centers do not interact with each other, and the tendency for competitive adsorption is less. Compared with other studies (Table 2), the maximum adsorption capacity of 200-Zn/TP is somewhat superior. To be able to draw more conclusions, it is necessary to compare

the adsorption capacity of adsorbents under the same conditions. However, this result is also remarkable in the effort to utilize water treatment sludge as H₂S adsorbent.

$$R_L = \frac{1}{1 + K_L \times C_{in}} \quad (4)$$

Table 2

Adsorbents	Conditions	Capacity, mg/g	Langmuir/Freundlich	References
Cu/PAC 450	T = 20 °C [H ₂ S] = 100–500 ppm Q = 2 mL/min	95.66	Langmuir (R ² = 0.9627)	[36]
BL-450-6	T = 293 K [H ₂ S] = 80–800 ppm Q = 1 L/min	25.00	Langmuir (R ² > 0.99)	[37]
Si-CHA	T = 298 K p = 0–190 kPa m = 0.73 g	194.48	Langmuir (R ² > 0.999)	[38]
MSA	T = 303 K p = 0–1000 kPa m = 5 g	120.36	Langmuir (R ² > 0.99)	[39]
ERS-8	T = 303 K p = 0–1000 kPa m = 5 g	192.44	Langmuir (R ² > 0.99)	[39]

Adsorbents	Conditions	Capacity, mg/g	Langmuir/Freundlich	References
TH300	[H ₂ S] = 50–400 ppm m = 3 g Q = 2.5 L/min	30.96	Langmuir (R ² = 0.99)	[3]
200-TP-Zn	T = 298 K [H ₂ S] = 1000–3000 ppm m = 10 g Q = 1 L/min	333.3	Langmuir (R ² = 0.9926)	This study

Regeneration adsorbent

The reusability of 200-Zn/TP material was investigated with different desorption methods, including heating (200, 300, and 400 °C) and air blowing (2 L/min). The result in Fig. 14 indicates that the adsorption capacity was different when the material was desorbed under different conditions and was much lower than the first adsorption capacity. When using the calcination method, the higher the temperature of the material being desorbed, the lower the adsorption capacity or the lower the adsorption efficiency achieved at reuse. This may be because the high temperature (higher than the processing temperature) could break the original structure of the material, thus reducing the adsorption efficiency. When using the method of air blowing through the material column, the adsorption capacity of the reuse is higher than that of the

regenerated materials by the calcination method, reaching 105.5 mgH₂S/g (reduced by 2.74 times compared to the original). In general, the results show that the efficiency of material reuse is not high. This may be because the mesopore structure of the starting material (Fig. 10) is not suitable for multiple reuse. In addition, the adsorption process of S²⁻ on the surface of the adsorbent as waste sludge and the interaction between S²⁻ and the adsorption centers can take place according to complicated processes, requiring further research to draw a suitable conclusion. Therefore, further study is needed to improve the regeneration of the adsorbent, in which, the partial oxidation of H₂S to elemental sulfur (S⁰) should be focused to recover S⁰ as a valuable product. Otherwise, without an effective recovery method, the adsorbed material with saturated H₂S must be disposed of as hazardous waste.

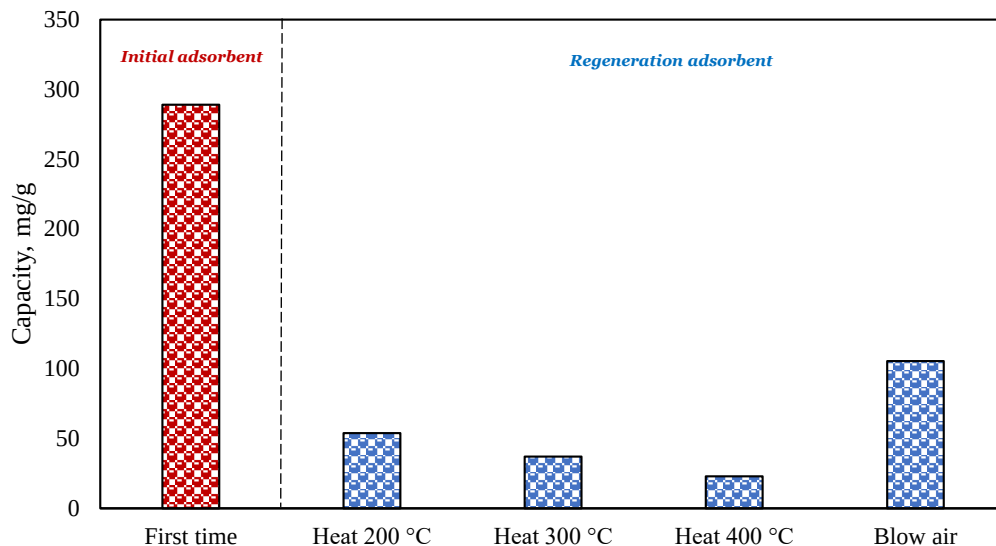


Fig. 14. Adsorption capacity of regenerated adsorbent by heating (200, 300, 400 °C) and by blowing air (operating conditions: 2000 ppm of H₂S, 10 g of adsorbent, and flow rate of 1 L/min)

Conclusions

In the context of the global energy and resource crisis, utilizing one waste to treat another one is a promising research direction that supports the circular economy. The research was successful in the modification of water treatment sludge into an effective adsorbent material. The experiments were conducted to assess the ability to adsorb H₂S in order to introduce biogas filtration in practical

applications. H₂S adsorption capacity reaches 235.54 mg/g using Zn-modified sludge calcined at 200 °C under suitable conditions of inlet H₂S concentration (1775 ± 169 ppm), adsorbent mass (5 g), and flow rate (1 L/min). The Langmuir maximum adsorption capacity was calculated to be 333.30 mg/g, which indicates that the material is promising for biogas filtration. However, the influence of environmental factors, particularly

the humidity of the input air, is an issue that needs clarification before the technology can be widely implemented. This study contributes an effective method for H₂S removal using solid waste that provides both economic and environmental benefits for the biogas and water treatment industries.

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