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PHYSICOCHEMICAL AND CHEMISORPTION PROPERTIES OF MODIFIED LOCAL BENTONITE SORBENTS FOR ACID GAS REMOVAL FROM EXPANDER GAS STREAMS

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Abstract

The removal of acidic components such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2) from expander gas streams is essential for improving process efficiency and preventing equipment corrosion in gas processing industries. In this study, modified chemisorbents based on locally available bentonite were synthesized through chemical modification and thermal activation and evaluated for acid gas removal under low-temperature conditions.

The modification significantly improved the structural properties of the sorbents, increasing the specific surface area from 62 to 176 m^2/g and pore volume from 0.18 to 0.41 cm^3/g. Sorption experiments showed that the H_2S adsorption capacity increased by approximately 3–4 times compared to natural bentonite, reaching 67 mg/g. Temperature studies confirmed the exothermic nature of adsorption, with optimal performance observed at 20–30°C. Dynamic column experiments demonstrated high sorbent efficiency and favorable mass transfer characteristics.

The results indicate that modified sorbents derived from local raw materials are promising candidates for industrial purification of expander gas streams, offering potential advantages in cost reduction, operational efficiency, and environmental safety.

Keywords: expander gas; chemisorption; modified bentonite; acid gas removal; hydrogen sulfide; carbon dioxide; adsorption capacity; local sorbents; gas purification; aluminosilicates.

Introduction

The removal of acid gases, primarily hydrogen sulfide (H_2S) and carbon dioxide (CO_2), from natural gas streams remains an important challenge in gas processing due to their detrimental effects on equipment integrity, process efficiency, and environmental safety. Expander units are widely used in hydrocarbon recovery and low-temperature separation processes; however, the gas streams leaving these units often contain residual acid components that may negatively affect downstream operations. Therefore, the development of efficient purification technologies suitable for low-temperature conditions is of significant industrial interest.

Conventional gas purification methods such as amine absorption, membrane separation, and cryogenic processes are effective but often associated with high energy consumption, operational costs, and process complexity [1–3]. In contrast, adsorption and chemisorption technologies offer advantages including operational simplicity, lower energy requirements, and adaptability to varying process conditions [4].

Solid sorbents based on aluminosilicates, zeolites, activated carbons, and metal oxides have demonstrated strong potential for acid gas removal. Sorption efficiency is largely governed by structural and physicochemical properties, including surface area, pore structure, and the nature of active adsorption sites [5–7]. Chemical modification of aluminosilicate materials, particularly through incorporation of metal species, can significantly enhance chemisorption performance and adsorption kinetics [6,8].

Recently, locally available mineral materials such as bentonite have attracted increasing attention due to their low cost, abundance, environmental compatibility, and regeneration capability [9]. Modified bentonite-based sorbents have shown promising performance in acid gas removal owing to their layered structure and ion-exchange capacity, which enable the formation of active chemisorption centers.

Despite these advances, limited information is available regarding the physicochemical and chemisorption properties of modified local sorbents specifically designed for expander gas purification under low-temperature conditions. Therefore, this study focuses on the development of modified bentonite-based sorbents and evaluation of their efficiency for H_2S and CO_2 removal from expander gas streams.

Local aluminosilicate bentonite obtained from the Zarafshan deposit was used as the precursor material for sorbent synthesis. The raw material was purified from mechanical impurities, dried at 110 °C for 6 h, and ground to a particle size of 0.1–0.5 mm. Metal salts including iron (III) chloride ($FeCl_3$), copper (II) sulfate ($CuSO_4$), and sodium hydroxide (NaOH) of analytical grade were used as modifying agents and prepared using distilled water.

Bentonite was selected due to its layered aluminosilicate structure, ion-exchange properties, and availability of surface functional groups suitable for adsorption and chemisorption processes [10].

Modified chemisorbents were synthesized through chemical modification followed by thermal activation. Bentonite samples were mixed with aqueous metal salt solutions in a solid-to-liquid ratio of 1:5 and stirred continuously for 6 h at ambient temperature to ensure uniform distribution of active components. The obtained samples were filtered and dried at 105 °C for 8 h.

Thermal activation was carried out in a muffle furnace at temperatures between 400–500 °C for 3 h. Thermal treatment promotes the formation of dispersed metal oxide active sites on the sorbent surface and enhances structural stability, leading to improved adsorption performance [11].

The structural and textural characteristics of the synthesized sorbents were determined using nitrogen adsorption–desorption analysis based on the Brunauer–Emmett–Teller (BET) method to evaluate specific surface area, pore volume, and average pore diameter. The BET technique is widely applied for characterization of porous materials and provides essential information for understanding adsorption behavior and surface reactivity [12].

Sorption experiments were conducted using a dynamic fixed-bed column system. The adsorption column had an internal diameter of 20 mm and a height of 300 mm and was packed with a known mass of sorbent. A model gas mixture simulating industrial expander gas composition was prepared with the following components:

CH_4 – 90–95%
CO_2 – 3–5%
H_2S – 0.2–1.0%
N_2 – balance

The gas flow rate was controlled using a mass flow controller, and experiments were performed at temperatures of 20–60 °C and pressures up to 0.5 MPa. The inlet and outlet concentrations of H_2S were measured using a gas analyzer. Dynamic adsorption experiments allow evaluation of sorbent performance under conditions close to industrial gas purification processes.

Adsorption kinetics were analyzed using a second-order kinetic model to determine adsorption rate constants and equilibrium capacity. Thermodynamic parameters, including Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were calculated from adsorption equilibrium data using standard thermodynamic equations. These parameters are commonly used to evaluate adsorption spontaneity and heat effects.

To evaluate the effectiveness of the synthesized chemisorbents derived from local raw materials, their structural, textural, and sorption properties were investigated comprehensively. The physicochemical characteristics of sorbents play a crucial role in determining the efficiency of acid gas removal from gas streams. In particular, parameters such as specific surface area, pore structure, and distribution of active adsorption centers significantly influence adsorption kinetics, thermodynamics, and overall sorption performance.

Chemical modification of local aluminosilicate minerals resulted in the formation of additional active centers and the development of a more accessible pore network within the sorbent structure. These structural improvements enhance the interaction between acidic gas molecules (H_2S and CO_2) and the sorbent surface, thereby increasing sorption capacity and selectivity. Similar structural improvements after modification of clay-based sorbents have been reported in recent studies, confirming the effectiveness of metal-functionalized aluminosilicates for gas purification applications. The structural parameters of synthesized sorbents were determined using BET analysis, and the results are presented in table 1.

Table 1 Textural parameters of sorbents

Sample	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)
Natural bentonite	62	0.18	11.6
Modified sorbent-1	148	0.32	8.9
Modified sorbent-2	176	0.41	7.4

The results indicate that chemical modification significantly improves the structural properties of the sorbents. The specific surface area increased nearly threefold compared to natural bentonite, while pore volume also increased substantially. This enhancement can be attributed to partial destruction of the layered structure during thermal treatment and formation of new mesoporous channels, which improve accessibility of adsorption sites.

A reduction in average pore diameter was observed for modified samples, indicating the formation of more uniform pore structures. Such structural transformation is beneficial for adsorption processes because smaller pores increase the probability of interaction between gas molecules and active centers. Similar trends have been reported for metal-modified clay sorbents used for acid gas removal, where increased surface area and controlled pore structure led to enhanced sorption efficiency.

From an industrial perspective, the increase in surface area and pore volume is particularly important, as it directly influences sorbent utilization efficiency and operational lifetime in fixed-bed adsorption systems. The adsorption capacities for H_2S and CO_2 are presented in table 2.

Table 2 Sorption capacity of sorbents

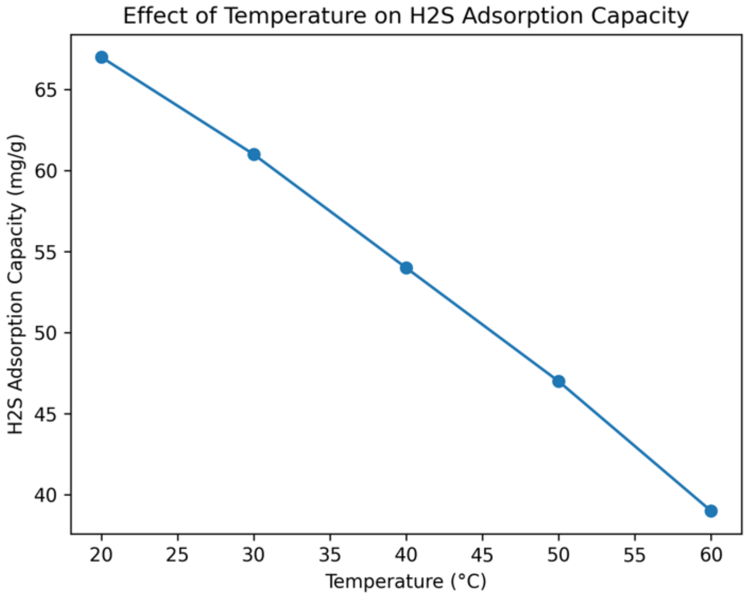
Sample	H_2S Adsorption (mg/g)	CO_2 Adsorption (mg/g)
Natural bentonite	18	9
Modified sorbent-1	54	28
Modified sorbent-2	67	34

The adsorption capacity of modified sorbents increased by approximately 3–4 times compared with natural bentonite. The highest H_2S adsorption capacity reached 67 mg/g, indicating significant improvement in sorption performance.

This enhancement can be explained by the formation of metal oxide active sites during modification, which promote chemisorption reactions between H_2S molecules and the sorbent surface. Metal ions such as Fe^{3+} and Cu^{2+} are known to interact strongly with sulfur-containing compounds through chemical bonding mechanisms, resulting in higher selectivity and adsorption capacity.

The relatively lower adsorption capacity for CO_2 compared to H_2S suggests that chemisorption mechanisms dominate the sorption process, as CO_2 removal is typically governed by weaker physical adsorption interactions on aluminosilicate surfaces.

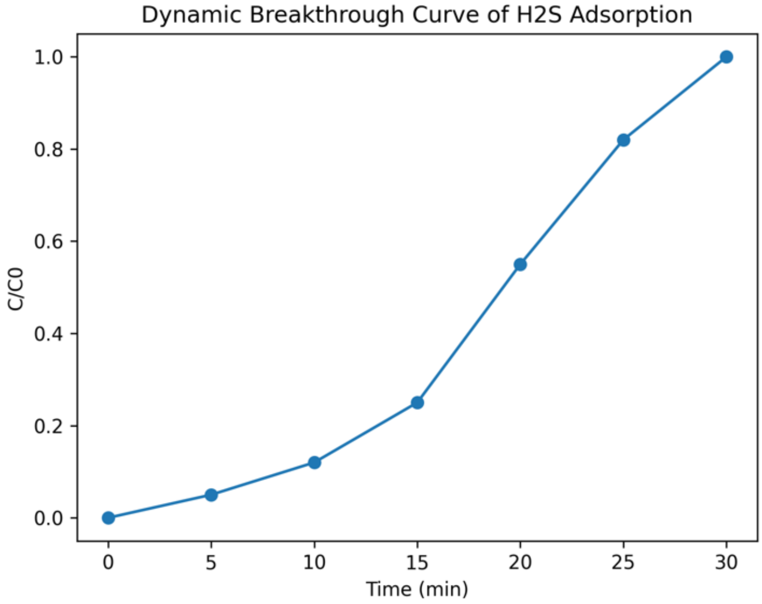
The effect of temperature on H_2S adsorption capacity is shown in figure 1.



The adsorption capacity decreases with increasing temperature, indicating that the adsorption process is exothermic in nature. At higher temperatures, increased molecular kinetic energy reduces the interaction time between gas molecules and active sites, thereby lowering sorption efficiency.

The highest adsorption capacity was observed in the temperature range of 20–30 °C, which corresponds well to the operating conditions of expander gas streams. This finding is particularly significant from a technological perspective, as it confirms the suitability of the synthesized sorbents for low-temperature gas purification processes without requiring additional cooling.

Dynamic adsorption behavior is essential for evaluating industrial applicability. The breakthrough curve obtained from column experiments is presented in figure 2.



The relatively long saturation time observed for modified sorbents indicates high dynamic adsorption capacity and efficient utilization of the sorbent bed volume. The gradual increase in the outlet concentration suggests uniform mass transfer within the adsorption column and absence of significant channeling effects.

Such dynamic performance is critical for industrial applications, as it directly influences operational cycle time, regeneration frequency, and overall process economics. The obtained results demonstrate that modified sorbents derived from local raw materials possess sufficient mechanical and sorption stability for continuous operation conditions.

Kinetic analysis showed that the second-order kinetic model provides a better correlation with experimental data, indicating that the adsorption process is primarily controlled by chemical interactions between gas molecules and active surface sites. This confirms that chemisorption is the dominant mechanism governing H_2S removal.

The overall adsorption mechanism likely involves the formation of metal sulfide species through chemical reactions between H_2S and metal oxide active centers on the sorbent surface. Such mechanisms have been widely reported for metal-modified sorbents and explain the high selectivity toward sulfur-containing compounds.

The modification of local bentonite significantly improves sorbent structure and increases the efficiency of H_2S removal due to the presence of reactive metal centers. Low-temperature conditions typical for expander gas streams were found to be optimal for adsorption performance, further confirming the applicability of the developed sorbents for industrial gas purification.

Modified chemisorbents based on local bentonite were successfully synthesized and evaluated for acid gas removal from expander gas streams. Chemical modification and thermal activation significantly enhanced structural properties, increasing the specific surface area and pore volume, which resulted in a 3–4 fold improvement in hydrogen sulfide adsorption capacity compared to natural bentonite.

The adsorption process exhibited exothermic behavior with optimal performance at 20–30 °C, consistent with expander gas operating conditions. Dynamic and kinetic analyses confirmed high sorption efficiency and indicated that chemisorption interactions between H_2S molecules and metal-containing active sites dominate the adsorption mechanism.

The developed sorbents demonstrate strong potential for industrial gas purification applications due to their high efficiency, low cost, and availability of local raw materials. Further studies should address regeneration performance and long-term operational stability.

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