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Computational Analysis of CO_2 Adsorption Performance in Amine-Grafted Activated Carbon

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ABSTRACT

Enhancing CO_2 adsorption remains a critical challenge in mitigating atmospheric CO_2 emissions. Carbon capture and storage (CCS) technology is pivotal in addressing this global issue. This study investigates the interactions between amine ($-NH_2$) functional groups and carbon molecules through machine learning simulations to improve adsorption efficiency cost-effectively. The findings reveal that amine-grafted activated carbon exhibits a potential energy of -715.865 kJ/mol, a pore size of 3.53 Å, a pore volume of 309.33 Å³, and a surface area of 274.07 Å². Conventional activated carbon has an average pore size of 1.25 Å, a pore volume of 500 Å³, and a surface area of 1000 m^2/g^{-1}. The functionalized material shows a 182.06% increase in pore size, which aligns with previous findings indicating that larger pore diameters enhance CO_2 adsorption rates by improving molecular accessibility and reducing steric hindrance. Additionally, functionalization with amine groups enhances adsorption through strong chemical interactions, compensating for lower surface area and pore volume. These results suggest the practical applicability of amine-functionalized carbon in industrial CCS applications, combining improved kinetics with economic feasibility.

Keywords: Carbon capture, Adsorption, Carbon, Amine.

1. Introduction

The pressing effects of global warming, primarily driven by carbon dioxide (CO_2), have highlighted the need for effective emission reduction strategies.CO_2, the most prominent greenhouse gas, is emitted on a massive scale, with global emissions reaching 37.49 billion metric tonnes in recent years [1]. In 1940, the amount of CO_2 emissions was just 4.87 billion tonnes, showing a nearly ninefold increase over 80 years. Thirteen of the last fourteen years (2000– 2014) were the warmest on record[2], underscoring the need for immediate action. Addressing this crisis demands innovative and effective strategies to mitigate CO_2 emissions.

Among the proposed solutions, Carbon Capture and Storage (CCS) technologies have shown promise in reducing CO_2 emissions by 80–90%. CCS approaches can be broadly categorized into:

- Post-combustion capture
- Pre-combustion capture
- Oxy-fuel combustion capture

Inspite of the advancement in CCS, challenges such as energy efficiency, material cost, and environmental sustainability persist. Among these, post-combustion capture using adsorption techniques has gained significant attention for its feasibility[3]. Adsorption, which involves adhering gas-phase CO_2 molecules onto a solid adsorbent's surface, offers a stable mechanism for CO_2 capture[4]. Unlike absorption, where CO_2 dissolves into a liquid medium[5], adsorption can leverage tailored materials to enhance capture efficiency under mild conditions. This study focuses on amine-grafted activated carbon (AC) as a potential adsorbent for post-combustion CO_2 capture. Amine-grafting introduces reactive functional groups that has higher affinity for CO_2 , even at low partial pressures, making it a feasible solution for industrial applications. The procedure of this work is done by integration of computational modeling and validation. This study states to bridge gaps in understanding the relationship between functionalization techniques, pore structure, and CO_2 capture efficiency. The findings are expected to contribute to the development of cost-effective, sustainable materials for large-scale carbon capture applications.

2. Literature Review

Researchers have extensively explored ways to synthesize, characterize, and optimize amine-based solid adsorbents for post-combustion CO_2 capture. Xu was the first to use amine-impregnated silica for CO_2 absorption, developing a "molecular basket" adsorbent[6]. This adsorbent, created using mesoporous silica supports (MCM41) and PEI, exhibited an adsorption capacity 24 times higher than MCM-41 alone and twice that of pure PEI[7]. Subsequent studies by Ma and Hicks introduced 'Tetraethylepentamine' (TEPA)-impregnated SBA-15, which demonstrated decreased adsorption capacity over time due to the leaching of TEPA from the surface[8],[9]. Furthermore, research showed that adsorbents' pore diameters directly influenced their CO_2 adsorption capabilities. The highest adsorption capacities were found in KIT-6 (dp= 6.5 nm), followed by SBA-15, SBA-16, MCM48, and MCM-41. These studies concluded that amine-functionalized adsorbents perform better at elevated

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temperatures. However, higher adsorption temperatures pose challenges in regeneration, as the amine may leach from the porous support. After analyzing the previous papers, we designed a 3D atomic structure of activated and amine-grafted activated carbon. After optimization, its structure co-originates into machine learning to identify pore size, volume, surface area, and potential energy. Another good example is the modification of covalent triazine frameworks with acetohydrazides enables the advancement of a sorbent with exceptionally high CO2 uptake capacity at low pressures (5.7wt% at 273K/0.15bar and 15.95wt% at 273K/1 bar) as well as good ideal selectivity (145.9) [10] Based on these findings, this study aims to design a 3D model of activated carbon and Amine-grafted activated carbon, applying machine learning to analyze structural characteristics.

Table 1 Amine-impregnation vs Amine-grafting

Adsorbent type	Amine-impregnated	Amine-grafted
Adsorption Capacity	High (Upto 3.18 mmol/g)	Moderate (up to 0.89 mmol/g)
Thermal Stability	Poor, susceptible to degradation	High-thermal stability
Amine Leaching	Significant at high temperature	Low amine leaching
Regeneration	Slow kinetics, issues with cyclic use	Improved regeneration stability
Production Complexity	Simple, scalable	Complex, costly

3. Simulation Methodology of this Study:

This Amine-grafted activated carbon simulation uses 'MD analysis' by Python. However, the initial input data file was created using Avogadro. Here, 'MD analysis' is used.

For molecular dynamics, 'Numpy' is used for numerical operations, and' ConvexHull' from "Scipy. spatial" is used for the molecule's shape. Here, 'Load_xyz(file_path)' is used to take the path to an XYZ file, and for pore size calculations, 'Calculate_pore_size (u, probe_radius=1.7)' is used.

Pore Radius is denoted by 'U' and refers to the size of a hypothetical sphere (or probe) used to explore the molecular surface. The radius of this sphere determines the areas it can access, essentially representing the dimensions of molecules that can potentially interact with the surface.

Pore Size: The pore size is directly related to pore radius. In simple terms, the pore size is the diameter of the pores within the molecular structure. Here, it is denoted by 'u.atoms.positions', and it refers to the positions of atoms that define the size of the pores or cavities within a molecular or material structure. The pore size is influenced by the arrangement and positions of atoms in the structure.

Pore Volume: The pore volume refers to the total volume that the pore occupies within the structure; it's calculated based on the size and number of pores. The larger the pore radius, the larger the volume of an individual pore, which contributes to the total pore volume. Here, it is denoted by 'hull. Volume' refers to the volume enclosed by the molecular surface, often calculated using the convex hull method. It can represent the available space within porous materials.

Surface Area: The surface area of a molecule includes the area of the outer surface plus the surfaces within the pores. A larger pore radius means that each pore has a larger surface area, which increases the total surface area of the molecule. Here, it is denoted by 'hull. Area' and The surface area of the molecule, often calculated using the convex hull method, refers to the total area of the molecular surface exposed to its surroundings. It represents the external surface of a molecule.

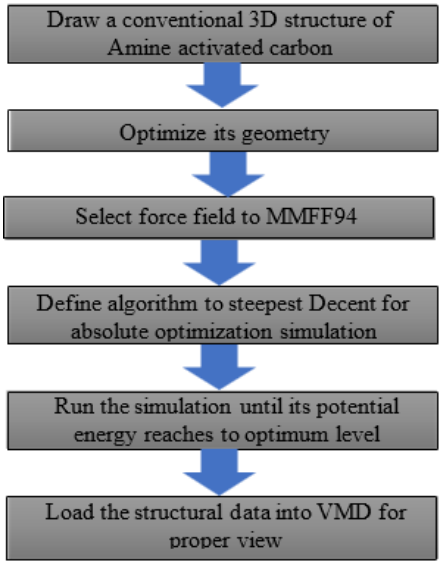
3.1 Libraries used for simulation:

- MDAnalysis: This library is used to analyze molecular dynamics simulations. It processes the input XYZ file from Avogadro.
- NumPy: The NumPy library performs numerical operations, such as matrix manipulations and mathematical computations necessary for analyzing molecular properties.
- SciPy.spatial.ConvexHull: The ConvexHull function is part of the SciPy library used to compute geometric boundaries of the molecular structure. This is important for calculating properties such as pore volume(hull. volume) and surface area(hull. area).

3.2 Key functions used:

- Load_xyz(file_path): This function reads the XYZ file containing molecular data.
- Calculate_pore_size(u, probe radius=1.7): This function uses molecular structure (u) and a defined probe radius to calculate the pore sizes accessible to the probe.

4. Flowchart of the simulation:



4.1 Activated Carbon Design

Phosphoric acid (H_3PO_4) is a dehydrating agent that chemically activates carbon to produce activated carbon (AC).

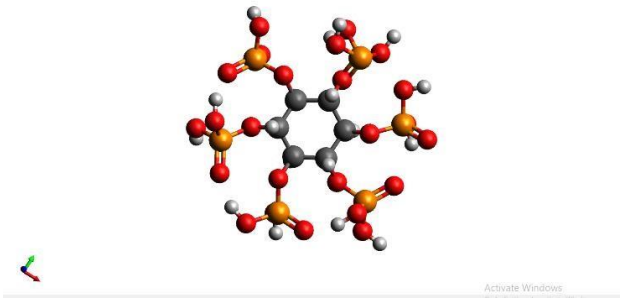


Fig1. Structural design of Carbon activated by Phosphoric acid

4.2 Amine-grafted Activated Carbon Design:

Amine-grafted activated carbon is primarily used for CO_2 capture due to its enhanced adsorption capacity. Here, activated carbon is doped with Ethylenediamine (EDA).

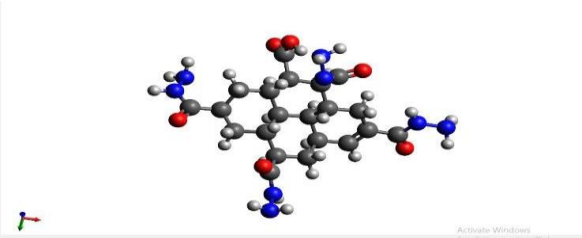
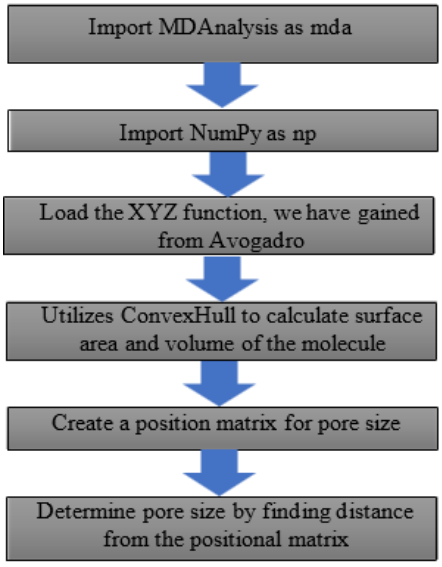


Fig 2. Structural design of Amine-grafted activated carbon

4.3 Molecular Dynamics Simulation for Porous Characteristics



5. Simulation results

Table 2 Simulation results

Characteristics	AC	AC-NH2
Potential Energy	-5710.03 KJ\mol	-715.865 KJ\mol
Pore Size	3.7334297 Å	3.5257108 Å
Pore Volume	208.09 $Å^3$	309.33 $Å^3$
Surface Area	218.16 $Å^2$	274.07 $Å^2$

From table 2, it seems the pore volume and surface area increased due to amine grafting, causing an increment in the adsorption capacity (**Table 2**). On the other hand, pore size decreases, proving the necessity of nitrogen doping in the activated carbon structure[11], [12]. The potential energy increased in amine-grafted activated carbon compared to normal activated carbon(**Table 2**). In physical systems, potential energy often represents the energy of interaction between particles or systems. For instance, when activated carbon interacts with adsorbates (like gases or liquids), the system's potential energy can become negative due to attractive forces[13]. In adsorption processes, this is a sign that the adsorbate is bound to the carbon surface and is at a lower energy state compared to when it was free[14].This suggests that the amine groups' interaction with the carbon surface led to higher energy levels[15]. The amine functionalization likely introduced new attractive forces, affecting the system's overall stability. Pore size decreased in amine-grafted activated carbon. This change could be due to amine groups altering the pore structure. The grafting process might have partially blocked or modified the existing pores, resulting in a smaller effective pore size. Interestingly, the pore volume increased in amine-grafted activated carbon **(Table 2).** This suggests that the amine groups created additional accessible space within the material. The grafting process likely expanded the pore network, allowing more adsorption sites for molecules. Surface area increased in amine-grafted activated carbon. This is intriguing because it contradicts the pore size reduction.

It is possible that the amine groups contributed to a more complex surface morphology, leading to increased surface area despite smaller pores.

6. Comparative Analysis

Table 3 Comparison of the porous characteristics based on the designs in Avogadro and MDAnalysis between AC and AC-NH_2

Parameter	AC	AC-NH_2	Impact
Adsorbate-Surface Interaction	Moderate interaction strength	Strong interaction strength	Lower energy suggests stronger adsorbate-surface interactions, enhancing adsorption capacity.
Pore Structure	Slightly smaller pores,	Larger pores, potentially better accessibility for adsorption	Larger pore size indicates higher adsorption rate
Pore Network	Moderate pore network connectivity	Enhanced and more accessible pore network	Increased pore volume suggests expanded pore networks, enhancing accessible

			space for adsorption.
Surface Active Sites	Fewer active sites for adsorption	Larger surface area, more active sites for adsorption	The increased surface area provides more active sites for adsorption, improving the material's capacity.

Table 4 Parametric study for Adsorption

Parameters	**Variable Range**	**Impact on CO2 Adsorption**
Pore Size	2nm to 6nm	Larger pores enhance adsorption
Amine Loading	30wt% to 50wt%	Higher loading increases adsorption
Temperature	25°C to 75°C	Elevated temperature improves adsorption
Pressure	0.1 bar to 1 bar	Low pressure favors selectivity

8. Conclusion

The energy problem is the burning question of the twenty-first century. Researchers worldwide are trying to solve this problem by creating new, feasible green energy sources. Besides exploring new green energy sources, we also have the responsibility to reduce CO_2 emissions and reverse the pollution we have caused. Carbon capture technology can serve an important role in this regard[16]. Carbon capture technology separates CO_2 from emissions sources like power plants or industrial facilities.

Acknowledging this CO_2 emission problem, the vision of this thesis is to run a simulated study based on the increment of adsorption capacity due to Amine-grafting in activated-carbon.

Our significant findings are:

- **Enhanced Adsorption Capacity**: Amine-grafting significantly improves the adsorption performance of activated carbon due to increased surface area and pore volume despite a slight reduction in pore size(**Table 3**).
- **Potential Energy and Interaction Strength**: The lower potential energy in AC-NH indicates stronger interactions between the amine-grafted carbon and adsorbates, suggesting more stable and efficient adsorption(**Table 2**).
- **Pore Structure Changes**: The grafting of amine groups slightly reduces pore size(**Table 2**), possibly due to partial blockages, but this is compensated by the increased pore volume and surface area, which facilitate enhanced adsorption.
- **Structural and Performance Trade-offs**: While the modification results in a more complex surface and increased adsorption sites, the pore size and potential energy changes suggest that careful control of the grafting process is needed to optimize material performance(**Table 3**).

Researchers and engineers can leverage these insights for tailored applications. Amine-grafted activated carbon can contribute in the field of adsorption, catalysis, gas separation, and carbon capture technology[17]. Captured CO_2 can later be used for Synthetic Natural Gas (SNG) production[18], an excellent renewable energy source for a more sustainable future.

9. Reference

[1] D. Y. C. Leung, G. Caramanna, and M. M. Maroto-Valer, "An overview of current status of carbon dioxide capture and storage technologies," 2014, *Elsevier Ltd*.

[2] "letters to nature 756," 2000. [Online]. Available: www.nature.com

[3] F. Raganati, F. Miccio, and P. Ammendola, "Adsorption of Carbon Dioxide for Post-combustion Capture: A Review," Aug. 19, 2021, *American Chemical Society*.

[4] A. Da, "Adsorption from theory to practice," 2001.

[5] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, and R. D. Srivastava, "Advances in CO2 capture technology-The U.S. Department of Energy's Carbon Sequestration Program," 2008, *Elsevier*.

[6] X. Xu, C. Song, J. M. Andrésen, B. G. Miller, and A. W. Scaroni, "Preparation and characterization of novel CO2 'molecular basket' adsorbents based on polymer-modified mesoporous molecular sieve MCM-41," *Microporous and Mesoporous Materials*, vol. 62, no. 1–2, pp. 29–45, Aug. 2003.

[7] X. Xu, C. Song, J. M. Andresen, B. G. Miller, and A. W. Scaroni, "Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-capacity adsorbent for CO2 capture," *Energy and Fuels*, vol. 16, no. 6, pp. 1463–1469, Nov. 2002.

[8] J. A. Delgado, M. A. Uguina, J. L. Sotelo, V. I. Águeda, A. Sanz, and P. Gómez, "Numerical analysis of CO2 concentration and recovery from flue gas by a novel vacuum swing adsorption cycle," *Comput Chem Eng*, vol. 35, no. 6, pp. 1010–1019, Jun. 2011.

[9] S. E. Zanco, L. Joss, M. Hefti, M. Gazzani, and M. Mazzotti, "Addressing the Criticalities for the Deployment of Adsorption-based CO2 Capture Processes," in *Energy Procedia*, Elsevier Ltd, 2017.

[10] Y. Fu *et al.*, "Acid/hydrazide-appended covalent triazine frameworks for low-pressure CO2 capture: Pre-designable or post-synthesis modification," *J Mater Chem A Mater*, vol. 5, no. 40, pp. 21266–21274, 2017.

[11] "French scientific medical journals confronted by developments in medical writing and the transformation of the medical press".

[12] Y.-C. Chiang, P.-C. Chiang, and C.-P. Huang, "Effects of pore structure and temperature on VOC adsorption on activated carbon," 2001.

[13] J. Y. Ge and J. Z. H. Zhang, "Use of negative complex potential as absorbing potential," *Journal of Chemical Physics*, vol. 108, no. 4, pp. 1429–1433, Jan. 1998.

[14] H. Y. Su, K. Sun, W. Q. Wang, Z. Zeng, F. Calle-Vallejo, and W. X. Li, "Establishing and Understanding Adsorption-Energy Scaling Relations with Negative Slopes," *Journal of Physical Chemistry Letters*, vol. 7, no. 24, pp. 5302–5306, Dec. 2016.

[15] D. Il Jang and S. J. Park, "Influence of amine grafting on carbon dioxide adsorption behaviors of activated carbons," *Bull Korean Chem Soc*, vol. 32, no. 9, pp. 3377–3381, Sep. 2011.

[16] T. Wilberforce, A. G. Olabi, E. T. Sayed, K. Elsaid, and M. A. Abdelkareem, "Progress in carbon capture technologies," *Science of the Total Environment*, vol. 761, Mar. 2021.

[17] A. Ayub, "MADE-TO-ORDER AMINE-GRAFTED SILICA MATERIALS FOR SINGLE-STAGE PURIFICATION OF BIOGAS AND LANDFILL GAS," 2021.

[18] A. Ayub, S. Ahsan, D. Meeroff, and M. Jahandar Lashaki, "Amine-grafted mesoporous silica materials for single-stage biogas upgrading to biomethane," *Chemical Engineering Journal*, vol. 445, p. 136497, Oct. 2022.