Phát triển và đặc trưng vật liệu composite bentonite – than hoạt tính từ vỏ trấu nhằm tăng cường khả năng hấp phụ khí H_2S

TÓM TẮT

Hydro sulfua (H_2S) là tạp chất chính trong biogas cần được loại bỏ hiệu quả để ngăn ngừa ăn mòn và ô nhiễm môi trường. Nghiên cứu này đánh giá quá trình tổng hợp và khả năng hấp phụ H_2S của vật liệu composite giữa bentonite và carbon hoạt tính từ vỏ trấu (SRH@Ben). Các vật liệu composite được chế tạo dưới các điều kiện hoạt hóa nhiệt và hóa học khác nhau, đồng thời được phân tích đặc trưng về cấu trúc, hình thái và thành phần hóa học bằng phương pháp hiển vi quang học, kính hiển vi điện tử quét phát xạ trường (FE-SEM), phổ tán xạ năng lượng tia X (EDS) và nhiễu xạ tia X (XRD). Kết quả cho thấy nhiệt độ hoạt hóa và hàm lượng vỏ trấu ảnh hưởng đáng kể đến khả năng hấp phụ, trong đó mẫu tối ưu (SRH@Ben 50%-450°C) đạt dung lượng hấp phụ H_2S là 2,23 mg/g. Quá trình hoạt hóa hóa học bằng KOH tiếp tục cải thiện dung lượng hấp phụ lên 2,34 mg/g nhờ tăng cường độ xốp và nhóm chức bề mặt. Phân tích so sánh cho thấy vật liệu SRH@Ben có hiệu suất hấp phụ vượt trội so với vật liệu hấp phụ gốc carbon thương mại (1,18 mg/g) và đạt hiệu quả tương đương với vật liệu gốc oxit sắt (2,46 mg/g). Kết quả này khẳng định tiềm năng của SRH@Ben như một giải pháp hấp phụ H_2S chi phí thấp và bền vững cho quá trình làm sạch biogas.

Từ khoá: *H_2S, bentonit, trấu, vật liệu composite, khả năng hấp phụ.*

Development and characterization of bentonite – activated carbon composite from rice husk for enhanced H_2S gas adsorption

ABSTRACT

Hydrogen sulfide (H_2S) is a major impurity in biogas that must be efficiently removed to prevent corrosion and environmental pollution. This study investigates the synthesis and adsorption performance of bentonite-rice husk activated carbon (SRH@Ben) composites for H_2S removal. The composites were prepared under varying thermal and chemical activation conditions, and their structural, morphological, and chemical properties were characterized using optical microscopy, field-emission scanning electron microscopy (FE-SEM), Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD). The results indicate that both activation temperature and rice husk content significantly influence adsorption capacity, with the optimal composite (SRH@Ben 50%-450°C) achieving an H_2S adsorption capacity of 2.23 mg/g. Further chemical activation with KOH enhanced the adsorption capacity to 2.34 mg/g due to increased porosity and surface functionality. Comparative analysis demonstrated that SRH@Ben composites outperformed commercial carbon-based adsorbents (1.18 mg/g) and exhibited comparable efficiency to iron oxide-based materials (2.46 mg/g). These findings highlight the potential of SRH@Ben composites as a cost-effective and sustainable alternative for biogas purification.

Keywords: *H_2S, bentonite, rice husk, composites, adsorption capacity.*

1. INTRODUCTION

Hydrogen sulfide (H_2S) is a major contaminant in biogas, posing serious environmental and operational challenges. Even at low concentrations, H_2S is highly toxic and corrosive, leading to severe damage to pipelines, gas storage systems, and energy conversion units such as internal combustion engines and fuel cells.[1] Moreover, the emission of H_2S contributes to air pollution and acid rain formation, necessitating its effective removal from biogas before utilization. Various H_2S removal techniques have been developed, including chemical scrubbing, catalytic oxidation, and biological filtration. However, these methods often suffer from high operational costs, complex maintenance, and secondary waste generation. Adsorption-based methods, particularly those utilizing low-cost, biomass-derived materials, have gained significant attention due to their cost-effectiveness, ease of operation, and environmental sustainability.[2] Activated carbon (AC) is widely employed in H_2S adsorption due to its high surface area, well-developed porosity, and tunable surface chemistry.[3] Among biomass-based precursors, rice husk-derived activated carbon (RHAC) is of particular interest due to its abundance, renewability, and ease of modification.

Rice husk-derived activated carbon has demonstrated excellent adsorption properties, attributed to its unique pore structure and ease of surface modification.[4] However, while activated carbon offers significant adsorption potential, its efficiency can be further improved by incorporating other materials that provide additional functional sites and structural stability. In one study, biochar produced from rice hulls through pyrolysis at 500°C exhibited a notable H_2S adsorption capacity of 382.7 mg/g. The adsorption kinetics aligned with the Yoon-Nelson model, suggesting a consistent mass transfer mechanism during the adsorption process.[5] Another investigation synthesized a triethylenetetramine (TETA)-grafted activated rice husk ash (TRI-A-RHA) to assess its efficacy in removing CO_2 and H_2S from biogas. The modified material demonstrated adsorption capacities of approximately 0.34 mmol/g for CO_2 and 0.14 mmol/g for H_2S at room temperature, attributed to its high surface area and effective amine functionalization.[6] These studies underscore the potential of rice husk-derived activated carbon as a cost-effective and efficient material for H_2S adsorption in biogas applications. Modifications such as amine grafting, hydrogel composite formation, and optimization of pyrolysis conditions can significantly enhance adsorption performance, offering valuable insights for developing sustainable biogas purification technologies.

Bentonite, a naturally occurring clay mineral, has been extensively studied for gas and liquid adsorption due to its high cation exchange capacity, layered structure, and strong affinity for polar molecules.[7,8] Bentonite based materials have been extensively studied for their potential in adsorbing hydrogen sulfide (H_2S) from biogas. Recent research has focused on enhancing the adsorption capacity of bentonite through various modifications. One study employed molecular simulations to investigate the adsorption of H_2S onto bentonite doped with cations such as Li^+, Na^+, and K^+. The findings indicated that these doped bentonites exhibit selectivity towards H_2S, suggesting their suitability for natural gas sweetening applications.[8] Another investigation explored the modification of bentonite using carbide slag, followed by high-temperature activation. The results demonstrated that the carbide slag-modified bentonite achieved a breakthrough adsorption capacity of 0.92 mg/g, significantly outperforming unmodified bentonite, which had a capacity of 0.06 mg/g. The enhanced performance is attributed to the active groups formed upon introducing $Ca(OH)_2$ from the carbide slag.[9] Collectively, these studies highlight that doping bentonite with specific cations or modifying it with industrial by-products like carbide slag can substantially improve its H_2S adsorption capabilities, making it a promising material for biogas purification.

Rice husk-derived activated carbon (RHAC) and bentonite are promising, cost-effective, and sustainable adsorbents for H_2S removal. RHAC provides high surface area and porosity, while bentonite offers structural stability and ion-exchange capacity. However, both materials have limitations. RHAC suffers from limited chemical stability, low affinity for acidic gases, rapid saturation, poor regeneration, moisture sensitivity, and sulfur deposition, reducing its long-term effectiveness. Similarly, bentonite has low surface area, limited adsorption capacity, susceptibility to moisture, mechanical instability, slow kinetics, and weak H_2S affinity, requiring modifications for improved performance.

To overcome these limitations, researchers have developed bentonite-activated carbon composites, which enhance adsorption capacity, improve mechanical strength, and reduce moisture sensitivity by combining the high porosity of activated carbon with the structural stability of bentonite.[10] Moreover, the modification of these materials through chemical activation or metal impregnation can significantly improve their selectivity and capacity for H_2S removal.[10,11] Investigating the adsorption behavior of H_2S on this composite can provide valuable insights into optimizing adsorbent performance for practical applications in air purification, biogas upgrading, and industrial gas treatment. Therefore, this study aims to: (1) Synthesize and characterize bentonite–rice husk activated carbon (SRH@Ben) composites under varying thermal and chemical activation conditions; (2) Evaluate their H_2S adsorption capacity through breakthrough curve analysis and (3) Compare their performance with commercial adsorbents to assess their practical applicability. The findings of this research will provide valuable insights into the development of cost-effective and environmentally sustainable adsorbents for biogas purification and industrial gas treatment applications.

2. EXPERIMENTAL

2.1. Materials

Commercial bentonite powder ($Al_2O_3{\cdot}4SiO_2{\cdot}H_2O$), sourced from India, was procured from Viet My Binh Dinh Co., Ltd. (655 Hung Vuong, Nhon Phu, Quy Nhon, Binh Dinh, Vietnam). Potassium hydroxide (KOH, 85%), manufactured by Xilong, was imported from China. Finely milled rice husk, with a particle size of less than 1 mm, was obtained from a local rice milling facility located in Quang Hy Hamlet, Phuoc Loc Commune, Tuy Phuoc District, Binh Dinh, Vietnam. In addition, large rice husks (1–3 mm particle size) and rice bran were also collected from the same facility for comparative purposes.

2.2. Material Fabrication

A total of 350 mL of distilled water was introduced into 200 g of a bentonite–milled rice husk mixture, with the proportions of the components varied systematically. The mixture was homogenized through continuous mechanical mixing for 15 minutes. The resulting bentonite/rice husk composite was subsequently molded into cylindrical pellets, each measuring approximately 6 mm in diameter and 1.5 cm in height. To evaluate the compressive strength of the SRH@Ben composite pellets, a uniaxial compression test was conducted using a manual cylindrical piston with a 2 cm diameter. The pellets, shaped as cylinders with a diameter of 0.6 cm and a height of 1.5 cm, were placed centrally beneath the piston. The applied force was gradually increased until a compressive stress of approximately 2 MPa was reached, which is sufficient for assessing the mechanical integrity of the pellet without inducing premature fracture. These pellets were initially air-dried under natural sunlight for a period of 2 days and 3 nights, followed by oven-drying at 90 °C for 12 hours. The dried composite was then subjected to anaerobic pyrolysis at 450 °C for 1.5 hours using a loosely covered ceramic crucible, which allowed the release of gaseous byproducts and prevented pressure buildup during the carbonization process. The pyrolysis was conducted in a Nabertherm LT3/12/B180 muffle furnace with a heating rate of 15 °C/min. Notably, no inert carrier gas such as nitrogen (N_2) or vacuum system was employed, in order to reduce operational complexity and cost. The final product was designated as SRH@Ben (SRH = Small Rice Husk, Ben = Bentonite). Following the same procedure, composite materials were fabricated using bentonite combined with larger rice husk (1–3 mm particle size) and rice bran. These samples were labeled as LRH@Ben and Bran@Ben, respectively. To optimize the H_2S adsorption capacity, the SRH@Ben composite was further activated by treatment with 0.15 M KOH at 90 °C for 1 hour. After activation, the material was dried at 90°C and underwent anaerobic pyrolysis at 650 °C for 30 minutes.

2.3. Characterization and Gas Adsorption Measurements

The surface morphology, chemical composition, and structural properties of the synthesized materials were comprehensively characterized using optical imaging, field-emission scanning electron microscopy (FE-SEM; HITACHI S-4800), Energy-Dispersive X-ray Spectroscopy (EDS) and X-ray diffraction (XRD; Bruker D2, equipped with Cu Kα radiation). A schematic representation of the experimental setup for H_2S gas adsorption measurements is provided in Figure 1. The H_2S gas concentration was precisely regulated using mass flow controllers (MFCs), with a certified H_2S gas cylinder (10,000 ppm, diluted in nitrogen) and high-purity N_2 (99.99%) serving as the carrier gas. The H_2S concentration was quantified before and after passage through the filtration column using a Dräger X-8000 multi-gas detector.

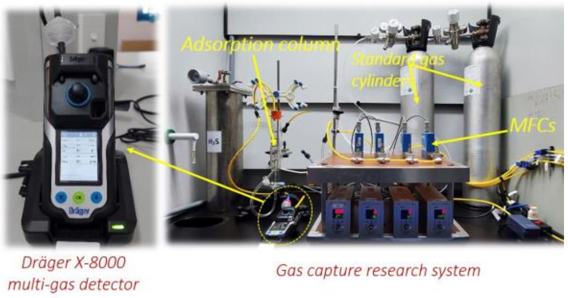

Figure 1. Experimental setup for H_2S gas adsorption study. The system comprises standard gas cylinders for controlled gas supply, mass flow controllers (MFCs) for precise gas flow regulation, an adsorption column containing the tested sorbents, and a Dräger X-8000 multi-gas detector for real-time monitoring of H_2S concentration at the outlet.

3. RESULTS

3.1. Morphology, structure, and chemical composition of composite materials

The optical images (Figure 2 and 3) provide a comparative analysis of SRH@Ben composites with varying rice husk (SRH) content subjected to different thermal treatments under anaerobic conditions. In the Figure 2, samples containing 30% SRH were thermally treated at 400 °C, 450 °C, and 500 °C. Notably, the material undergoes significant morphological and color changes as the temperature increases.

Figure 2a shows the surface morphology of the SRH@Ben 30 % composite material after anaerobic pyrolysis at 350 °C. The sample exhibits a relatively rough surface with minimal shrinkage or structural damage, indicating that the temperature was sufficient to initiate carbonization without causing thermal degradation. The dark color suggests the beginning stages of carbon formation. However, the structure remains partially preserved, and no significant cracking or pore development is observed at this stage, implying that further increases in temperature may enhance the porosity and carbon content of the material. The sample treated at 400 °C (Figure 2b) exhibits a dark and compact appearance, while the sample treated at 450 °C (Figure 2c) retains a similar structure but displays a more developed texture. At 500 °C (Figure 2d), the surface becomes rougher and more porous, indicating potential structural degradation at elevated temperatures. In contrast, the pure bentonite sample treated at 450 °C (Figure 2e) demonstrates a distinctly different morphology, characterized by a lighter color and a denser structure.

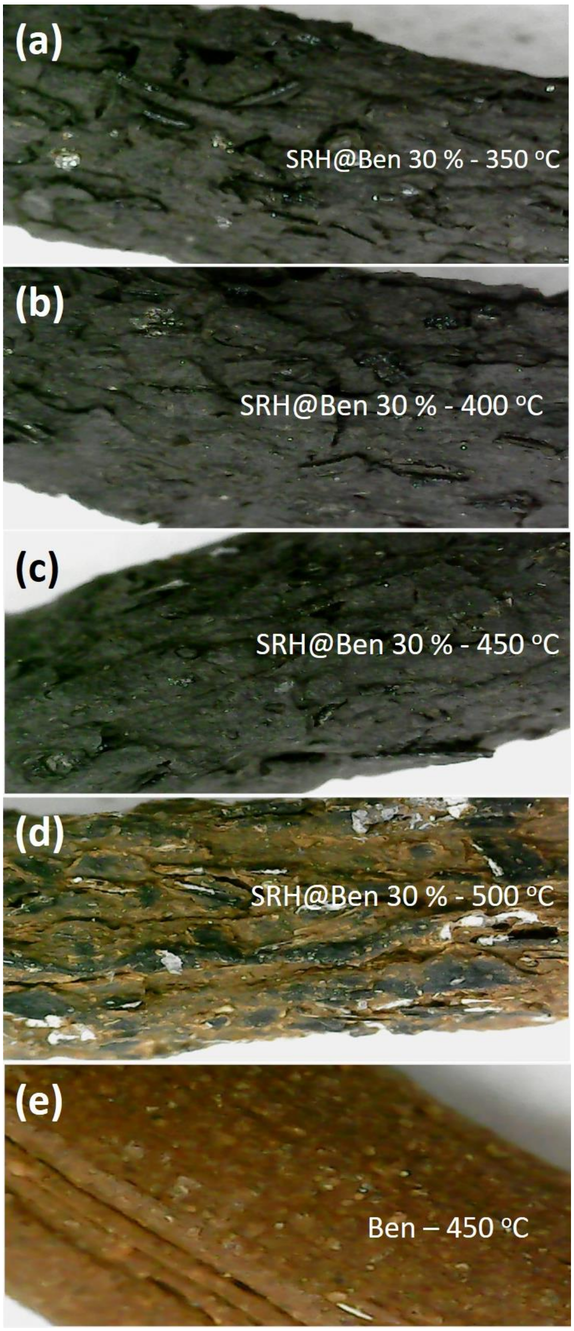

Figure 2. Optical images of SRH@Ben composites with 30% rice husk content treated under anaerobic conditions at different temperatures: (a) 350 °C (b) 400 °C, (c) 450 °C, (d) 500 °C. Image (e) shows the pure bentonite sample treated at 450 °C.

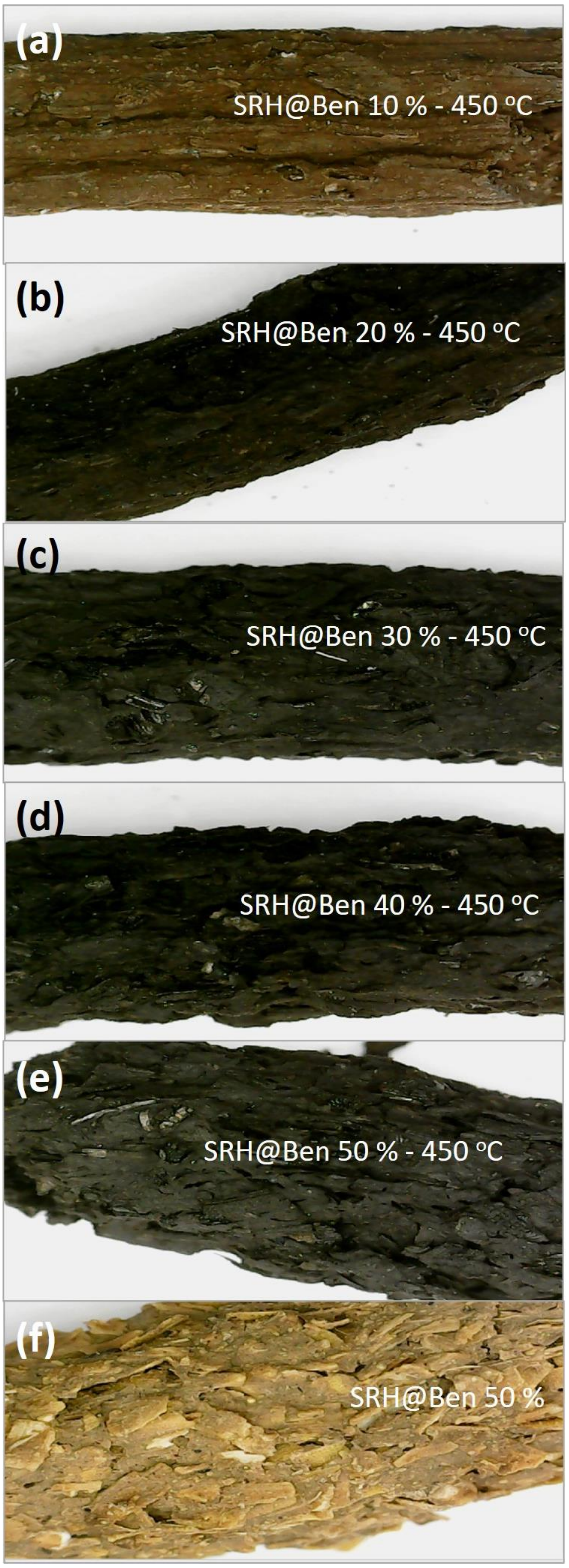

Figure 3. Optical images of SRH@Ben composites with varying rice husk content treated at 450 °C: (a) 10 %, (b) 20 %, (c) 30 %, (d) 40 %, (e) 50 %. Image (f) represents the SRH@Ben 50 % sample before thermal treatment.

Figure 3 illustrates the effect of SRH content on the composite structure at a fixed temperature of 450 °C. As the SRH ratio increases from 10 % to 50 % (Figures 3a–e), the material progressively darkens and develops a more compact texture, likely due to enhanced carbonization. The SRH@Ben 50 % sample treated at 450 °C (Figure 3e) exhibits the most uniform and dense structure, consistent with its highest H_2S adsorption efficiency observed in the study. Importantly, the non-thermally treated SRH@Ben 50 % sample (Figure 3f) appears significantly lighter in color with a more fibrous structure, underscoring the substantial transformation induced by thermal treatment. These observations demonstrate that both the thermal treatment temperature and the SRH content critically influence the final morphology and textural properties of the composite materials, which in turn directly affect their adsorption performance.

The SEM images provide a comparative analysis of the morphological evolution of SRH@Ben composites subjected to different thermal treatments under anaerobic conditions. At 350 °C (Figure 4a), the material exhibits a relatively compact and smooth surface with minimal porosity, indicating that thermal decomposition has not yet progressed significantly. As the temperature increases to 400 °C (Figure 4b), surface roughness becomes more pronounced, accompanied by the emergence of microvoids, suggesting the onset of structural modification and partial volatilization of organic components.

At 450 °C (Figure 4c), the material displays a well-developed porous structure with enhanced surface roughness, indicative of effective carbonization and increased surface area. The formation of interconnected pore networks at this temperature likely facilitates improved adsorption capacity, making this condition optimal for gas adsorption applications. However, at 500 °C (Figure 4d), noticeable structural degradation is observed, with the material exhibiting a more fragmented and brittle morphology. The excessive thermal treatment may have led to the collapse of microporous structures and potential carbon burnout, reducing its mechanical integrity and adsorption efficiency.

The progressive morphological transformations observed in the SEM images highlight the critical role of thermal treatment in tailoring the physicochemical properties of the composite. 450 °C appears to be the optimal temperature, striking a balance between structural stability and porosity enhancement, thereby maximizing the material's suitability for gas adsorption applications such as H_2S removal. Conversely, excessive heating at 500 °C may lead to undesirable material degradation, compromising its functional performance.

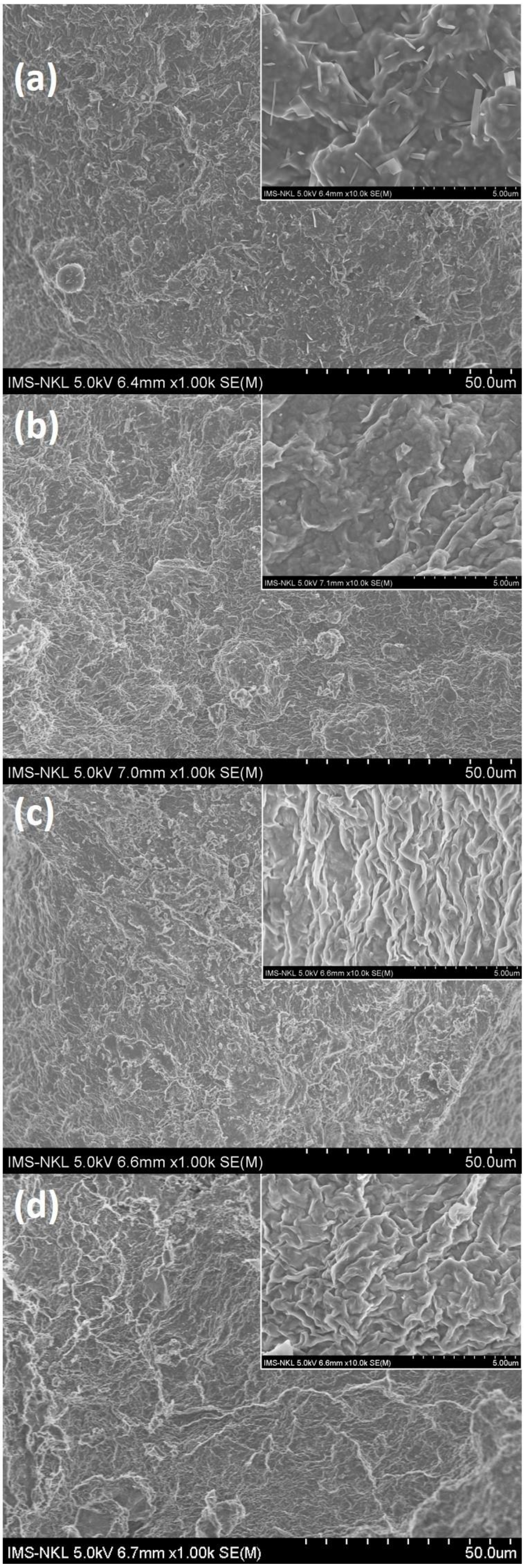

Figure 4. SEM images of SRH@Ben composites with 30 % rice husk treated at different temperatures: (a) 350 °C, (b) 400 °C, (c) 450 °C, and (d) 500 °C. The inset images display higher magnification views (×10.0k) of each sample.

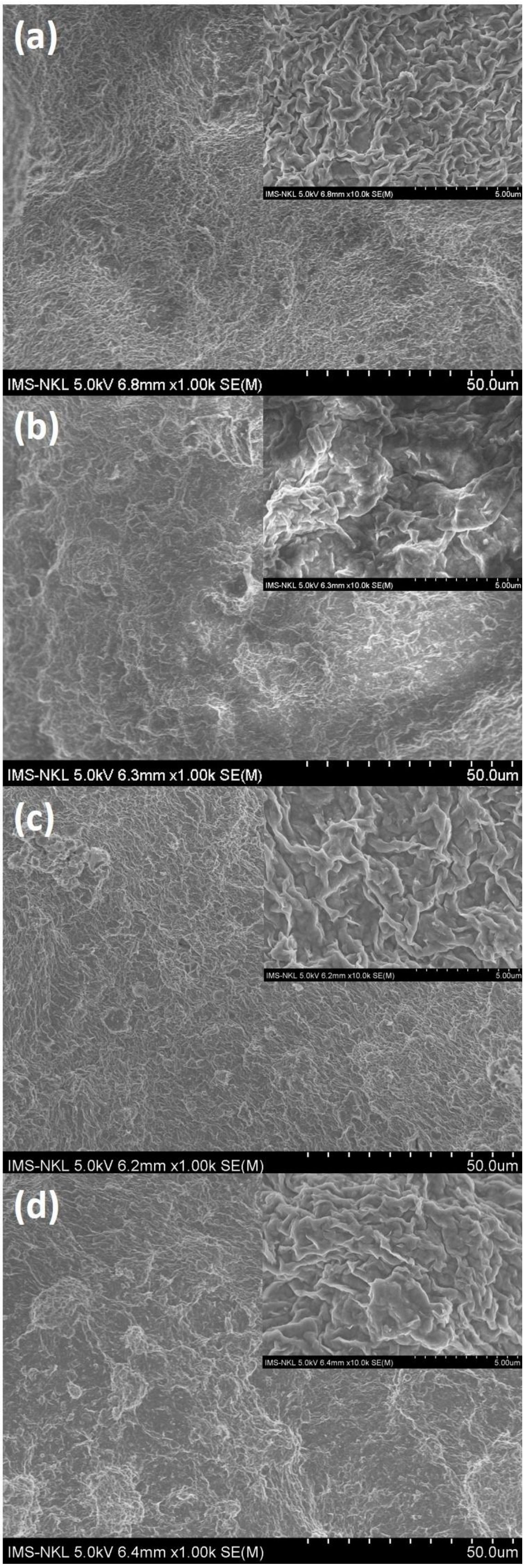

Figure 5. SEM images of SRH@Ben composites treated at 450 °C with varying rice husk contents: (a) 10 %, (b) 20 %, (c) 40 %, and (d) 50 %. The inset

images (magnified at ×10.0k) provide a closer view of the surface morphology.

The SEM images illustrate the influence of rice husk content on the morphological characteristics of SRH@Ben composites pyrolyzed at 450 °C. At a low rice husk content (10 %, Figure 5a), the surface appears relatively compact with limited porosity. The material maintains a somewhat dense structure, indicative of incomplete structural transformation and insufficient development of porous networks.

As the rice husk content increases to 20 % (Figure 5b), a noticeable change in morphology is observed, with the emergence of microvoids and enhanced surface roughness. This suggests a higher degree of decomposition and carbonization, leading to an increase in available adsorption sites. At 40 % rice husk content (Figure 5c), the porous structure becomes more pronounced, characterized by a well-interconnected network of micro- and mesopores. This transformation significantly enhances the material's surface area, which is beneficial for adsorption-based applications, particularly in gas capture.

At the highest rice husk content of 50 % (Figure 5d), the composite exhibits the most developed porous structure, with an intricate network of wrinkles and voids. The increased textural complexity suggests an optimal balance between carbonization and porosity formation, enhancing the material's adsorption potential. However, excessive porosity may compromise mechanical stability, making the material more fragile under certain operational conditions.

Overall, the 40–50 % rice husk content range appears to be optimal for achieving a well-structured porous network while maintaining material integrity. This suggests that a higher proportion of biomass precursor facilitates effective porosity development, thereby improving the composite's adsorption capacity, particularly for applications such as H_2S gas removal.

The EDS results in Figure 6 provide insights into the elemental composition of SRH@Ben composites and its variation with processing conditions. In Figure 6a, the elemental composition of SRH@Ben 30 % composite subjected to anaerobic pyrolysis at 350 °C, 400 °C, 450 °C, and 500 °C is shown. The major detected elements include C, O, N, Al, Si, Na, Mg, Ca, and Fe. Figure 6b illustrates the effect of rice husk content (10 %, 20 %, 30 %, 40 %, and 50 %) on the elemental composition of SRH@Ben composites pyrolyzed at 450 °C. To enhance the reliability of the analysis, EDS measurements were conducted at three distinct locations on each sample. The average atomic percentages of key elements (C, O, N, Al, and Si) were calculated and are presented in Figures 6c and 6d.

In Figure 6c, the elemental composition of SRH@Ben (30 % rice husk) is analyzed as a function of carbonization temperature (350–500 °C). Oxygen (O) remains the dominant element, with its content increasing slightly with temperature before stabilizing around 450 °C. This trend suggests the progressive oxidation of carbonaceous species or the retention of oxygenated functional groups. In contrast, the carbon (C) content decreases slightly with increasing temperature, likely due to thermal decomposition and gasification processes. The nitrogen (N) content remains relatively stable, indicating minimal nitrogen loss within the investigated temperature range. Silicon (Si) and aluminum (Al), originating from the bentonite structure, are present in minor quantities, with their concentrations remaining nearly unchanged across the temperature range. These results suggest that 450 °C is an optimal carbonization temperature, as it maintains a balanced elemental composition favorable for adsorption applications.

Figure 6d examines the influence of varying rice husk content (10–50 %) at a fixed carbonization temperature of 450 °C. The oxygen content shows a decreasing trend as the rice husk percentage increases, which can be attributed to the higher degree of carbonization of organic matter. Conversely, the carbon content increases with higher rice husk content, consistent with the expectation that a greater amount of organic precursor leads to enhanced carbon deposition. The concentrations of Si and Al remain relatively stable, confirming that the bentonite matrix is not significantly affected by the rice husk content. The final sample in Figure 4d represents SRH@Ben with 50 % rice husk, which was activated using a 0.15 M KOH solution followed by thermal treatment at 650 °C for 30 minutes. This sample exhibits a notable change in elemental composition, with a significant increase in potassium (K) content. The higher K concentration indicates the successful incorporation of KOH-derived residues into the material, which can enhance porosity and catalytic properties. Additionally, the oxygen content increases slightly compared to non-activated samples, likely due to the formation of oxygen-containing surface functionalities during activation. The enhanced porosity and modified surface chemistry of this KOH-activated sample suggest its potential for improved adsorption and catalytic performance.

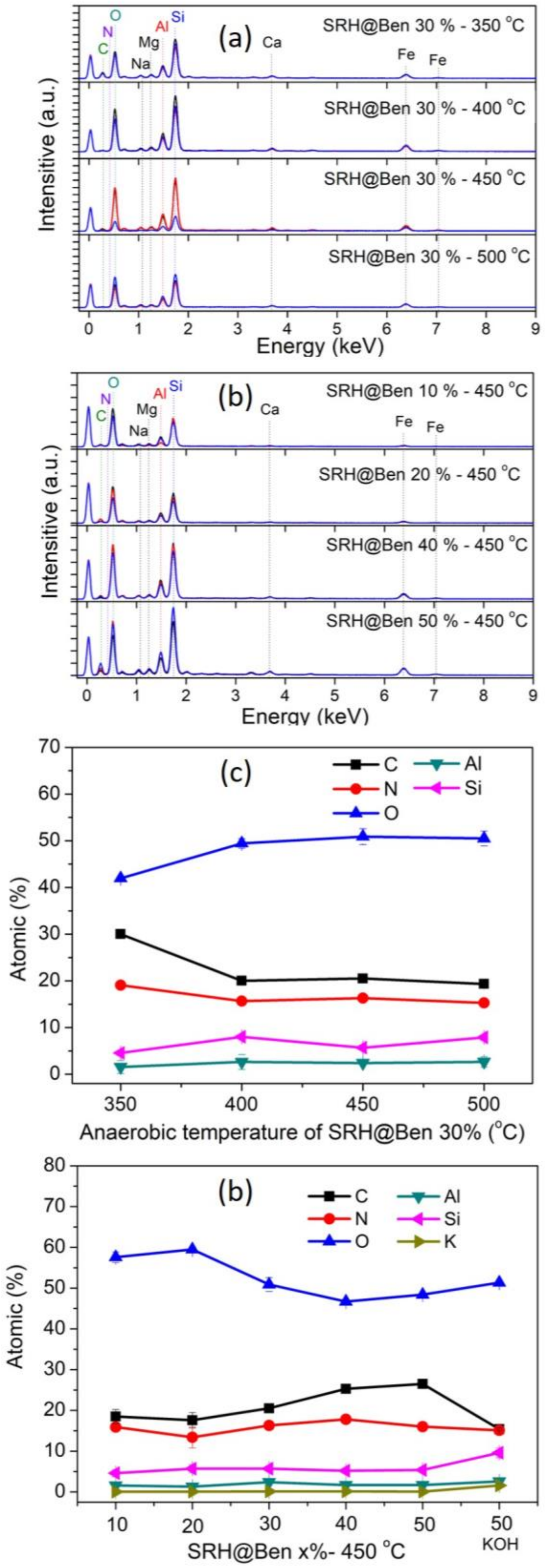

Figure 6. EDS spectra and atomic composition of SRH@Ben composites: (a) EDS spectra of SRH@Ben 30 % pyrolyzed at different temperatures (350, 400, 450, and 500 °C), (b) EDS spectra of SRH@Ben composites with varying rice husk content (10–50 wt%) pyrolyzed at 450 °C, (c) Atomic percentages of main elements (C, N, O, Al, Si) as a function of pyrolysis temperature for SRH@Ben 30 % and (d) Atomic percentages of elements (C, N, O, Al, Si, K) as a function of rice husk content for composites pyrolyzed at 450 °C.

Overall, these results demonstrate the significant influence of carbonization temperature, rice husk content, and chemical activation on the structural and elemental composition of SRH@Ben composites. These parameters can be systematically tailored to optimize the material for specific adsorption or catalytic applications.

The XRD patterns presented in Figure 7 provide insights into the structural evolution of SRH@Ben composites as a function of rice husk content and carbonization temperature. Figure 7a illustrates the XRD spectra of SRH@Ben samples with varying rice husk content (10–50 %) carbonized at 450 °C. The broad diffraction humps centered around 20–30° (2θ) indicate the presence of amorphous silica and/or carbon, primarily derived from the rice husk phase. As the rice husk content increases, the intensity of this amorphous peak becomes more pronounced, suggesting a higher concentration of silica within the composite. Notably, the absence of sharp crystalline peaks in the XRD patterns confirms the predominantly amorphous nature of the materials. Minor variations in peak intensity across different compositions indicate that the structural integrity of the bentonite matrix remains largely unaffected by the increasing rice husk content. The characteristic peaks at diffraction angle, 2θ = 20.7°, 26.5°, 36.3°corresponds to the planes (110), (210) and (124) of the bentonite material. These XRD patterns are in good agreement with the standard JCPDS file (card no.01-088-0891).

Figure 7b depicts the XRD patterns of SRH@Ben composites with 30 % rice husk, subjected to anaerobic treatment at temperatures ranging from 350 °C to 500 °C. A progressive increase in the intensity of the broad peak around 20–30° (2θ) is observed with rising temperature, further confirming the presence of amorphous silica and/or carbon structures. The gradual disappearance of minor crystalline features at higher temperatures suggests enhanced decomposition of organic matter and structural reorganization of silica phases. Despite these changes, the overall amorphous nature of the samples remains consistent, underscoring the thermal stability of the composite framework. These results demonstrate that SRH@Ben composites exhibit predominantly amorphous characteristics due to the incorporation of rice husk-derived silica and bentonite. The extent of amorphous phase formation is influenced by both rice husk content and processing temperature, with higher rice husk content and elevated temperatures promoting increased silica enrichment. Importantly, the structural integrity of the bentonite matrix remains intact, making these composites promising candidates for adsorption and catalytic applications that require high-surface-area amorphous materials. The characteristic peaks at diffraction angle, 2θ = 26.5°, 36.3°corresponds to the planes (210) and (124) of the bentonite material.

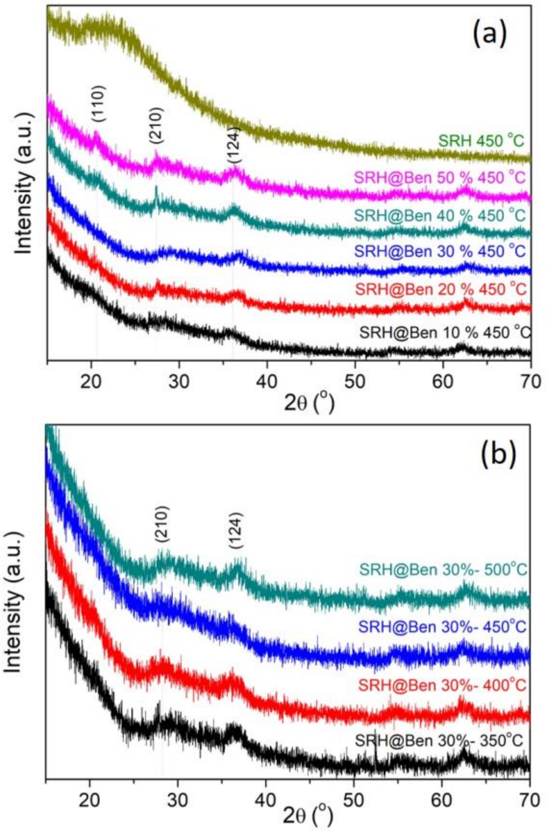

Figure 7. XRD patterns of SRH@Ben composites: (a) Effect of rice husk content (10–50 %) at 450 °C; (b) Effect of carbonization temperature (350–500 °C) on SRH@Ben with 30 % rice husk.

The H_2S adsorption performance of the synthesized materials is systematically evaluated in Figure 6, which illustrates the temporal variation of H_2S outlet concentration under different experimental conditions.

In Figure 8a, the H_2S outlet concentration profiles are compared for various composites, including Bran@Ben 30 %, LRH@Ben 30 %, SRH@Ben 30 %, and pure bentonite (Ben), treated at 400 °C and 450 °C. The "Free" curve, representing the control experiment without any adsorbent, shows a rapid increase in H_2S concentration, reaching saturation within a short time. In contrast, all composite materials exhibit significantly lower H_2S outlet concentrations, indicating effective adsorption capabilities. Among the tested samples, SRH@Ben treated at 450 °C demonstrates the lowest H_2S outlet concentration, suggesting superior adsorption efficiency. This can be attributed to its optimized structural and textural properties, which enhance active site availability for H_2S capture. Notably, the adsorption performance of Bran@Ben and LRH@Ben composites is also commendable, though slightly inferior to SRH@Ben, likely due to differences in porosity and surface chemistry. Pure bentonite (Ben) treated at both 400 °C and 450 °C shows significantly higher H_2S outlet concentrations, reaching saturation quickly. This indicates that pure bentonite has limited adsorption capacity compared to the composites, highlighting the importance of incorporating rice husk-derived components to enhance adsorption performance.

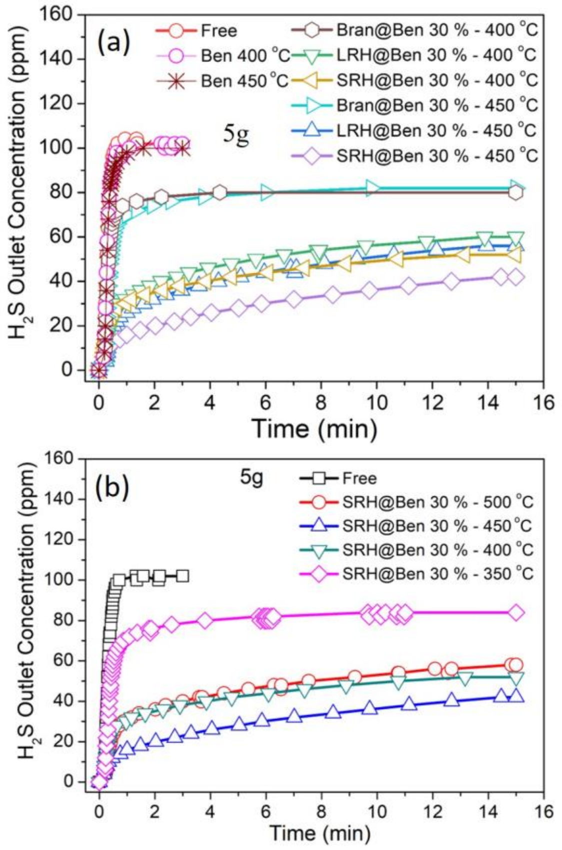

Figure 8. H_2S outlet concentration profiles over time for (a) different composites (Bran@Ben 30 %, LRH@Ben 30 %, SRH@Ben 30 %, and pure bentonite) thermally treated at 400 °C and 450 °C, and (b) SRH@Ben 30 % composites subjected to

carbonization at varying temperatures (350 °C to 500 °C).

Figure 8b further investigates the impact of carbonization temperature on SRH@Ben 30 %. The results reveal that increasing the carbonization temperature from 350 °C to 450 °C markedly enhances H_2S removal efficiency, likely due to the improved porosity and active site availability. However, at 500°C, a slight decline in performance is observed, possibly due to excessive thermal degradation leading to reduced surface functionality. Notably, SRH@Ben450 °C outperforms other samples, reinforcing the optimal thermal activation conditions for maximizing H_2S adsorption efficiency. These findings underscore the critical role of thermal treatment in tuning the physicochemical properties of the adsorbents for effective gas removal applications.

The H_2S adsorption performance, as illustrated in Figure 9 (using 5 g of material for each sample), offers critical insights into the impact of rice husk content and chemical activation on adsorption efficiency, along with a comparative evaluation against commercial adsorbents. Figure 9(a) highlights the effect of varying rice husk content on the H_2S adsorption performance of SRH@Ben composites. Among the tested samples, SRH@Ben 50 % exhibits the most efficient H_2S removal, maintaining the lowest outlet concentration over an extended duration. This superior adsorption performance can be attributed to the increased presence of carbonaceous material, which enhances pore development and active surface sites, leading to improved gas capture capability. In contrast, composites with lower rice husk content (10–20 %) show a rapid breakthrough, indicating limited adsorption capacity due to insufficient carbon content and surface area.

Notably, rice husk content beyond 50 % was not investigated in this study due to mechanical limitations in pellet formation. At higher rice husk ratios, the structural integrity of the composite pellets significantly deteriorates, making them prone to breakage and fragmentation. This mechanical instability compromises practical applicability, as fragile pellets would result in increased pressure drop and handling difficulties in industrial adsorption systems. Therefore, the 50 % rice husk composite was identified as the optimal formulation, balancing enhanced adsorption efficiency with sufficient mechanical strength for real-world applications.

Figure 9(b) compares the optimal composite, SRH@Ben 50%-450 °C, with its KOH-activated counterpart (0.15 M) and two commercial adsorbents: a carbon-based pellet (Com. Pellet C) and an iron oxide-based pellet (Com. Pellet F_xO_γ). The activation with KOH further improves H_2S adsorption, as evidenced by a lower breakthrough concentration and prolonged retention time, likely due to enhanced surface area and active functional groups. Comparatively, the commercial carbon pellet exhibits significantly weaker performance, with rapid saturation, while the iron oxide pellet demonstrates superior efficiency, approaching the adsorption behavior of the optimized SRH@Ben 50 % - 450 °C-KOH sample. These findings underscore the efficacy of tailored bentonite-carbon composites in H_2S removal applications, with potential competitiveness against commercial adsorbents.

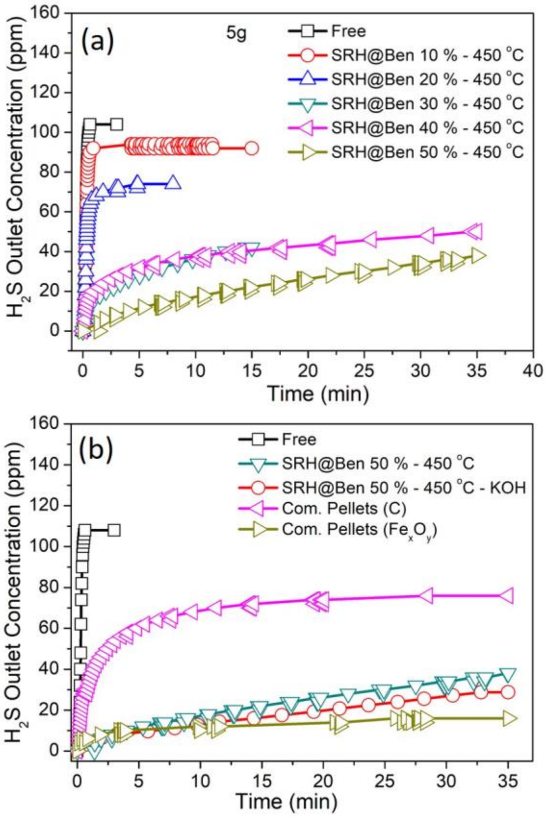

Figure 9. H_2S adsorption performance of SRH@Ben composites: (a) Effect of rice husk content (10–50 %) on H_2S breakthrough behavior; (b) Comparison of the optimized SRH@Ben 50 % - 450 °C composite, with and without KOH activation, against commercial adsorbents (carbon-based and iron oxide-based pellets).

The adsorption capacity (Cs) is one of the key factors for evaluating the adsorption performance of the filter material. The H_2S adsorption capacity is determined by integrating the area above the breakthrough curve, considering the inlet H_2S concentration, adsorbent mass, and flow rate. It is calculated using the following equation:[12]

$$C_s = 10^{-3}\frac{M_s FP}{m_a} C_{\mathrm{Sin}} \int_0^{t_b} \left(1 - \frac{C_{Sout}}{C_{\mathrm{Sin}}}\right) dt$$

where: C_s is the H_2S adsorption capacity (mg/g); M_s is the molecular weight of sulfur (32 g/mol); m_a is the mass of the adsorbent (g); C_{Sin} is the inlet H_2S concentration (108 ppm ≈ 150.538 mg/m^3); C_{Sout} is the outlet H_2S concentration (mg/m^3); F is the total gas flow rate (0.2 L/min); and t_b is the adsorption time until the outlet concentration exceeds the breakthrough point (min). In this study, the H_2S capture capacity is evaluated at $t = 35$ minutes to facilitate a comparative analysis of the performance of different samples.

The H_2S adsorption capacities of the synthesized materials, measured at $t = 35$ minutes, are presented in the Figure 10. The results reveal significant variations in performance among the tested samples, highlighting the influence of composition and activation on adsorption efficiency.

The SRH@Ben 50 % sample treated at 450 °C demonstrates an H_2S adsorption capacity of 2.23 mg/g, reflecting moderate performance. This is attributed to its optimized rice husk content and carbonization temperature, which enhance porosity and active site availability. Further improvement is observed in the SRH@Ben 50 % sample activated with KOH, which achieves a capacity of 2.34 mg/g. This enhancement is likely due to the chemical activation process, which increases surface area and introduces functional groups that facilitate H_2S capture.

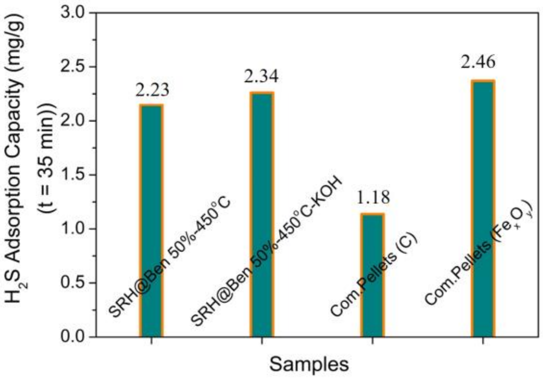

Figure 10. H_2S adsorption capacity (mg/g) of various materials, including SRH@Ben composites and commercial pellets, measured after 35 minutes of adsorption using 5 g of material for each sample.

Note: Due to the time-consuming nature and complexity of the H_2S adsorption measurements—requiring separate sample preparation, and precise quantification for each run—replicate experiments were not performed in this study. However, strict control of experimental conditions and careful instrument calibration were employed to ensure the reliability of the results. Further studies involving replicate measurements are planned to assess the statistical variations in adsorption performance.

When compared to commercial pellets, the synthesized SRH@Ben samples exhibit significantly superior performance. The commercial pellet Com.Pellets (C) shows a notably lower adsorption capacity of 1.18 mg/g, less than half that of the SRH@Ben materials. This stark difference underscores the effectiveness of the tailored composition and activation processes used in the fabrication of SRH@Ben composites. Additionally, the adsorption capacity of the SRH@Ben samples is comparable to that of the commercial pellet Com.Pellets (Fe_xO_y), which achieves 2.46 mg/g. This indicates that the synthesized materials are not only highly efficient but also competitive with commercially available alternatives.

The superior performance of the SRH@Ben samples can be linked to their enhanced structural properties, such as increased porosity and the presence of oxygen-containing functional groups, which are critical for H_2S adsorption. These findings highlight the potential of the synthesized materials as cost-effective and sustainable solutions for H_2S capture, offering performance that rivals or exceeds that of commercial products.

4. DISCUSSION

4.1. Effect of thermal treatment and rice husk content on adsorption performance

The adsorption performance of the SRH@Ben composites was strongly influenced by thermal treatment temperature and rice husk content, as evidenced by the breakthrough curves and adsorption capacity measurements. The optimal composite, SRH@Ben 50% - 450 °C, exhibited the highest H_2S adsorption capacity (2.23 mg/g), which can be attributed to a well-developed porous structure and enhanced surface reactivity. Increasing the carbonization temperature from 350 °C to 450 °C led to an improvement in adsorption performance due to the removal of volatile organic compounds and the formation of micropores and mesopores. However, at 500 °C, a slight decline in adsorption capacity was observed, likely due to excessive structural degradation and reduced surface functionalities.

Similarly, the increase in rice husk content (10–50 %) resulted in enhanced adsorption performance, with the highest efficiency observed at 50 % rice husk content. This is likely due to the increased carbon content, which contributes to a higher surface area and greater availability of active sites for H_2S adsorption. However, further increasing the rice husk content beyond 50 % was not explored in this study due to structural instability, as composites with higher rice husk content tend to be mechanically weaker and more prone to disintegration during handling and testing.

4.2. Mechanism of H_2S Adsorption on SRH@Ben Composites

The adsorption of H_2S onto SRH@Ben composites is governed by a combination of physisorption, chemisorption, and catalytic oxidation mechanisms, facilitated by the structural and chemical properties of both activated carbon (from rice husk) and bentonite.

4.2.1. Physisorption via porous structure

The well-developed pore structure of the carbonized rice husk phase provides a high surface area and multiple adsorption sites for H_2S molecules. The presence of micropores enhances van der Waals interactions, allowing gas molecules to be retained within the porous network. Additionally, mesopores play a critical role in gas diffusion, facilitating the accessibility of active sites within the material. The increase in adsorption capacity after KOH activation (from 2.23 mg/g to 2.34 mg/g) further supports this, as KOH treatment is known to enhance porosity and improve the dispersion of functional groups on the adsorbent surface.

4.2.2. Chemisorption via functional groups

The interaction between H_2S and SRH@Ben composites is also influenced by the oxygen-containing functional groups present on the activated carbon surface, such as carboxyl (-COOH), hydroxyl (-OH), and carbonyl (-C=O) groups. These functional groups can react with H_2S, forming surface-bound sulfur species (e.g., elemental sulfur or polysulfides), thereby enhancing adsorption efficiency. The presence of bentonite further contributes to adsorption through its hydrophilic nature and cation exchange capacity, which facilitates the trapping of H_2S molecules via electrostatic interactions.

4.2.3. Catalytic oxidation and sulfur deposition

A portion of the adsorbed H_2S is likely oxidized into elemental sulfur (S) or sulfate (SO_4^{2-}) under ambient conditions. The presence of metal oxides in bentonite may serve as catalytic sites, accelerating this oxidation process. The sulfur species formed during adsorption may block adsorption sites over time, leading to gradual saturation. This explains why, after extended adsorption cycles, a reduction in breakthrough time was observed, indicating progressive deactivation of adsorption sites due to sulfur deposition.

4.3. Comparison with Commercial Adsorbents

To evaluate the practical applicability of SRH@Ben composites, their adsorption performance was compared with commercial adsorbents, including carbon-based (Com. Pellet C) and iron oxide-based (Com. Pellet F_xO_y) materials. The results indicate that: (1) SRH@Ben 50 % - 450 °C (2.23 mg/g) outperformed commercial carbon-based adsorbents (1.18 mg/g), demonstrating the superior adsorption efficiency of the composite material; (2) KOH-activated SRH@Ben (2.34 mg/g) exhibited adsorption capacity comparable to iron oxide-based adsorbents (2.46 mg/g), suggesting that the composite material is a viable alternative to more expensive commercial sorbents.

These findings emphasize that the synergy between bentonite and activated carbon significantly enhances H_2S removal efficiency, making SRH@Ben a cost-effective and sustainable solution for biogas purification.

5. CONCLUSION

In conclusion, this study demonstrates the successful synthesis and optimization of SRH@Ben composites for H_2S adsorption, highlighting the critical role of tailored composition, thermal treatment, and chemical activation in enhancing adsorption performance. The SRH@Ben 50 % - 450 °C composite, with its uniform and dense structure, achieved an H_2S adsorption capacity of 2.23 mg/g, which increased to 2.34 mg/g after KOH activation. These values are more than double that of the commercial carbon-based pellet (1.18 mg/g) and comparable to the iron oxide-based pellet (2.46 mg/g), underscoring the superior performance of the synthesized materials. The enhanced adsorption capacity is attributed to the optimized porosity, surface area, and functional groups introduced through thermal and chemical activation. These findings position SRH@Ben composites as cost-effective, sustainable, and highly efficient alternatives for H_2S capture, with significant potential for industrial applications. Future work will focus on scaling up production and evaluating long-term performance under real-world conditions.

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