CHEMICAL ENGINEERING TRANSACTIONS
VOL. 122, 2025

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Bohong Wang, Guo Ren Mong, Petar S. Varbanov

ISBN 979-12-81206-23-6; **ISSN** 2283-9216

DOI: 10.3303/CET25122014

Polyaniline as a Selective Adsorbent for NO_2, SO_2 and H_2S: Thermal Influence and Gas – Specific Trends

Anh Kien Le, Tuan Viet Tran, Van Linh Nguyen*

Institute for Tropical Technology, 57A Truong Quoc Dung Street, Ward Phu Nhuan, Ho Chi Minh City, Vietnam
linh.vittep@gmail.com

This study presents a comprehensive analysis of polyaniline's adsorption capacity for three gases: nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and hydrogen sulfide (H_2S). Adsorption isotherms were investigated at various temperatures (293 K, 298 K, 303 K, 308 K, 313 K) to evaluate the effect of temperature on adsorption capacity. The results show that polyaniline exhibits superior adsorption capacity for SO_2 of 250mg/g at 293 K and 10^5 Pa, achieving the highest adsorption capacity, followed by H_2S of 200 mg/g and NO_2 of 190 mg/g under the same reaction conditions. Notably, polyaniline demonstrated SO_2 adsorption capability even at low fugacity. Increasing temperature reduced the adsorption capacity for all gases, consistent with the physisorption process. This study provides deep insights into the interaction between polyaniline and these gases, paving the way for the design of polyaniline-based adsorbent materials.

1. Introduction

Air pollution stands as one of the most pressing environmental challenges humanity faces, with widespread and severe impacts on public health, natural ecosystems, and global climate stability. Rapid urbanization and an increasing number of vehicles have led to the accumulation of various pollutants in the atmosphere, most notably toxic gases like nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) (Bhandarkar., 2013). These gases not only degrade air quality but also directly contribute to health and environmental problems.

NO_2 and SO_2 are primary byproducts of incomplete or high-temperature combustion of fossil fuels in energy industries, metallurgy, chemical production, and from internal combustion engine exhaust (Hannun and Razzaq., 2022). When released into the atmosphere, NO_2 and SO_2 can react with water vapor and other oxidizing agents to form nitric acid (HNO_3) and sulfuric acid (H_2SO_4), leading to acid rain. Acid rain not only corrodes buildings and infrastructure but also severely degrades agricultural land, reducing crop yields, harming aquatic life, and destroying forests, thereby upsetting ecological balance. From a human health perspective, even short-term inhalation of NO_2 and SO_2 can irritate the respiratory tract, leading to coughing, shortness of breath, and chest tightness (Ćurić et al., 2021). Long-term exposure to low concentrations or acute exposure to high concentrations can exacerbate chronic respiratory diseases such as asthma and chronic obstructive pulmonary disease, and increase the risk of cardiovascular diseases, even leading to premature death.

Alongside NO_2 and SO_2, H_2S is another highly toxic gas, often overlooked in general discussions about air pollution but posing a serious threat in specific environments. H_2S is a product of anaerobic decomposition of organic matter, common in landfills, wastewater treatment systems, stagnant ponds, as well as in the oil and gas extraction industry and pulp production (Smet et al., 1998). A prominent characteristic of H_2S is its distinctive rotten egg smell at low concentrations, but more alarmingly, at high concentrations, it rapidly paralyzes the olfactory nerves, preventing victims from detecting the presence of this toxic gas. H_2S directly attacks the central nervous system and respiratory system, potentially causing nausea, dizziness, loss of consciousness, convulsions, and at very high concentrations, leading to respiratory failure, coma, and almost immediate death. Controlling and eliminating H_2S is extremely important for industrial safety and public health.

Given the immense challenges posed by these toxic gases, developing effective and sustainable solutions for adsorbing and removing them from the environment is a top priority. Traditional technologies such as activated carbon adsorption, alkaline solution absorption, or catalytic oxidation, while somewhat effective, often come with

Paper Received: 2 August 2025; Revised: 24 September 2025; Accepted: 15 December 2025
Please cite this article as: Le A.K., Tran T.V., Nguyen V.L., 2025, Polyaniline as a Selective Adsorbent for NO_2, SO_2 and H_2S: Thermal Influence and Gas – Specific Trends, Chemical Engineering Transactions, 122, 79-84 DOI:10.3303/CET25122014

significant limitations. Activated carbon has a good adsorption capacity but it is difficult to fully regenerate and can become saturated quickly (Zanella et al., 2014). Liquid absorption processes often generate secondary waste streams that require costly and complex treatment. Catalytic methods typically require high temperatures and specialized reaction conditions, increasing operating costs and making them unsuitable for widespread application at room temperature. These limitations have driven the scientific and engineering communities to continuously seek new adsorbent materials with superior characteristics in terms of performance, reusability, stability, and optimal cost, especially materials that can operate effectively under ambient environmental conditions.

Polyaniline (PANi), one of the most extensively studied conductive polymers, has emerged as a promising candidate for gas adsorption and sensing applications. PANi possesses a range of properties including electrical conductivity that can be flexibly tuned through doping, good chemical and thermal stability, simple and low-cost synthesis, and strong interaction with various gas molecules (Mais et al., 2021). This capability stems from PANi conjugated structure, which allows for electronic interactions and redox reactions with gas molecules, leading to changes in the polymer's surface physical and chemical properties. The development of nanotechnology has opened new opportunities to optimize PANi (Ahmad et al., 2017). Synthesizing PANi in nanostructures (nanofibers, nanotubes, nanoparticles, or in combination with other nanomaterials like graphene) can significantly increase its specific surface area, enhance the number of active adsorption sites, improve mass transfer rates, thereby substantially boosting adsorption efficiency and sensitivity.

Minisy and colleagues studied the adsorption of organic substances onto polyaniline-based nanocomposite structures (Minisy et al., 2021). Polyaniline-based composites proved to be better dye adsorbents than polyaniline material alone. Dye adsorption followed pseudo-second-order kinetics and was well described by the Temkin isotherm model. The maximum adsorption capacity achieved was 111 mg/g. Oussama and colleagues investigated the synthesis of polyaniline-based nanocomposite materials for the removal of cefixime. A hybrid $Bi_{12}TiO_{20}$/PANi system was proposed as a catalyst (Baaloudj et al., 2023). Results showed that this hybrid system could remove very high concentrations of Cefixime, up to 30 mg/L, with nearly 100% removal within just 2 h. Despite the recognized potential of PANi in treating exhaust gases, there remains a significant gap in comprehensive studies comparing PANi adsorption capabilities for various important pollutant gases like NO_2, H_2S, and SO_2 under the same controlled experimental conditions. Detailed investigation into the effect of temperature on the adsorption process is crucial for evaluating the practical applicability of the material in different environments and operating conditions.

This study aims to comprehensively evaluate the adsorption capacity of Polyaniline for NO_2, H_2S, SO_2, focusing on determining detailed adsorption isotherms at different temperatures using the Grand Canonical Monte Carlo (GCMC) simulation method to elucidate the relationship between fugacity, temperature, and adsorption capacity. The paper will meticulously analyze the adsorption results, compare the adsorption performance among the three gases, and explain the influence of temperature. This research will not only provide critical insights into the interactive mechanisms between PANi and pollutant gases but also reinforce PANi potential as an effective and sustainable adsorbent material, opening new prospects for future air pollution control and environmental monitoring solutions.

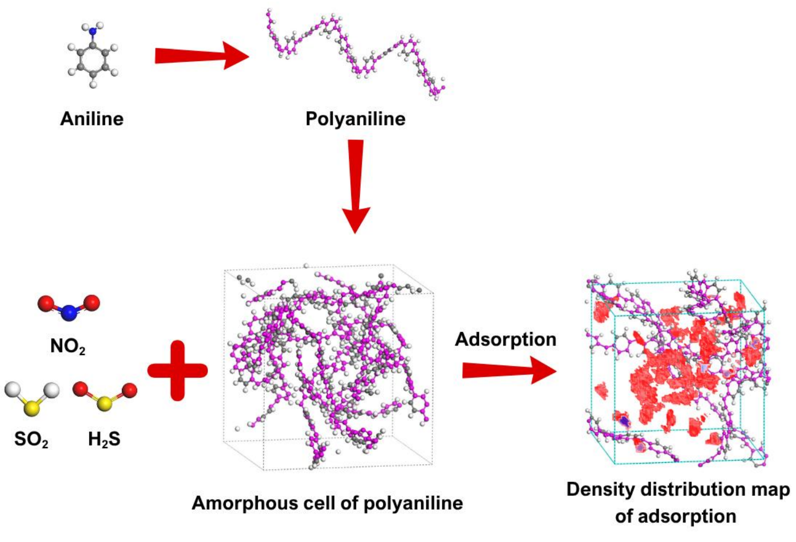

Figure 1: Models

2. Materials and Methods

2.1 Material Model

The polyaniline structure was constructed using the Amorphous Cell Tools module in BIOVIA Material Studio 2017 software (BIOVIA., 2017). Polyaniline molecules were randomly packed into a 23.89 Å cubic simulation cell with three-dimensional periodic boundary conditions. Van der Waals interactions were set to 12.5 Å, and the Ewald summation method with an accuracy of 10^{-3} KCal.mol-1 was used to account for long-range electrostatic interactions (Figure 1).

2.2 Simulation method

Calculations used the Sorption Tools module with an optimized molecular potential for the condensed phase force field. The parameters selected included critical state parameters and van der Waals parameters. One of the create, translate, rotate, and delete operations in the Monte Carlo steps was chosen for adsorbates, which were considered rigid spheres in the simulation. The adsorption process at various fugacity values ranging from 10^{-8} to 10^{5} Pa was performed through a series of simulations (Jiang et al., 2022).

2.3 Adsorption energy

In quantum chemical calculations, determining the adsorption energy (E_{ads}) is one of the most crucial parameters. Where: $E_{surf+gas}$ is total energy of the adsorbate and the gas molecule; E_{surf} is the surface energy of the isolated adsorbent; E_{gas} is the energy of the isolated gas molecule.
Adsorption energy indicates the strength of the interaction between an adsorbate molecule and the adsorbent. It is typically calculated based on the total energies of the individual systems using the following Eq(1) (Bahamon et al., 2021). Calculating the adsorption energy aims to clarify the interaction mechanism between molecules and surfaces, playing a crucial role in materials research.

$$E_{ads} = E_{surf+gas} - E_{surf} - E_{gas} \tag{1}$$

3. Results and Discussion

3.1 Effect of Temperature

Results showed that polyaniline exhibited the highest adsorption capacity for SO_2, followed by H_2S and the lowest for NO_2. By studying adsorption isotherm at various temperatures (293 K, 298 K, 303 K, 308 K, 313 K), a consistent trend was observed: the adsorption capacity of polyaniline for all three gases tended to decrease as temperature increased.

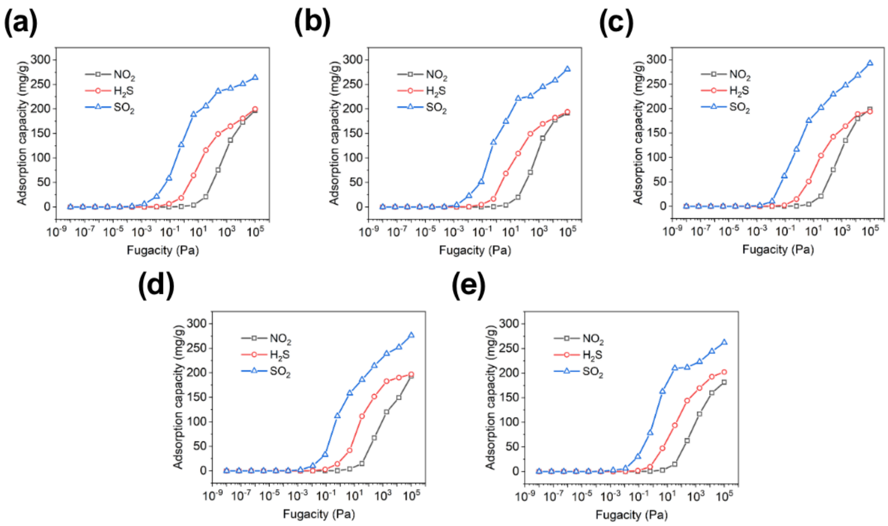

Figure 2: Adsorption isotherm with different temperature: (a) 293 K, (b) 298 K, (c) 303 K, (d) 308 K, (e) 313 K

In Figure 2, SO_2 demonstrated the superior adsorption capacity, with H_2S and NO_2 trailing. The optimal temperature for adsorption was 303 K, where SO_2 achieved an impressive 293 mg/g, H_2S reached 200 mg/g and NO_2 registered 198 mg/g all measured at 10^5 Pa. As the temperature climbed from 293 K to 303 K, the gases' adsorption capacities improved. Pushing the temperature beyond 303 K to 308 K caused a noticeable drop in adsorption. The lowest capacities were observed at 313 K, with SO_2 at 260 mg/g, H_2S at 180 mg/g and NO_2 at 170 mg/g, also at 10^5 Pa.

This distinct difference in adsorption capacity can be explained based on the physicochemical properties of each gas molecule and their interaction capabilities with polyaniline. SO_2 is a strong polar molecule (dipole moment 1.62 D) and is acidic (Yang et al., 2024). It can interact strongly with amine and imine groups on the polyaniline chain through hydrogen bonding and Lewis's acid-base interactions. H_2S also has weaker acidity (dipole moment 0.97 D), allowing interaction with polyaniline (Gautam and Panda., 2021). Conversely, NO_2 is a free radical, and although it has reactive potential, its physical adsorption interaction with polyaniline appears weaker than that of the other two gases.

The trend of decreasing adsorption capacity with increasing temperature is characteristic of physisorption. As temperature increases, the kinetic energy of gas molecules increases, reducing their ability to be retained on the adsorbent surface and simultaneously promoting desorption. Despite this decline, polyaniline still showed significant adsorption capacity at 313 K, which is important for practical applications where ambient temperature can fluctuate.

3.2 Comparison between Gas Pairs

Figure 3 provides a more detailed insight into the differences in polyaniline's simultaneous adsorption capabilities for these gases investigated at 303 K.

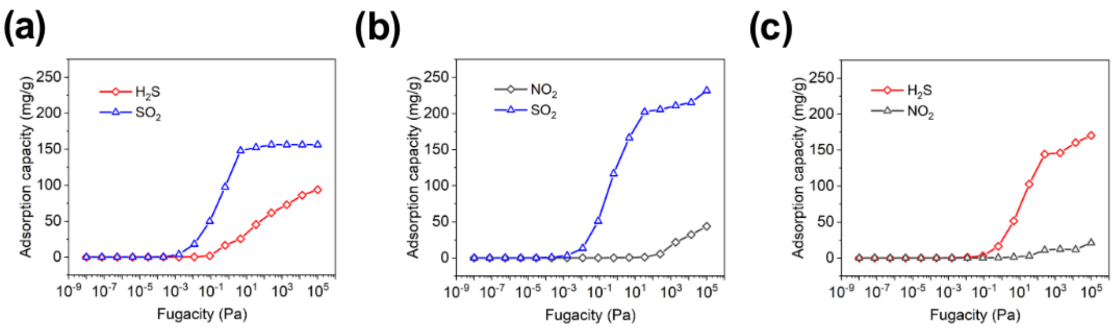

Figure 3: Adsorption isotherm with different pairs of gases: (a) SO_2 H_2S, (b) SO_2, NO_2, (c) H_2S, NO_2

Figure 3a clearly shows polyaniline's superiority in adsorbing SO_2 over H_2S. While SO_2 reached a maximum adsorption capacity of over 150 mg/g and began absorbing at very low fugacity, H_2S reached approximately 100 mg/g at high fugacity and began absorbing at higher fugacity. Figure 3b highlights a very large difference between SO_2 and NO_2. SO_2 maintained very high adsorption capacity, while NO_2 was hardly adsorbed at low fugacity and only reached very limited adsorption capacity (below 50 mg/g) even at the highest fugacity. Figure 3c shows that H_2S was adsorbed much more effectively than NO_2. The adsorption capacity of H_2S increased rapidly after 10^{-1} Pa and reached high levels, while NO_2 remained near zero for most of the fugacity range and only showed a slight increase at very high fugacity.

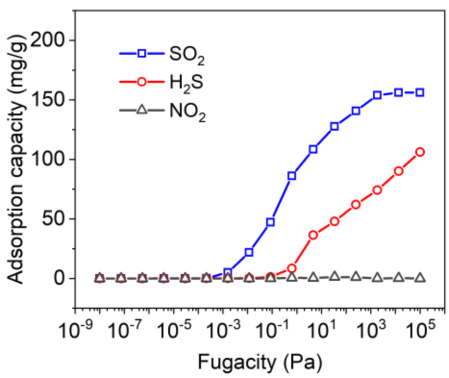

Figure 4: Adsorption isotherm with three gases at once

Figure 4 shows the clearest preference order when all three gases were combined simultaneously. Polyaniline exhibited high selectivity for SO_2 and H_2S, while NO_2 remained completely unresponsive in the simultaneous presence of the three gases. The results show that polyaniline's SO_2 adsorption capacity was significant, reaching over 150 mg/g, H_2S adsorption capacity was moderate, around 105 mg/g, and it was almost ineffective in adsorbing NO_2. These comparative analyses reaffirm the overall adsorption order and provide further evidence of polyaniline's selectivity for SO_2 and H_2S over NO_2.

3.3 Adsorption Energy

In order to study the adsorption interaction between the gases and polyaniline, the adsorption energy values were investigated. The order of adsorption strength was SO_2 (-18.2 $KCal.mol^{-1}$)> H_2S (-12.8 $KCal.mol^{-1}$) > NO_2 (-8.2 $KCal.mol^{-1}$). For H_2S and NO_2 the deformation energy was negligible, indicating that adsorption was primarily due to direct interaction without much structural change (Figure 5).

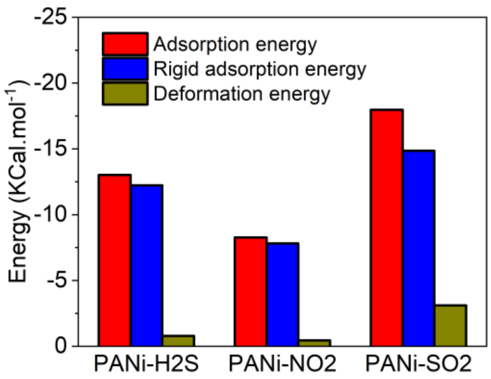

Figure 5: Adsorption energy

This might suggest that these interactions are more physical in nature or weak chemical interactions that do not significantly alter the molecular shape. For SO_2 deformation energy contributed a significant portion to the total adsorption energy (Li et al., 2023). This means that SO_2 adsorption may involve a stronger chemical interaction (chemisorption) or require significant structural rearrangement of both SO_2 and PANi to optimize bonding. This deformation, though requiring energy, was compensated by very strong adsorption interactions (Li et al., 2021). These results suggest that PANi has great potential for more effective SO_2 adsorption or sensing compared to H_2S and especially NO_2. Analysing energy components (total adsorption energy, rigid adsorption energy, deformation adsorption energy) provides deep insights into the adsorption mechanism. For SO_2, it appears that a chemisorption process is occurring, requiring a slight energy sacrifice for deformation to achieve a very stable bonding state.

4. Conclusion

This study provided a quantitative analysis of polyaniline's adsorption capacity for NO_2, H_2S, SO_2 under different temperature conditions. Our findings indicate that polyaniline exhibits the best adsorption capacity for SO_2, reaching 250 mg/g at 293 K and 10^5 Pa. This is followed by H_2S and NO_2, with adsorption capacities of 200 mg/g and 190 mg/g, respectively, under the same conditions. Further studies on the co-adsorption of gas pairs and the formation of adsorption bonds, analyzed through adsorption energy parameters, further corroborate this overall adsorption order and provide insights into polyaniline's selectivity towards SO_2, H_2S, NO_2. The insights gained from this study will contribute to the development and optimization of polyaniline-based adsorbent materials for air pollution control applications. Future studies can focus on exploring polyaniline variations or combining with other simulation techniques to gain a deeper understanding of adsorption mechanisms.

Acknowledgments

This research was supported by the Institute for Tropical Technology.

References

Ahmad A., Yunos M.Z., Harun Z., Hassan M.F., Adzila S., Arifin A.M.T., Rahman M.N.A., Haq R.H.A., 2017, Effect of polyaniline on surface properties of polysulfone membrane, Chemical Engineering Transactions, 56, 691-696.

Baaloudj O., Nasrallah N., Kenfoud H., Bourkeb K.W., Badawi A., K., 2023, Polyaniline/Bi12TiO20 hybrid system for cefixime removal by combining adsorption and photocatalytic degradation, ChemEngineering, 7(1), 4.

Bahamon D., Khalil M., Belabbes A., Alwahedi Y., Vega L.F., Polychronopoulou K., 2021, A DFT study of the adsorption energy and electronic interactions of the SO2 molecule on a CoP hydrotreating catalyst, RSC advances, 11(5), 2947-2957.

Bhandarkar S., 2013, Vehicular pollution, their effect on human health and mitigation measures, Vehicle Engineering, 1(2), 33-40.

BIOVIA Dassault Systèmes, Material studio., 2017, v17.1.0.48, San Diego: Dassault Systèmes.

Ćurić M., Zafirovski O., Spiridonov V., 2021, Air quality and health, Essentials of medical meteorology, Springer, 143-182.

Gautam S.K., Panda S., 2021, Effect of moisture and molecular weight of polyaniline on H2S sensing characteristics, Sensors Actuators B: Chemical, 344, 130323.

Hannun R.M., Razzaq A.H.A., 2022, Air pollution resulted from coal, oil and gas firing in thermal power plants and treatment: A review, IOP Conference Series: Earth and Environmental Science, IOP Publishing.

Jiang Y., Xu X., Liu B., Zhou C., Wang H., Qiu J., Zeng Z., Ge Y., Li L., 2022, Optimal pore size design guided by GCMC molecular simulation for VOCs adsorption, Microporous Mesoporous Materials, 341, 112081.

Li B., Gao W., Jiang Q., 2021, Electronic and geometric determinants of adsorption: fundamentals and applications, Journal of Physics: Energy, 3(2), 022001.

Li J., Chang J., Cheng S., Wang Z., Zhao Y., Zhou B., Ma C., Zhang L., Wang T., Song Z., 2023, New insights into the influence of SO2 as an activator on the physicochemical properties of carbon materials and the influence of S-doping on SO2 adsorption: Experimental and density functional theory study, Chemical Engineering Journal, 474, 145902.

Mais L., Mascia M., Casula E., Palmas S., Vacca A., Rodriguez J., 2021, Electrochemical synthesis of polyaniline/metal-based anodes and their use in microbial fuel cell, Chemical Engineering Transactions, 84, 193-198.

Minisy I.M., Salahuddin N.A., Ayad M.M., 2021, Adsorption of methylene blue onto chitosan–montmorillonite/polyaniline nanocomposite, Applied Clay Science, 203, 105993.

Smet E., Lens P., Langenhove H.V., 1998, Treatment of waste gases contaminated with odorous sulfur compounds, Critical Reviews in Environmental Science Technology, 28(1), 89-117.

Yang Y., Yu J., Jiang X., Lai K., Miao J., 2024, Insight into the interaction between amino acids and SO2: Detailed bonding modes, Journal of Molecular Modeling, 30(8), 291.

Zanella O., Tessaro I.C., Féris L.A., 2014, Desorption-and decomposition-based techniques for the regeneration of activated carbon, Chemical engineering technology, 37(9), 1447-1459.