

OPTIMIZATION AND FUNCTIONALIZATION OF POROUS POLYMERS FOR POST-COMBUSTION CARBON CAPTURE

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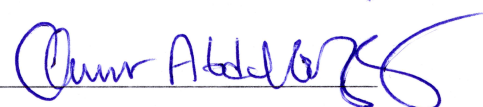
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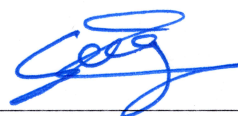
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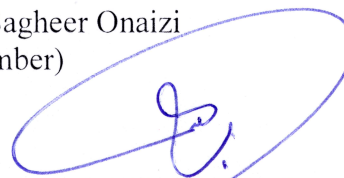
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|To my family, for their unwavering support, patience, and encouragement throughout this journey. To my parents, who instilled in me the value of education. And to my mentors, for their invaluable guidance and inspiration |

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LIST OF ABBREVIATIONS

CO₂	:	Carbon dioxide
CCS	:	Carbon capture and storage
POPS	:	Porous organic polymers
RMS	:	Response surface methodology
DAC	:	Direct air capture
TLC	:	Thin-Layer Chromatography
FID	:	Flame Ionization Detector
SEM	:	Scanning Electronic Microscopy
DVS	:	Dynamic Vapor Sorption
CCD	:	Central Composite Design
DF	:	Degrees of freedom
FTIR	:	Fourier Transform Infrared Spectroscopy
EDX	:	Energy Dispersive X-ray
ATR	:	Attenuated Total Reflectance
PXRD	:	Powder X-ray Diffraction

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ABSTRACT

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Amidst growing global efforts to combat climate change, the capture and sequestration of CO₂ from industrial emissions is becoming increasingly critical. In this work, phenolic resin-based porous polymers were synthesized, optimized, and functionalized to enhance their CO₂ adsorption capabilities. Surface area optimization was achieved using response surface methodology (RSM), identifying temperature, reaction time, and catalyst amount as key parameters for maximizing surface area, resulting in an optimized value of 857.5 m²/g.

The polymer was functionalized with amine-containing silanes, specifically APTS and ABTES, to improve its CO₂ uptake. Among the functionalized samples, the APTS-functionalized polymer (OPTP-8-APTS) exhibited the highest CO₂ adsorption capacity, reaching 2 mmol/g at 273 K and 1 bar. This enhancement was attributed to the successful incorporation of amine groups, as confirmed by FTIR, SEM-EDX, and elemental analysis, which showed a uniform distribution of nitrogen and silicon.

Thermal stability was evaluated using thermogravimetric analysis (TGA), where the functionalized polymers displayed thermal stability to 400 °C. Furthermore, cyclic adsorption–desorption tests demonstrated the durability of the functionalized polymers, as they maintained their CO₂ adsorption capacity over multiple cycles. These findings suggest that the functionalized phenolic resin-based polymers, particularly those modified with APTS, hold immense potential for industrial CO₂ capture applications due to their enhanced adsorption performance, thermal stability, and long-term durability.

ملخص الرسالة

الاسم الكامل: محمود عاطف عبد الله

عنوان الرسالة: تحسين بناء وتخصيص البوليمرات المسامية لاحتجاز الكربون بعد الاحتراق

التخصص: الهندسة الكيميائية

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في ظل الجهود العالمية المتزايدة لمكافحة تغير المناخ، أصبح احتجاز وتخزين ثاني أكسيد الكربون من الانبعاثات الصناعية أمرًا بالغ الأهمية. في هذه الدراسة، تم تصنيع البوليمرات المسامية القائمة على الفينول، وتحسينها، وتعديلها لتعزيز قدرتها على امتصاص ثاني أكسيد الكربون. تم تحقيق تحسين مساحة السطح باستخدام منهجية الاستجابة السطحية، حيث تم تحديد درجة الحرارة، ووقت التفاعل، وكمية المحفز كعوامل رئيسية لتحقيق أقصى قدر من مساحة السطح، مما أدى إلى قيمة محسنة تبلغ 857.5 م²/جم.

تم تعديل البوليمر بوحدة السيليكا المحتوية على الأمينات، وتحديدًا APTS و ABTES، لتحسين امتصاصه لثاني أكسيد الكربون. من بين العينات المعدلة، أظهر البوليمر المعدل بـ APTS أعلى قدرة امتصاص لثاني أكسيد الكربون، حيث وصلت إلى 2 ملي مول/جم عند 273 كلفن وضغط 1 بار. ويعزى هذا التحسن إلى الدمج الناجح لمجموعات الأمين، كما تم تأكيده باستخدام تقنيات التحليل الطيفي بالأشعة تحت الحمراء (FTIR)، ومجهر المسح الإلكتروني (SEM-EDX)، والتحليل العناصر، والتي أظهرت توزيعًا متجانسًا للنيتروجين والسيليكون.

تم تقييم الاستقرار الحراري باستخدام التحليل الحراري الوزني (TGA)، حيث أظهرت البوليمرات المعدلة استقرارًا حراريًا يصل إلى 400 درجة مئوية. علاوة على ذلك، أظهرت اختبارات الامتصاص والتجديد الدورية متانة البوليمرات المعدلة، حيث حافظت على قدرتها على امتصاص ثاني أكسيد الكربون عبر عدة دورات. تشير هذه النتائج إلى أن البوليمرات المسامية القائمة على الفينول، وخاصة تلك المعدلة بـ APTS، تحمل إمكانات كبيرة لتطبيقات احتجاز ثاني أكسيد الكربون الصناعية نظرًا لأدائها المحسن في الامتصاص، واستقرارها الحراري، ومتانتها على المدى الطويل.

CHAPTER 1:

INTRODUCTION

1.1 Overview

Greenhouse gas emissions has emerged as a paramount concern in the context of global environmental in recent years. The intensification of human activities, such as the combustion of fossil fuels, deforestation, industrialization, and modern agricultural practices, has led to a significant increase of the concentration of these gases in the atmosphere. Among all greenhouse gases, carbon dioxide is considered as the major contributor due to the huge amount being emitted each year. Fig. 1 shows the drastic increase in CO₂ emissions from energy generation activities and industrial processes during the last century. Scientists proposed many solutions to mitigate carbon emissions such as improving the efficiency of current processes or developing sustainable and cost-effective energy sources, for example solar, wind, biomass and geothermal energy [1–3]. Among various strategies to mitigate atmospheric CO₂ levels, developing efficient and cost-effective materials for CO₂ capture, particularly from post-combustion sources, stands out as a critical technological challenge [4–6]. CCS offers a dual benefit by mitigating emissions from existing sources and enabling the continued use of fossil fuels during the transition to cleaner energy alternatives [7]. CCS process starts by capturing CO₂ from exhaust gas of combustion process referred to as post-combustion capture. Typically, an

amin-based solution is used as a solvent in a process called absorption in order to capture CO₂ by feeding the flue gas to a packed column where CO₂ is selectively absorbed and separated from other gases.

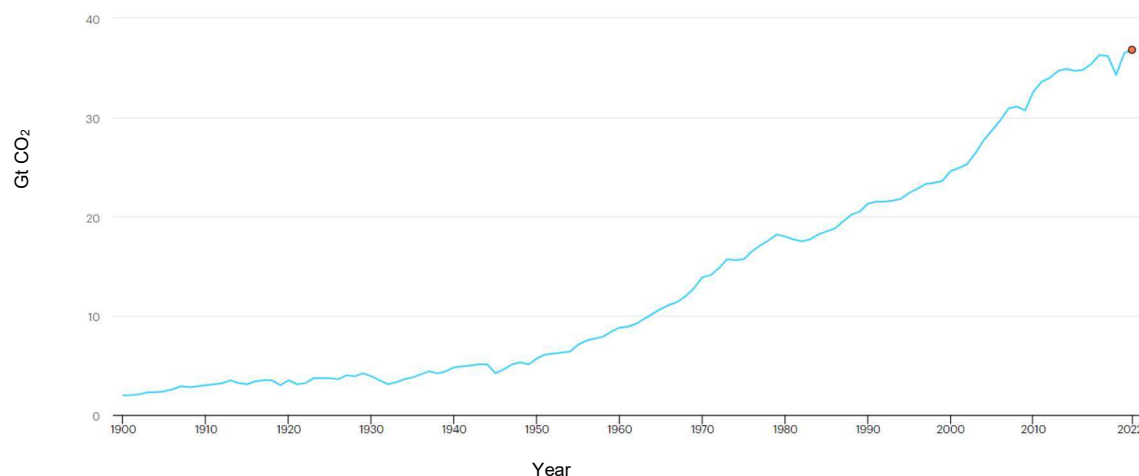


Fig. 1. CO₂ emissions from energy generation and industrial activities, 1900-2022 [8].

Then, the rich solution is stripped, releasing CO₂ and is recycled back to the absorption column (Fig. 2). However, aqueous amine solutions have a very high specific heat, resulting in large energy consumption that represents approximately 25–40% of energy produced from power plant. Therefore, shifting to a less energy intensive method would make CO₂ capture a more economical and appealing method [9,10].

Adsorption is the process by which gas or liquid molecules stick to a solid surface to form a layer or film. Unlike absorption, where particles are taken up by the bulk of material, adsorption is a surface phenomenon attaching molecules to the solid surface by weak forces such as van der Waals, hydrogen bonding and electrostatic interactions, which in this case called a physisorption. On the other hand, chemical adsorption or chemisorption involves a stronger chemical bond forming between adsorbate (gas or liquid) and adsorbent (solid).

This type is usually more specific and can remove a small traces of gas or liquid from a stream, making it particularly useful for CO₂ capture where the concentration is usually very low [11].

The other less common post-combustion carbon capture processes are membrane filtration and cryogenic distillation. In the case of membrane filtration, a selective membrane is utilized to separate CO₂ from other gases by exploiting a high pressure as the driving force [12]. While cryogenic distillation cools down the exhaust gas stream to the CO₂ sublimation temperature (-100 to -135 °C) then separated solid CO₂ particles from other gases [13]. Nowadays, a cost-effective capture of CO₂ is essential to mitigate the greenhouse effect on environment. Adsorption using porous material requires significantly less energy to regenerate compared to amine-based absorption process.

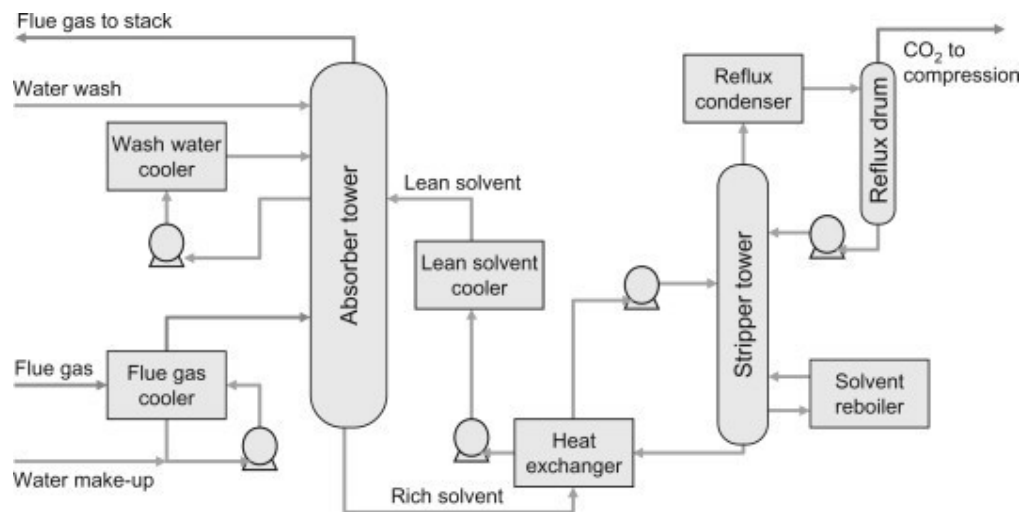


Fig. 2. CO₂ capture using absorption system [14].

This reduction in regeneration energy is attributed to the low heat capacity of solid sorbent compared to that of amine solution with large amounts of water. The ideal solid sorbent is

required to be cost-effective and to have a selectivity, high capacity, and sorption-desorption rate for CO₂.

1.2 Literature review

1.2.1 What is adsorption?

The phenomenon of adsorption was discovered a long time ago. The term “adsorption” itself was first introduced by the German physicist Heinrich Kayser in 1881 [15]. Also, in 19th century both John Tyndall and Michael Faraday observed gas adhering to a solid surface, laying the groundwork for early understanding of adsorption [16]. However, the twentieth century was the time of major breakthroughs in adsorption, when Irving Langmuir developed the first theoretical model explaining the relationship between gas concentration and adsorption on the surface [17]. Not long after that, the trio Stephen Brunauer, Paul Hugh Emmett, and Edward Teller developed their own isotherm model (BET) which is still used today as a standard to calculate the surface area of solid sorbent [18]. World war I was the first time when adsorption has been practically used as activated carbon was recognized for its ability to adsorb the toxic gases such as, chlorine, phosgene, and mustard, providing protection to individuals [19].

1.2.2 Materials used for CO₂ capture

In the context of carbon capture, researchers began actively exploring adsorption for carbon capture as concerns about climate change increases. In many reviews, the ideal CO₂ absorbent should have several properties such as high CO₂ capacity and selectivity, fast kinetics, low cost, and chemical, thermal and mechanical stability [11,20]. Not surprisingly, given their widespread use as a well-known adsorbent, activated carbons have been thoroughly investigated for the purpose of carbon capture. Maniara et al.,

investigated the use of biomass-based activated carbons, particularly those derived from coconut and palm shells, and highlighted potential for CO₂ capture due to their surface area, porosity, and functional groups [21]. Also, Pevida et al, and Liu et al, both found that the introduction of basic nitrogen functionalities into activated carbons can enhance their selectivity and capacity for CO₂ capture [22,23]. Nevertheless, Numerous studies have demonstrated that the presence of water has a negative impact on CO₂ capacity because of the water's capacity to competitively adsorb. This is particularly the case for post-combustion CO₂ capture for example, the flue gases of natural gas and coal power plants contains the double amount of water to CO₂ per unit volume [24]. Wang et al, did a comparative study on two different activated carbon. The result shows a significant decrease of activated carbon capacity to CO₂ of wet sample comparing to a dry sample [25].

Another promising class of material for CO₂ capture are zeolites, which are a group on naturally occurring or synthetically produced crystalline minerals with unique structure and ability of molecular sieving [26]. A range of zeolites have been explored for CO₂ adsorption, with promising results. Liu et al, found that zeolite 13X (APGIIA) possesses a high capacity for CO₂ adsorption and is applicable to temperature swing and vacuum pressure swing adsorption. [27]. Thakkar et al, demonstrated the potential of 3D-printed zeolite monoliths, which have comparable adsorption uptake to powder sorbents and good mechanical stability [28]. Miyamoto et al, highlighted the effectiveness of pure silica CHA type zeolite for CO₂ separation, with a high adsorption capacity and selectivity [29]. Lee et al, explored the use of zeolitic sorbents derived from waste fly ash, finding that calcium ions were particularly effective for CO₂ adsorption [30]. These studies collectively suggest

that zeolites, including 13X, pure silica CHA type, and those derived from waste fly ash, hold promise for CO₂ adsorption applications. However, the presence of H₂O in zeolite significantly reduces its capacity for CO₂ adsorption, as demonstrated by molecular simulations in 13X zeolite [31]. This effect is further influenced by the cation type, particle size, and the presence of co-adsorbed water [32]. The inhibitory effect of water on CO₂ adsorption is particularly strong, leading to a decline in the Henry constant [33].

Additionally Porous organic materials, especially materials which can be tailored to achieve high CO₂ adsorption selectivity and capacities [34], are pivotal in advancing CCS technologies. Metal-organic frameworks (MOFs) [35,36] and porous polymers such as covalent organic frameworks (COFs) [37,38], porous aromatic frameworks (PAFs) [39], and covalent triazine frameworks (CTFs) [40] have been extensively studied for their potential to adsorb CO₂ from industrial waste gases. In addition, recent studies focused on developing heteroatom-doped porous carbon materials to enhance CO₂ capture. Saho et al. developed a N-doped porous carbon derived from chitosan, which demonstrated an exceptional CO₂ uptake of 4.4 mmol/g at 298 K and 1 bar [41]. Similarly, Liu et al. and Bai et al. produced sulfur-doped porous carbon materials with significant CO₂ uptake capacities [42,43]. Nevertheless, the substantial cost associated with the starting materials and low yield stand as a barrier to their large-scale industrial implementation.

1.2.3 Porous Organic Polymers for CO₂ capture

POPs have shown great potential for CO₂ capture due to their high surface area, stability, and structural flexibility [44]. Specific types of POPs, such as the ultra-microporous BILP-101, have demonstrated exceptional CO₂ uptake and selectivity, making them promising materials for this application [45]. The use of ionic POPs has also been explored, with their

ability to convert CO₂ into cyclic carbonates being a notable advantage [46]. Recent research has focused on engineering the pore environment of POPs to enhance their CO₂ affinity and catalytic activity, further improving their performance in CO₂ capture and conversion [47].

Porous phenolic resin-type polymers have gained attention due to their cost-effectiveness, robust thermal stability, chemical resistance, and structural versatility [48,49]. The typical structure of phenolic resin features a three-dimensional network where phenol units are linked by methylene bridges [50]. This construction yields a densely cross-linked matrix, which gives phenolic resin its unique properties. Among various synthesis methods, solvothermal is the most common way to synthesize phenolic resin, where the phenolic monomers react with an aldehyde source in the presence of a catalyst within a solvent under controlled temperature and pressure. Phenolic resin polymers are of particular interest in carbon capture technology due to their ability to selectively adsorb CO₂ from gas mixtures [49,51]. Recent studies have demonstrated the efficacy of hierarchically porous phenolic resin-type polymers and phenolic resin-based activated carbon spheres in CO₂ capture and conversion. A hierarchically porous phenolic resin-type polymer was successfully prepared through a solvothermal reaction, showcasing high CO₂ adsorption and efficient catalytic conversion for CO₂ cycloaddition [49]. In addition, Wickramaratne and Jaroniec highlighted in their work the importance of small micropores in CO₂ capture by phenolic resin-based activated carbon spheres achieving substantial amounts of CO₂ adsorption at 273 K and ambient pressure [52].

1.2.4 Response Surface Methodology (RSM) optimization for CO₂ capture applications

Optimization plays a pivotal role in bridging the gap between research and market application. It serves as a critical pathway for transforming theoretical models and experimental prototypes into viable products that can be efficiently manufactured, marketed, and used on a large scale [53,54]. The one-factor-at-a-time approach has commonly been used to optimize the operational factors of various processes, but it fails to account for the interactions between the variables and the response. In contrast, RSM serves as a useful alternative, having been broadly applied to investigate both the individual and combined effects of different variables [55].

In the context of CO₂ capture, a range of studies have explored the optimization of both materials and operational parameters involved in the adsorption process. Taheri et al. employed RSM and artificial neural networks (ANNs) to optimize the CO₂ capture process using a novel mesoporous amine-based nano-adsorbent. Their study focused on optimizing temperature, pressure, and CO₂ concentration during the adsorption process [56]. Jedli et al. also applied RSM to investigate the effects of process variables on CO₂ adsorption on activated carbon, identifying pressure and temperature as key factors [57]. Malekbala et al. used RSM to enhance the formation yield of carbon nanofiber-coated monolith for CO₂ capture and found that post-modification with amine improved CO₂ adsorption [58]. Gil et al, used response surface methodology to identify the best activation parameters for CO₂ capture, achieving a 9.3 wt.% adsorption capacity [59]. Khurana et al, proposed an integrated approach for adsorbent and process design, expanding traditional optimization to include adsorbent isotherm characteristics [60]. González et al, developed sustainable

carbon adsorbents from biomass residues, optimizing activation conditions to maximize CO₂ adsorption capacity [61].

1.2.5 Amine-functionalized polymer-based sorbents

Amine-functionalized polymer-based sorbents have gained significant attention for CO₂ capture applications due to their enhanced adsorption capacities and regeneration potential [62,63]. These sorbents are primarily synthesized via two main approaches: (i) the synthesis of copolymers using amine-containing monomers and (ii) post-synthesis modification through the incorporation of amine groups into a polymer matrix, either by impregnation or covalent functionalization [64].

In the impregnation method, amine-rich polymers such as polyethyleneimine (PEI) are physically impregnated into the porous structure of a polymer support. The amine groups in the impregnated polymer offer multiple active sites for CO₂ adsorption. Due to the high concentration of amines, this method often results in significant CO₂ uptake. However, a major limitation of this approach is the potential for amine leaching during operation, particularly in the presence of moisture, which can lead to diminished long-term performance. Recent studies have explored amine-impregnated porous polymers for enhanced CO₂ capture. Li et al. developed a hierarchical porous polymer impregnated with polyethyleneimine (PEI), achieving a CO₂ adsorption capacity of 3.029 mmol/g through physicochemical synergistic adsorption [65]. Similarly, Sami et al. synthesized amine-impregnated polymer aerogels with a CO₂ capture capacity of 2.34 mmol/g, demonstrating fast kinetics and stable regeneration [66]. Varghese & Karanikolos reviewed various amine-bearing polymer functionalities for CO₂ capture, highlighting the importance of increasing amine functional groups and enhancing CO₂-philicity [67].

Covalent functionalization involves chemically tethering amine-containing molecules to the polymer support through covalent bonds. This process is achieved by reacting the amine groups with functional groups on the polymer, such as hydroxyl (-OH) or chloride groups. Covalent bonding ensures that the amine groups are securely attached to the polymer backbone, resulting in more stable sorbents compared to those produced by the impregnation method. This enhanced stability and improved the durability of the sorbent, allowing for better cyclic performance during repeated adsorption and desorption cycles.

In the context of this study, the functionalization of silica sorbents using silane amines begins with the preparation of the silica surface, where hydroxyl groups (-OH) are introduced, providing reactive sites for the attachment of silane molecules [20]. Silane amines, such as APTES, contain both a reactive silane group and an amine group [68]. The silane group reacts with the surface hydroxyl groups on the silica, forming strong covalent Si-O-Si and Si-O bonds (Fig. 3). This covalent bonding ensures that the amine groups remain exposed on the silica surface, ready to interact with CO_2 molecules. The exposed amine groups on the surface significantly enhance the CO_2 capture capacity by providing multiple active sites for CO_2 adsorption. In the absence of H_2O , these groups often form carbamates when they capture CO_2 , while in the presence of H_2O , they can form ammonium bicarbonate [69]. By leveraging the hydroxyl groups of the optimized polymer, the same functionalization and CO_2 adsorption mechanisms can be applied, promoting enhanced CO_2 capture performance.

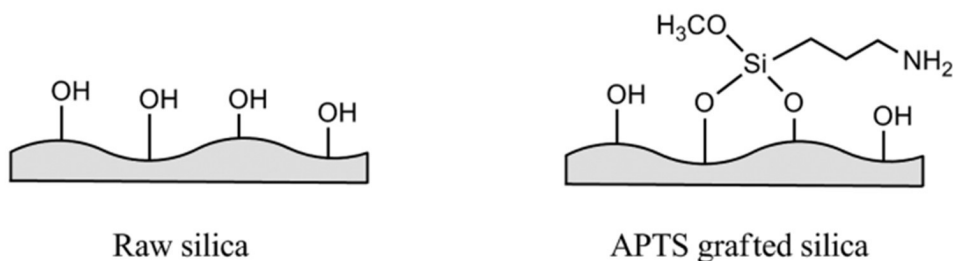


Fig. 3. Functionalization of silica using silane-amine [70].

1.3 Proposed Work

The synthesis conditions significantly contribute to the economic viability of producing porous polymers on a commercial scale. By identifying the optimal reaction temperatures, catalyst amounts, and reaction time, this study lays the groundwork for cost-effective production processes, essential for commercial success. Furthermore, this work illustrates how optimization can lead to polymers with a higher surface area, a critical factor in CO₂ adsorption. High surface area polymers offer increased CO₂ capture capacities, making them more practical for use in CCS technologies. The optimization process not only focuses on performance and cost but also considers the environmental impact of the synthesis process. The carbon footprint associated with producing this material is consequently reduced by minimizing reaction times and temperatures. This aspect is particularly relevant in the context of CO₂ capture technologies, where the overarching goal is to mitigate the impact of climate change. The polymer with optimized parameters was named OPTP-8 (stands for optimized polymer). Substituting to the optimization, the polymer undergoes a functionalization step using two different silane-amine. The functionalized polymers are then evaluated and characterized using different techniques to

test its selectivity, capacity and heat of adsorption for CO₂. In addition, the highest performance polymer among the functionalized ones is then investigated for its DAC ability and stability.

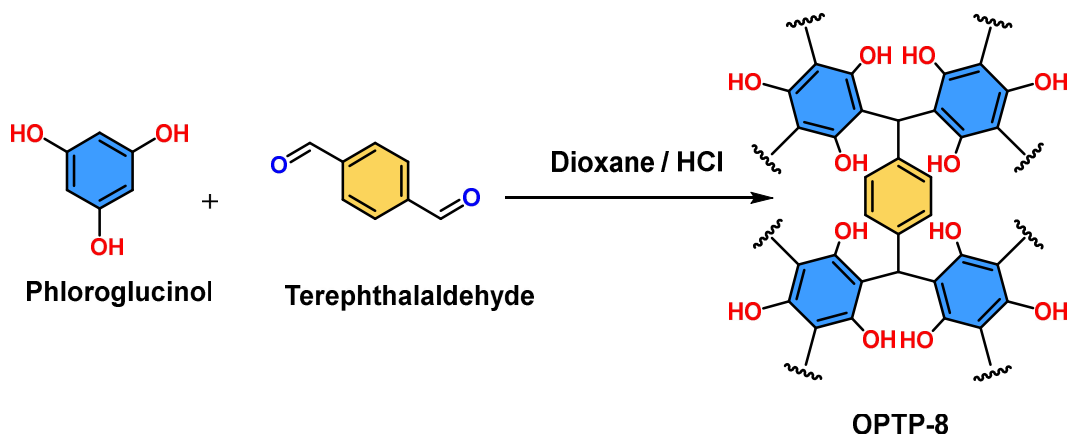


Fig. 4. Synthesis procedure of OPTP-8.

To the best of the author's knowledge, this study represents the first attempt to optimize the synthesis and subsequent functionalization of phenolic resin-based porous polymers, specifically targeting surface area enhancement for CO₂ capture applications. Previous optimization studies have predominantly focused on optimizing the adsorption process by exploring parameters such as temperature, pressure, and concentration while often neglecting the properties of the sorbent itself. This underscores the significance of the current research. Additionally, prior functionalization methods have largely employed the impregnation technique, which is prone to instability over extended use. In contrast, the phenolic resin-based polymer (Fig. 4) was selected for this study due to its low-cost precursor materials and its straightforward, energy-efficient synthesis process.]

CHAPTER 2:

SYNTHESIS AND OPTIMIZATION

2.1 Materials and methods

2.1.1 Chemicals

Methanol (purity $\geq 99.9\%$), 1,3,5-trihydroxybenzene (phloroglucinol, 98%), and benzene-1,4-dicarboxaldehyde (terephthalaldehyde, 99%) were purchased from Merck. 1,4-Dioxane (purity $>99.5\%$) was purchased from Loba Chemie. Tetrahydrofuran (THF) (purity $>99.5\%$) was purchased from Duksan Pure Chemicals. All chemicals and solvents were used as received without further treatment or purification.

2.1.2 Synthesis

This OPTP-8 was prepared in a 50 mL autoclave by mixing phloroglucinol (0.5 g, 4.0 mmol) and terephthalaldehyde (TA) (0.4 g, 3.0 mmol) in 1,4-dioxane (20 mL). The resultant mixture was stirred and sonicated to dissolve all suspended solid. Based on each run, the catalyst HCl (37%) was added accordingly, and a well-closed autoclave has been placed in an oven at a specific temperature (150–250 °C) and time (12–36 hours) of each run. The reaction product was then washed by THF and methanol using the filtration method several times. The product was further washed with methanol using Soxhlet for one day to ensure the removal of all contaminants then vacuum dried at 75 °C. The resultant polymer was a brown-colored light powder.

2.1.3 Sorption analysis

The sorption analysis for both CO₂ and N₂ uptake was performed on a sample of the polymer (approximately 0.25 g) using an Autosorb® high vacuum physisorption analyzer (Anton Paar). The surface area was determined using Brunauer–Emmett–Teller (BET) in accordance with IUPAC guidelines. Prior to the test, the sample was activated under vacuum at 120 °C for 12 hours [71].

2.1.4 Characterization

CHNS elemental analysis was performed using IATROSCAN® MK-7 equipped with thin-layer chromatography (TLC), with a flame ionization detector (FID). A high-resolution image of synthesized polymer morphology was taken using scanning electronic microscopy (SEM) purchased from SEMoscope® IEM 11+. Before analysis, the polymer sample was coated with a thin layer of gold to enhance the conductivity. The stability test was carried out using dynamic vapor sorption (DVS) vacuum sorption analyzer, which is a gravimetric sorption instrument manufactured by Surface Measurement Systems Ltd.

2.1.5 Response surface optimization

The optimal values of synthesis parameters of temperature, catalyst amount, and reaction time were determined by RSM using the Desing Expert® software (Stat-Ease, Inc., Minneapolis, MN). Basically, the optimization process involves three major steps: (1) performing the statistically designed experiments, (2) estimating the coefficients in a mathematical model, and (3) predicting the response and checking the adequacy of the model. An empirical model was developed to correlate the response (BET surface area) to the three studied factors (catalyst amount, reaction time, and reaction temperature) which is based on the second-order quadratic model as given by Eq. (2.1).

$$Y = \beta_0 + \varepsilon + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_{ii}^2 \quad (2.1)$$

where Y is the response variable; β_0 is the intercept; β_i , β_{ij} and β_{ii} are coefficients of the linear effect, double interactions; x_i , x_j are the independent variables or factors and ε is the error.

A central composite design (CCD) statistical technique was used to build a quadratic model for the response variable. The main goal of CCD is to efficiently explore the relationships between multiple independent variables (factors) and one or more dependent variables (responses). CCD consists of three groups of experimental runs:

1. Center points: Experimental runs at middle values of independent variables, which are repeated to estimate the error and the curvature in the response surface.
2. Factorial points: These are the corner points of a multidimensional cub, providing the linearity and interaction information about the system.
3. Axial points: Points along the axis of the cube at a certain distance from the center. The distance from the center to the axial point is often denoted by α (alpha).

Axial points are chosen to estimate the curvature of the response surface. Also, they are used to ensure the design is rotatable, which means the variance of the predicted response is constant at all points that are equidistant from the center. Fig. 5 illustrates the CCD and highlights the position of each point type in three-dimensional space.

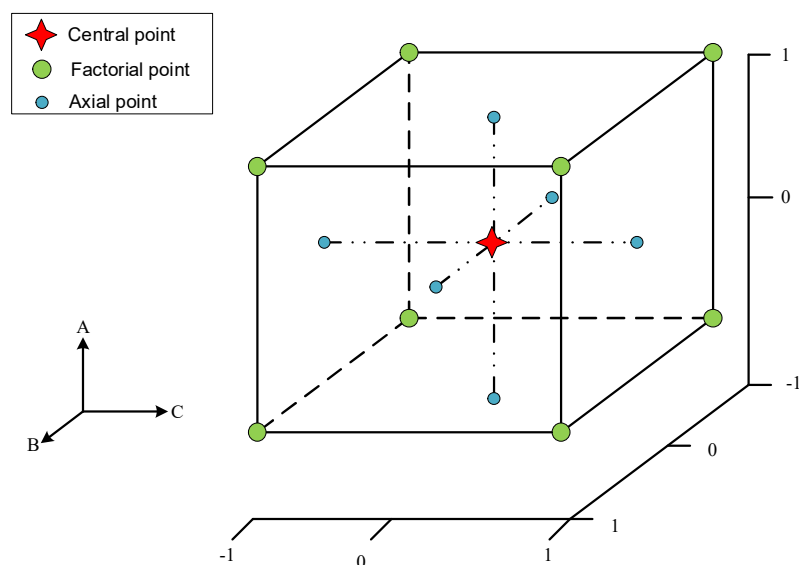


Fig. 5. Graphical representation of experimental data points in the CCD.

In CCD, the independent variables are represented using dimensionless coded variables denoted by +1, 0, and -1. The use of dimensionless or coded variables allows for the simplification of the mathematical relationships in the response surface model. Instead of working with actual values that might have different units and scales, a dimensionless variable is used to standardize the experimental runs and make the coefficients in the polynomial model directly comparable.

The surface area is one of the most essential properties of porous materials. A porous polymer with simple steps to synthesize and high surface area can be a promising candidate for commercialization. In addition, a high surface area would allow the functionalization of the polymer without a significant compromise on capacity. For the above reasons, a phenolic resin-type porous polymer (OPTP-8) was tuned for optimal surface area by investigating three independent variables of temperature, catalyst amount, and reaction time. Through initial screening, the range of model factors was set to be 150–250 °C for temperature, 1–2 mL of catalyst amount and 12–36 hours for reaction time. The center

point at 200 °C, 1.5 mL, and 24 hours, was repeated three times to ensure the reliability and accuracy of the model. The independent variable range and corresponding coded level are listed in Table 1

Table 1. Independent variables for surface area optimization with corresponding coded levels

Independent variable	Symbol	Coded level		
		-1	0	+1
Temperature (°C)	A	150	200	250
Reaction time (hour)	B	12	24	36
Catalyst amount (mL)	C	1	1.5	2.5

2.2 Result and discussion

2.2.1 Model development

A suggested set of experiments based on independent variable ranges was generated using the Design-Expert software. Following the synthesis and washing of the polymer, the resin sorbent resulting from each experimental run was investigated for its BET surface area (APPENDIX-I). The resultant surface area for each run is used to generate a coded quadratic model as shown in Eq. (2.2). The model contains three main types of terms: a liner term, which represents the effect of each factor independently; an interaction term, which represents the effect of dual interaction between factors; and a quadratic term, representing the curvature or nonlinear effects of each factor. The three main types of terms are donated as A, AB, and A2, respectively. The terms were evaluated based on their significance using F-value and p-value; the non-significant terms such as AB were omitted.

$$\begin{aligned}
\text{Surface area} = & 1022.95 + 113.13 \times A + 56.18 \times B - 1.03 \times C \\
& + 16.07 \times AC + 26.43 \times BC - 162.01 \times A^2 - 87.56 \times B^2 \\
& + 126.48 \times C^2
\end{aligned} \quad (2.2)$$

The complete list of experiments used to calculate the model is shown in Table 2, with the corresponding BET surface area and Yield of each run.

Table 2. Experimental design matrix for surface area optimization

Run	A: Temperature (°C)	B: Reaction time (h)	C: Catalyst (mL)	BET surface area (m ² /g)	Yield (%)
1	200	12	1.5	845.9	69.8
2	150	24	1.5	663.7	79.1
3	250	24	1.5	1006.3	83.5
4	200	24	1	1144.2	70.44
5	250	36	1	1028.4	91.5
6	250	12	1	941.6	83.6
7	150	36	1	832.4	91.77
8	200	24	1.5	1075.0	67.9
9	150	12	2	692.9	81.6
10	200	24	2	1102.8	73.5
11	150	12	1	807.6	79.1
12	250	12	2	966.0	87.1
13	200	24	1.5	1026.4	70.4
14	200	36	1.5	973.1	73.5
15	200	24	1.5	1071.1	80.4
16	150	36	2	898.2	94.62
17	250	36	2	1083.7	93.4

2.2.2 Statistical analysis

Analysis of variance (ANOVA) is a statistical method used to analyze the differences among the means of different levels of factors and identify which factors significantly affect the response. Table 3 illustrates some elements of ANOVA for the regression model. The purpose of calculating the sum of squares (SS) is to measure the variance attributed to each component. Results indicate that factor A (temperature) has the highest value of SS either as a factor or a quadratic term; hence, the model is highly affected (attributed) by the synthesis temperature. While the rest of the model components have comparable SS values, the C (catalyst amount) has the lowest SS value, suggesting low attribution to the model.

Table 3. Statistical evaluation of the regression model and model terms using ANOVA

Source	Sum of squares	df ^a	Mean square	F-value	p-value
Model	299100	8	37388.77	13.69	0.0006
A	128000	1	128000	46.85	0.0001
B	31559.34	1	31559.34	11.55	0.0094
C	10.69	1	10.69	0.0039	0.9517
AC	2065.99	1	2065.99	0.7564	0.4098
BC	5588.41	1	5588.41	2.05	0.1905
A²	70324.16	1	70324.16	25.75	0.0010
B²	20540.68	1	20540.68	7.52	0.0254
C²	42863.39	1	42863.39	15.69	0.0042
Lack of fit	20393.05	6	3398.84	4.66	0.1871

^aDegrees of freedom

The degrees of freedom (df) indicated the number of variables that are free to vary in each term, and mean square (MS) is simply SS divided by df to allow for easy comparison between factors. F-value represents the ratio of the mean square of the component to the mean square of the residuals, where a F-value of 4 or above indicates a more significant

effect on the response variable. From Table 3, the overall model has an F-value of 13.96, suggesting that the model is significant. Also, the temperature term has the highest F-value among all model terms, implying the significance of synthesis temperature on the polymer surface area. Another ANOVA indicator, which is the p-values, are calculated for each F-value to determine the probability that the observed effect could occur by chance, a number of less than 0.05 of the p-value for the model indicates that the model is significant and there is only a 0.06% chance that an F-value which represent the significant of the model have occurred due to noise [72].

The lack of fit refers to a specific test that evaluates how well a statistical model fits the observed data. It helps to determine whether the model is too simple to capture the underlying relationship between the variables. A model with a significant lack of fit indicates that the model does not adequately represent the data. In such a case, the model might need to be revised or expanded to better capture the complexity of the data. Conversely, a non-significant lack of fit suggests that the model sufficiently fits the data, implying that the model's complexity is appropriate for the observed variability, and there is no evidence to suggest that the model is missing critical components or interactions. The lack of fit for the model of polymer surface area had an F-value of 4.66, suggesting that the lack of fit is not significant and that the model is of significance.

Standard deviation is the amount of variation or dispersion in a set of values. A low standard deviation indicates that the values tend to be close to the mean of the set, while a high standard deviation indicates that the values are spread out over a broader range. Meanwhile, the coefficient of determination or R^2 is a statistical measure of how close the data are to the fitted regression line, ideal R^2 is equal to one. A reasonable accurate model

that fits the data should have a difference of less than 0.2 between predicted and adjusted R^2 . Predicted R^2 measures how well the model predicts new observations from the model data. Adjusted R^2 is a modified R^2 value that considers the number of independent variables in the model relative to the number of data points. An advantage of using adjusted R^2 is to prevent overfitting. Overfitting occurs when a model becomes too tailored to the specific sample and captures noise rather than the underlying relationship, which usually results in poor predictive performance on new data.

Lastly, adequate precision, also known as the signal-to-noise ratio, is a measure used in the context of the design of experiments and regression analysis to assess the reliability of the predicted values from a statistical model. A model with a ratio greater than 4 is considered to have sufficient signal-to-noise ratio to be useful. In simpler terms, the effects of changing the factors (signal) are more pronounced compared to the variability (noise) of the model predictions. Table 4 gives the standard deviation, R^2 (normal, adjusted, and predicted), and adequate precision, respectively of the surface area model.

Table 4. Descriptive statistical measures for the model

Statistical measure	Value
Standard deviation	52.26
R^2	0.93
Adjusted R^2	0.86
Predicted R^2	0.68
Adequate precision	12.19

The visual patterns in Fig. 6. provide a quantitative understanding of the experimental results. When combined with ANOVA and statistical measures like R^2 , a more comprehensive interpretation can be formed regarding the model's accuracy and the significance of the variables involved. Fig. 6a presents a plot of the predicted versus actual values for each run. The 45° line represents the ideal scenario where the predicted values are equal to the experimental values. In this case, the plot shows a strong correlation between the actual and predicted values with only minor deviations from the 45° line. Fig. 6b displays a plot of externally studentized residuals versus the run number, with the two red horizontal lines representing the 95% confidence interval for a t-distribution. Externally studentized residuals are a type of standardized residual used in regression analysis to identify outliers. They are calculated by dividing the residual by an estimate of its standard deviation, which accounts for the variability in the data. A value outside the range of ± 4.46 , which corresponds to the 95% confidence interval of the t-distribution, would typically be considered an outlier. However, according to Fig. 6b, no values in this study were considered to be outliers.

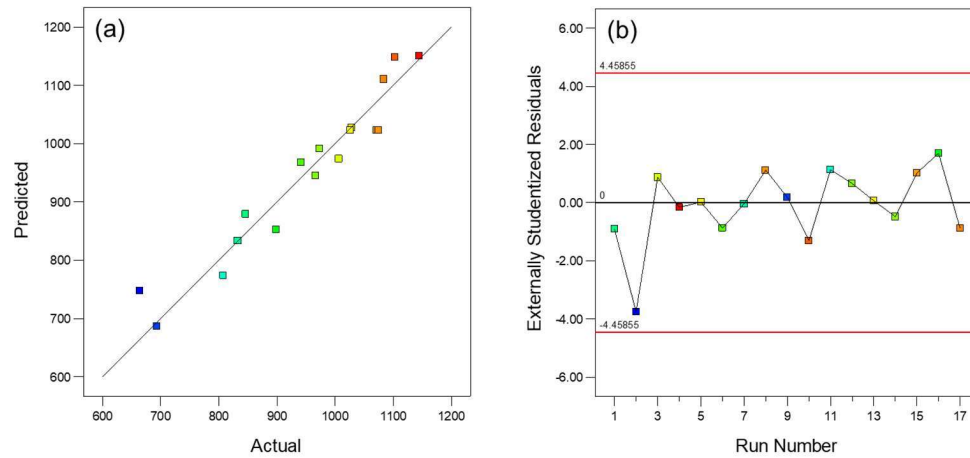


Fig. 6. (a) Predicated data from the model vs. actual data of the experiments. (b) Number of each run vs externally studentized residuals.

2.2.3 Effect of factors and their interactions

Based on ANOVA analysis, both temperature and reaction time significantly affect the surface area in both linear and quadratic terms, as evidenced by F-values greater than 4 and p-values less than 0.05. Meanwhile, the amount of catalyst only shows a significant effect on the surface area in its quadratic term. This underlines the importance of considering a full quadratic model, indicating a curvature in the response surface. This means the response variable may either increase to a maximum point and then decrease, or decrease to a minimum point and then increase, as the level of the factor varies.

Although the factors show significant effects in their linear and quadratic terms, interaction terms in the model can further refine the understanding of how factors jointly influence the response. Fig. 7. illustrates the interactions between catalyst amount and reaction time (a), and catalyst amount and temperature (b) on surface area, denoted in the model by terms BC and AC, respectively.

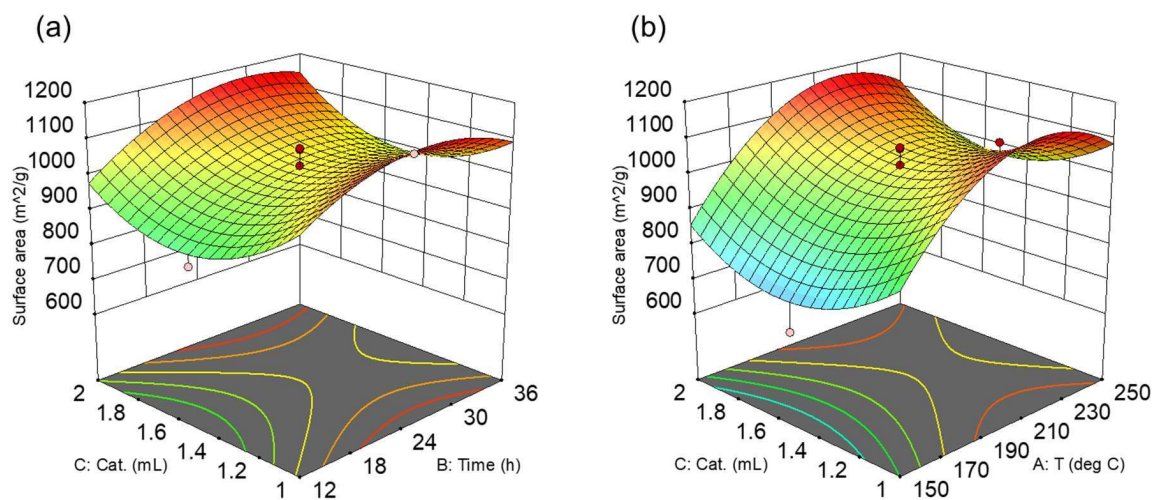


Fig. 7. Three-dimensional response surface graphs of the surface area versus (a) catalyst amount and time (b) catalyst amount and temperature.

2.2.4 Optimization and model validation

The optimization and model confirmation processes were conducted utilizing the tools provided by Design Expert®. The primary objective was to identify the optimal combination of factors that would yield the highest possible surface area while also considering the environmental impact associated with each independent variable. Specifically, minimizing temperature and reaction time is crucial as it reduces energy consumption and, consequently, lowers carbon emissions. On the other hand, the catalyst amount was kept in range since it has the lowest effect on the surface area. Table 5 highlights the goal, importance, and range of values for model factors and response.

Table 5. Optimization goals and constraints for maximizing polymer surface area

Factor/Response	Code	Goal	Importance	Limits	
			Scale 1–5	Lower	Upper
Temperature (°C)	A	Minimize	3	150	250
Reaction time (h)	B	Minimize	3	12	36
Catalyst amount (mL)	C	In range	–	1	2
Surface area (m ² /g)	Y	Maximize	5	664	1144

The software generated 30 different solutions for optimization. Among these, the solution with the highest desirability was chosen (162 °C, 23.4 hours, and 2 mL). According to the software, this most desirable solution is expected to yield a surface area of 952.5 m²/g. Fig. 8a depicts a contour plot illustrating the effect of temperature versus reaction time, alongside the corresponding desirability in Fig. 8b, while the catalyst amount was held constant at 2 mL.

To verify the model's validity and accuracy, the proposed optimal reaction conditions were replicated three times. These experiments yielded an average surface area of 860 m²/g with a standard deviation of 52.3, which falls within the 95% confidence interval. This confirms the model's reliability and accuracy.

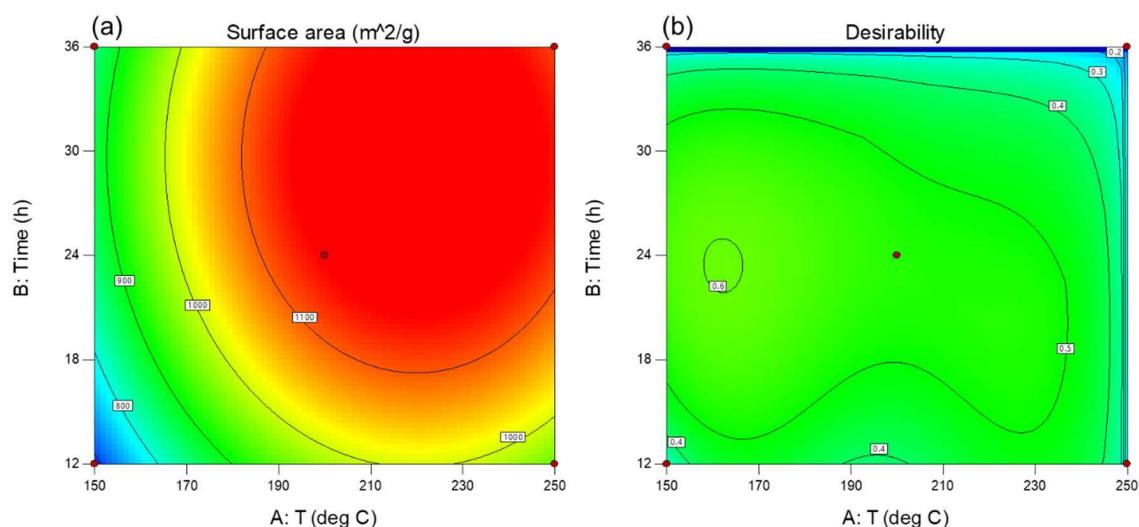


Fig. 8. Contour plots of (a) temperature vs. reaction time where catalyst amount has been set to 2 mL. The red dot in the center represents the proposed optimal condition and (b) the effect of temperature and reaction time on desirability.

2.2.5 Structure characterization

a. Elemental analysis

The elemental analysis experiments were conducted for the prepared polymers to evaluate the effect of cross-linking on the chemical composition and the results are presented in Table 6. It is worth mentioning that a very low concentration of nitrogen and sulfur (<0.72%) was detected, which could be attributed to some contamination in the elemental analysis instrument, or it could be due to the trapped nitrogen gas adsorbed from the atmosphere. Interestingly, as the reaction temperature increases from 150 to 200 °C, the percentage of carbon atoms increases from 62.21 to 64.15%, respectively, along with a decrease in the amount of hydrogen and oxygen atoms. This could be attributed to the

increase in the degree of cross-linking within the polymer as the temperature rises. The cross-linking likely results from condensation reactions where oxygen-containing groups are consumed.

Furthermore, upon increasing the temperature to 250 °C, a notable increase in the carbon content associated with a reduction in the oxygen content was observed, indicating a higher degree of cross-linking at higher temperatures. Increased cross-linking usually leads to more rigid polymers with higher thermal and mechanical stability. Moreover, the strong correlation between the theoretical elemental content and the experimental data at the highest synthesis temperature corroborates with the higher degree of cross-linking. This suggests the polymer could possibly have the desired structure at a high temperature.

Table 6. Elemental analysis of the polymer at different temperatures, along with the theoretical values

Run	N%	C%	H%	S%	O% balanced
16 (150 °C)	0.72	62.21	4.89	0.35	31.83
10 (200 °C)	0.55	64.15	4.58	0.08	30.64
17 (250 °C)	0.67	68.11	4.98	0.14	26.10
Theoretical^a	–	67.22	5.92	–	26.86

^aThe theoretical elemental analysis was calculated using the ChemDraw[®] software.

b. Surface morphology

The morphological characteristics of the synthesized polymer were studied using SEM. SEM images were obtained to provide a visual assessment of the polymer's surface texture and porosity, which are critical attributes for effective CO₂ capture. As illustrated in the SEM images (Fig. 9), the polymers exhibit a range of microstructures indicative of a highly porous network. At 100x magnification, the polymer particles are shown to have an

irregular shape with a rough surface texture. This topography is favorable for adsorption as it increases the available surface area for interaction between adsorbent and adsorbate [73]. The images at 200x and 500x provide a closer view of the surface irregularities and the porous nature of the material, and they also reveal more detailed features, including the presence of different pore sizes. At a higher magnification of 2.0k, the surface roughness and pores size variety are clearer, providing a visual validation of the polymer's textural properties, which are hypothesized to contribute to its high CO₂ adsorption capacity.

The pore size distribution of OPTP-8 was determined using QSDFT methods (APPENDIX-I). The polymer consistently exhibited a microporous structure with pore sizes less than 2 nm under all test conditions [71]. However, the data indicates a trend where an increase in temperature leads to enhanced curing of the reaction, resulting in a higher degree of cross-linking. This increased cross-linking contributes to a greater volume of micropores within the structure, thereby enhancing the CO₂ adsorption capacity.

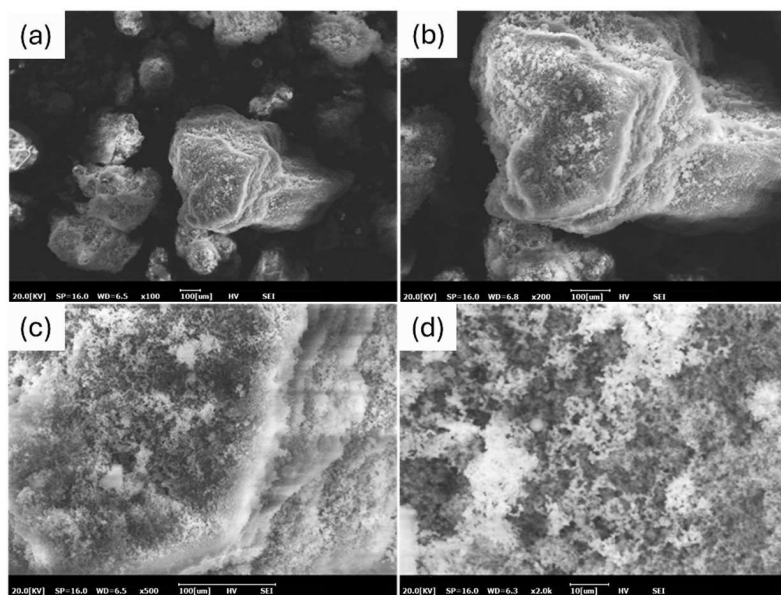


Fig. 9. SEM images of polymer surface at different magnifications (a) 100x, (b) 200x, (c) 500x, and (d) 2.0k.

2.2.6 Polymer stability test

Stability testing is a crucial analysis for evaluating new adsorption materials with potential for CO₂ capture. Recent studies on CO₂ adsorption materials often include more than five adsorption cycles to demonstrate the material's stability and suitability for industrial applications [41,43,74,75]. OPTP-8 was investigated for its cyclic CO₂ capture performance. For the initial run, the sample was activated by raising the temperature to 120 °C under vacuum for 12 hours. Subsequent runs involved reactivating the sample for 6 hours at 100 °C under vacuum. The experiments were conducted in dynamic mode, maintaining a steady flow of CO₂ while controlling the pressure and monitoring the sample weight. Fig. 10 illustrates 15 cycles of CO₂ adsorption on OPTP-8. The uptake of the first run was taken as 100 percent of the polymer's capacity. Subsequent runs exhibited lower capacities compared to the first run due to less rigorous activation conditions.

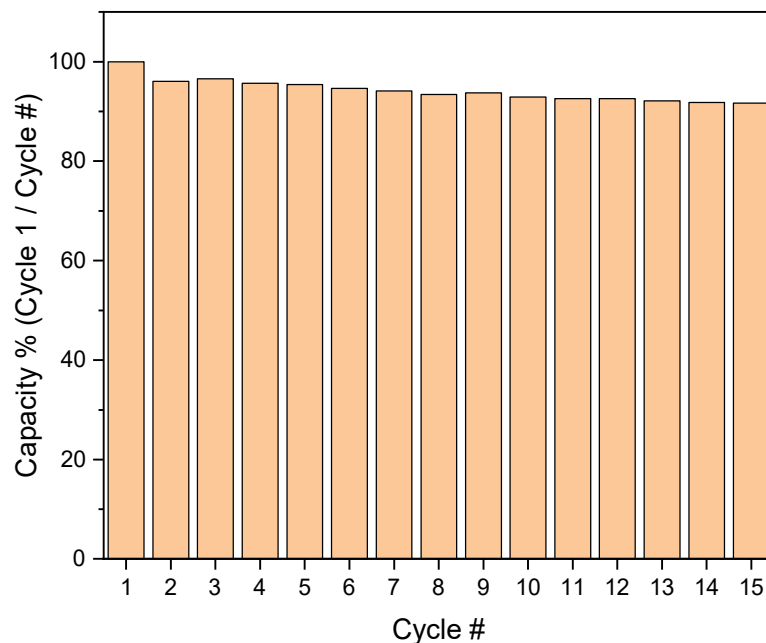


Fig. 10. CO₂ adsorption cyclic stability test of OPTP-8.

CHAPTER 3:

FUNCTIONALIZATION

2.3 Materials and methods

2.3.1 Chemicals

All solvents, including methanol, 1,4-dioxane, and tetrahydrofuran (THF), were procured from Sigma–Aldrich, Loba Chemie, and Duksan Pure Chemical, respectively. The reactants, specifically 1,3,5-trihydroxybenzene (phloroglucinol) and benzene-1,4-dicarboxaldehyde, were sourced from Sigma-Aldrich. Silane-amine reagents, namely (3-aminopropyl)trimethoxysilane (APTS), was obtained from Alfa Aesar, while (4-aminobutyl)triethoxysilane (ABTES) was purchased from Gelest. All chemicals were of laboratory grade and were used as received without further purification.

2.3.2 Synthesis

a. Pristine polymer

The pristine polymer of OPTP-8 was prepared according to the previous optimized synthesis method.

b. Functionalization

In a 50 mL rounded-bottom flask, the functionalized polymers of OPTP-8-APTS, and OPTP-8-ABTES were synthesized by mixing pristine polymer OPTP-8 (0.5 g), with silane-amines (2.5 ml) in solvent consisting of ethanol (5 mL) and deionized water (2.5 mL). The reaction mixture was heated to 80 °C and stirred continuously for 48 hours. Subsequently, the mixture was allowed to cool at room temperature, and the precipitate

formed was separated from the liquid phase using centrifugation. The precipitate was then washed three times with methanol to remove any unreacted reagents and by-products. The purified product was dried in a vacuum oven at 80 °C. The resultant yields were 0.996 g and 0.519 g for OPTH-8-APTS and OPTH-8-ABTES, respectively.

2.3.3 Characterization

CHNS elemental analysis was conducted to determine the material composition, utilizing an IATROSCANTM MK-7 elemental analyzer equipped with a flame ionization detector (FID) and thin-layer chromatography (TLC). Morphological images of the polymers were obtained using a Scanning Electron Microscope (SEM), specifically the SEMoscopeTM IEM 11+ from Invenso. The instrument was equipped with an Energy Dispersive X-ray (EDX) analyzer to determine the silicon and oxygen composition of the samples. To enhance the conductivity of the samples, a thin layer of gold was sputter-coated onto the surfaces at a current of 4 mA for 30 seconds. During SEM analysis, an electron gun with an acceleration voltage of 20 kV and an emission current of 54 μ A was employed. Additionally, Fourier Transform Infrared Spectroscopy (FT-IR) was conducted to identify the functional groups present in the polymers. The analysis was performed using a NicoletTM iS10 FT-IR spectrometer from Thermo Fisher Scientific, equipped with an Attenuated Total Reflectance (ATR) accessory for non-destructive analysis. The FT-IR spectra were recorded over a wavenumber range of 400 to 4000 cm^{-1} , providing detailed information on the chemical functionalities of the polymer samples. The thermal stability of the polymers, along with their decomposition mechanisms, was evaluated using a TA Q500TM Thermogravimetric Analyzer (TGA). The analysis was conducted at a heating rate of 10 °C/min under a continuous flow of dry air. Furthermore, the crystallinity of the

materials was assessed using powder X-ray diffraction (PXRD). The PXRD analysis was performed using a Rigaku MiniFlexTM II diffractometer, operating at a scan rate of 2 degrees per minute with Cu $K\alpha$ radiation, over a range of 5-40 degrees. The stability test was carried out using dynamic vapor sorption (DVS) vacuum sorption analyzer, which is a gravimetric sorption instrument manufactured by Surface Measurement Systems Ltd

2.3.4 Sorption analysis

The porous properties of polymers, along with their amine functionalization, are critical factors that influence their potential applications. Therefore, extensive sorption experiments were conducted using AutosorbTM high vacuum analyzer from Anton Paar to investigate the adsorption behavior of these polymers. To assess the impact of functionalization on the polymer porosity, including surface area and pore size, nitrogen (N₂) uptake measurements were performed at 77 K, following the IUPAC recommended procedures [71]. Prior to the sorption experiments, each polymer sample was activated by heating under vacuum conditions at 120 °C for 12 hours to remove any adsorbed moisture and gases. The resulting adsorption isotherms were subsequently analyzed by fitting it in the range of 0.5-0.3 of p/p_0 to obtain the surface area using Brunauer-Emmett-Teller (BET) model [71]. The same isotherms were also used to estimate the pore size distribution using QSDFT model assuming (slit/ cylinder/ sphere) pores [76]. In addition, CO₂ and N₂ uptakes were measured at two different temperatures, 273 K and 298 K, using the same instrument. The samples were activated by heating under vacuum conditions at 130 °C for 4 hours before these measurements. The isotherms obtained were then fitted to the Fredrich-Langmuir model, and the fitting parameters were used to calculate both isosteric enthalpy of adsorption (Q_{st}), providing insights into the nature of adsorption process [77].

Furthermore, the Ideal Adsorbed Solution Theory (IAST) was employed to evaluate the effectiveness of functionalization for CO₂ adsorption in the presence of N₂ [78].

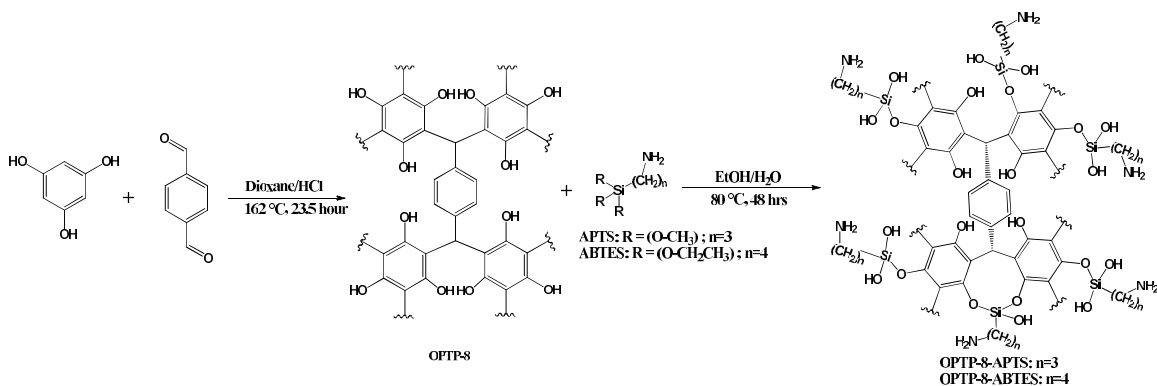


Fig. 11. Synthesis and functionalization procedure of polymers presented in this study

2.4 Results and discussion

2.4.1 Vibrational Resonance Spectroscopy

The strong chemical interaction with CO₂ molecules through the amine groups can significantly enhance the CO₂ adsorption capacity of the functionalized POPs compared to the pristine polymer. As shown in Fig. 11, the chemical grafting of the aminoalkyl-trialkoxysilane with the hydroxy groups of OPTP-8 structure results in direct covalent bonding of the aminoalkyl silane groups to the deprotonated phloroglucinol motif [79,80]. The functionalization of the phloroglucinol-based OPTP-8 with APTS and ABTES groups was confirmed by FTIR. In the FTIR spectra Fig. 12. of the polymer samples, several characteristic peaks were identified, corresponding to different functional groups, confirming the successful functionalization of the base polymer. The broad absorption peak at approximately 3400 cm⁻¹, observed in all samples, corresponds to O–H stretching vibrations, indicative of hydroxyl groups (–OH), or N–H stretching, characteristic of primary or secondary amine groups. The peak at approximately 1604 cm⁻¹ is attributed to

both C=C stretching in aromatic rings and N-H bending in amines. The peak at approximately 1440 cm^{-1} corresponds to C-H bending vibrations, likely arising from alkyl chains or methyl groups present in the polymer structure.

Additionally, the strong peak at around 1040 cm^{-1} is assigned to Si-O-Si stretching vibrations, likely resulting from the hydrolysis of silane groups. The peak at approximately 1115 cm^{-1} can be attributed to a combination of C-N stretching from amine groups, Si-O-C stretching from silane linkages, and C-O stretching from hydroxyl groups. The absorption band at around 920 cm^{-1} is associated with Si-OH bending, confirming the presence of silanol groups on the surface of the material, which are likely from unreacted silanol groups post-functionalization. Finally, the peak at approximately 680 cm^{-1} is indicative of N-H wagging, a characteristic vibration of primary or secondary amines, and is present only in the functionalized polymers. The FTIR spectra of the functionalized POPs exhibited a similar fingerprint to OPTP-8 with additional characteristics around 920 cm^{-1} for Si-OH, and around 680 cm^{-1} for N-H bending in amines. These new bands indicated the successful introduction of amino groups, which were absent in the FTIR spectrum of the pristine

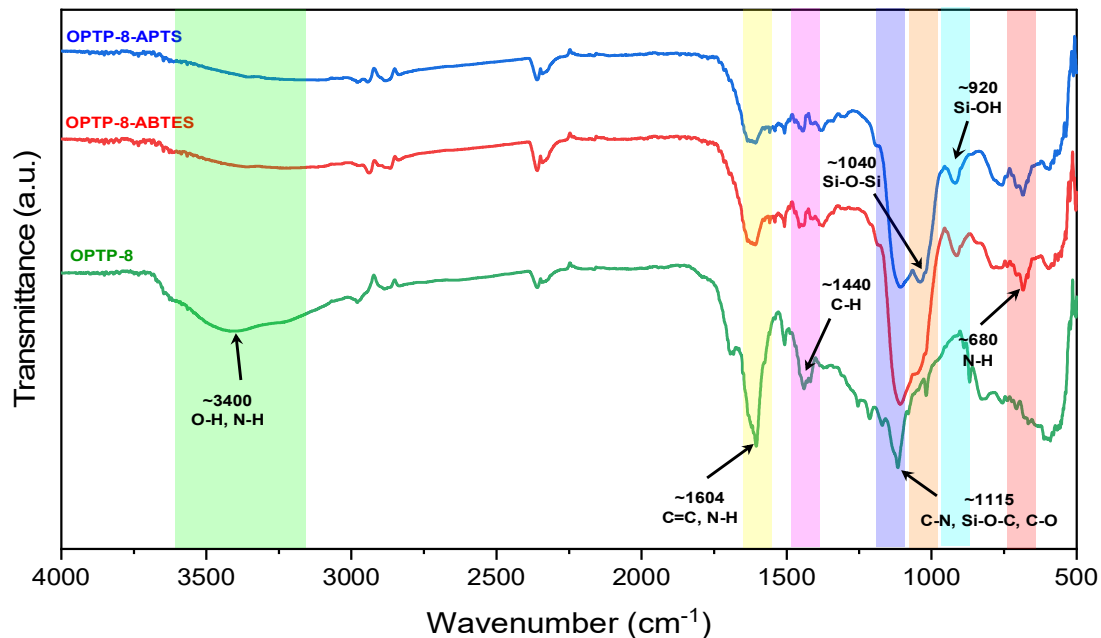


Fig. 12. FTIR spectra for polymers presented in the study.

2.4.2 Morphological and Elemental analysis

The morphological and elemental composition of the pristine and functionalized polymers were analyzed using SEM coupled with EDX, as shown in Fig. 13. The SEM images provide insight into the surface morphology of the polymers, while the EDX maps and spectra offer detailed information regarding the elemental distribution. The SEM image of pristine polymer (Fig. 13c) shows a relatively smooth surface morphology, indicating that the material has a uniform structure. The EDX mapping confirms the dominant presence of Carbon and Oxygen atoms with a very low concentration on Nitrogen, consistent with the elemental composition of the unfunctionalized polymer. Functionalization with APTS (Fig. 13a) and ABTES (Fig. 13b) resulted in noticeable changes in the surface morphology. Both functionalized samples show a more textured surface, probably due to the introduction of functional groups and silane compounds. The EDX mapping for each functionalized polymer indicates a more homogeneous distribution of Silicon and Nitrogen across the surface compared to the pristine sample, suggesting successful functionalization.

In the EDX spectra, Silicon peaks are much more pronounced in the functionalized samples, confirming the incorporation of silane-amine groups into the polymer matrix.

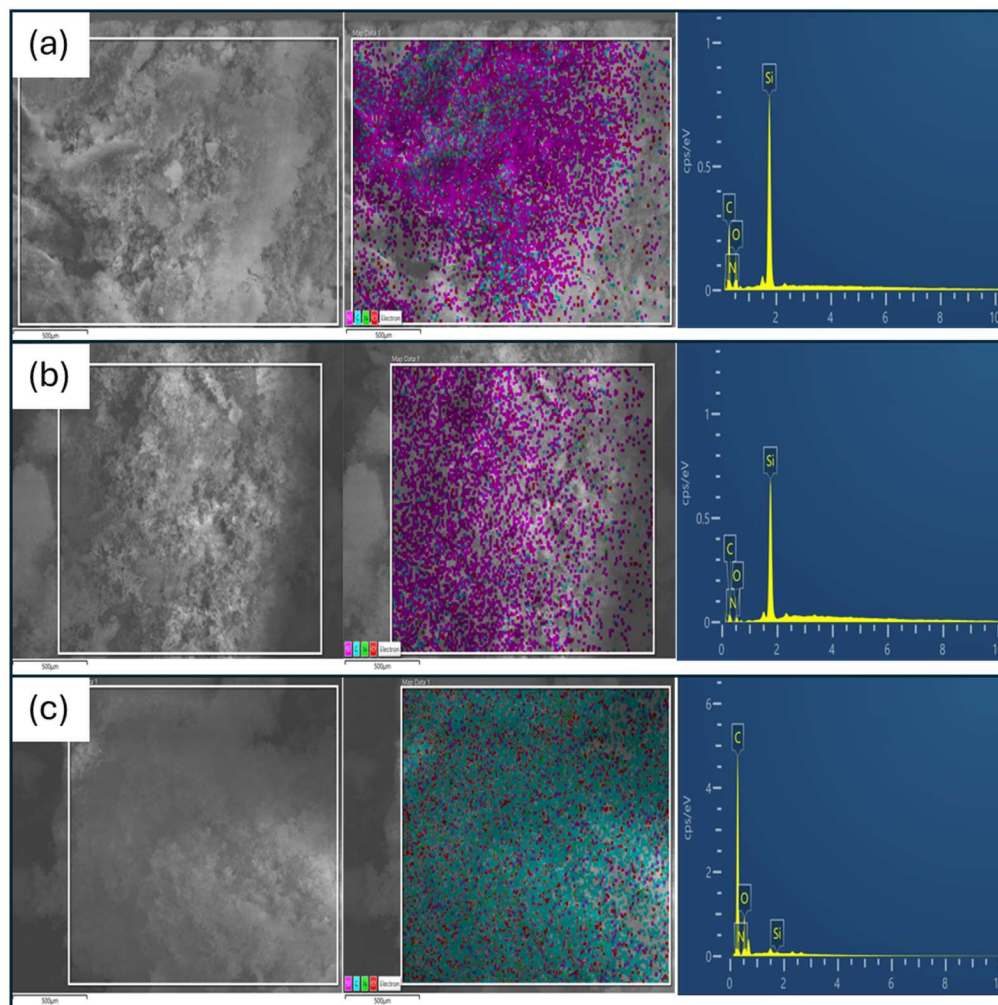


Fig. 13. SEM along with EDX for pristine (c) and functionalized polymers OPTP-8-APTS and OPTP-8-ABTES as (a) and (b), respectively.

The XRD patterns of the pristine and functionalized polymers (Fig. 14) provide further insights into the structural change following functionalization. The pristine polymer exhibits a broad peak around 22° , indicative of an amorphous structure. After functionalization, both OPTP-8-APTS and OPTP-8-ABTES show slight shifts and slight increase in the intensity of this peak, which suggests that the functionalization process

affects the polymer's overall crystallinity. The functionalized polymers exhibit more prominent peaks, confirming the introduction of new functional groups and their interaction with the polymer backbone.

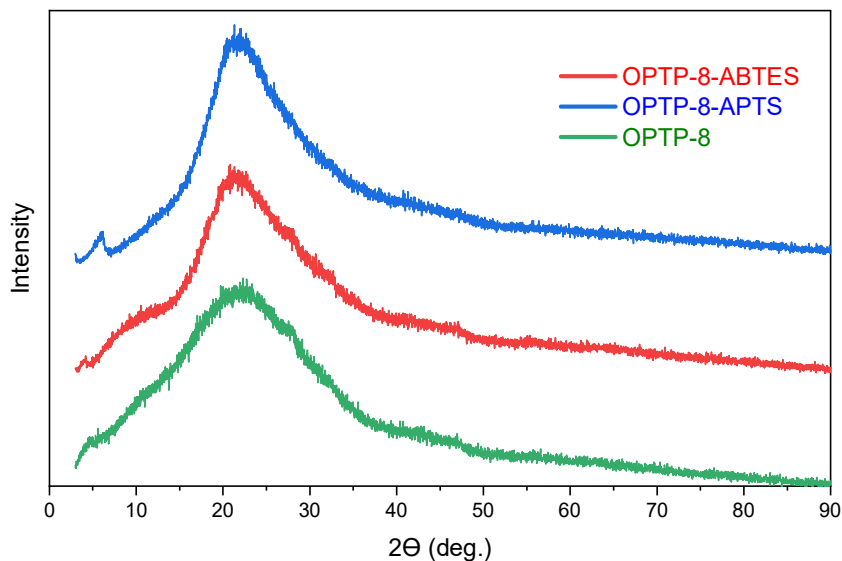


Fig. 14. XRD spectra of pristine and functionalized polymers.

Elemental analysis of the pristine polymer (OPTP-8) and the functionalized polymers (OPTP-8-APTS and OPTP-8-ABTES) was performed to quantify the content of key elements, including nitrogen, carbon, hydrogen, and sulfur, as shown in the Table 7. The results indicate significant differences between the pristine and functionalized polymers. The pristine polymers consist predominantly of carbon and hydrogen, reflecting their unfunctionalized nature. The low nitrogen content confirms the absence of nitrogen-containing functional groups. The result also shows, after functionalization with APTS, the nitrogen content increased significantly to 6.43%, indicating the successful introduction of amino groups from APTS. Additionally, the carbon content decreased to 47.69%, which can be attributed to the incorporation of silicon-based functionality from APTS. The hydrogen content increased slightly to 5.59%. On the other hand, functionalization with ABTES also resulted in an increase in nitrogen content, rising to 4.29%, though lower than

that observed in APTS-functionalized polymer. The carbon content in this sample was 52.54%, reflecting the contribution of the silane groups. The hydrogen content was slightly higher at 5.70% compared to pristine polymer.

Table 7. Elemental analysis of the pristine and functionalized polymer.

Run	N%	C%	H%
OPTP-8-APTS	6.43	47.69	5.59
OPTP-8-ABTES	4.29	52.54	5.70
OPTP-8	0.57	63.50	4.77

2.4.3 Adsorption Study

The CO₂ adsorption performance of the functionalized polymers was evaluated to determine their efficacy and potential for practical applications compared to the pristine polymer. The results indicate that all samples exhibit a Type I isotherm (Langmuir isotherm), characteristic of monolayer adsorption and microporous materials. The presence of microporosity was further confirmed by the DFT analysis (APPENDIX-I), which also revealed that functionalization resulted in partial pore blockage and a reduction in surface area from 857.5 m²/g for OPTP-8 to 36.7 m²/g and 128.3 m²/g for OPTP-8-APTS and OPTP-8-ABTES, respectively.

Despite having the lowest surface area, OPTP-8-APTS (Fig. 15a) demonstrated a higher CO₂ adsorption capacity of 2 mmol/g compared to 1.4 mmol/g for OPTP-8-ABTES (Fig. 15), under the same temperature and pressure conditions. This suggests that functionalization with APTS leads to a more efficient sorbent compared to ABTES, offering superior CO₂ adsorption performance. While the pristine polymer exhibits a higher

CO₂ uptake compared to the functionalized polymers, the selectivity, as determined using ideal adsorbed solution theory (IAST) (Fig. 16), demonstrates superior performance for the functionalized polymers over the parent material. The calculations were performed under DAC conditions, assuming a CO₂ concentration of 400 ppm. The polymer functionalized with APTS displayed a selectivity that was 100 times greater than that of the unfunctionalized polymer.

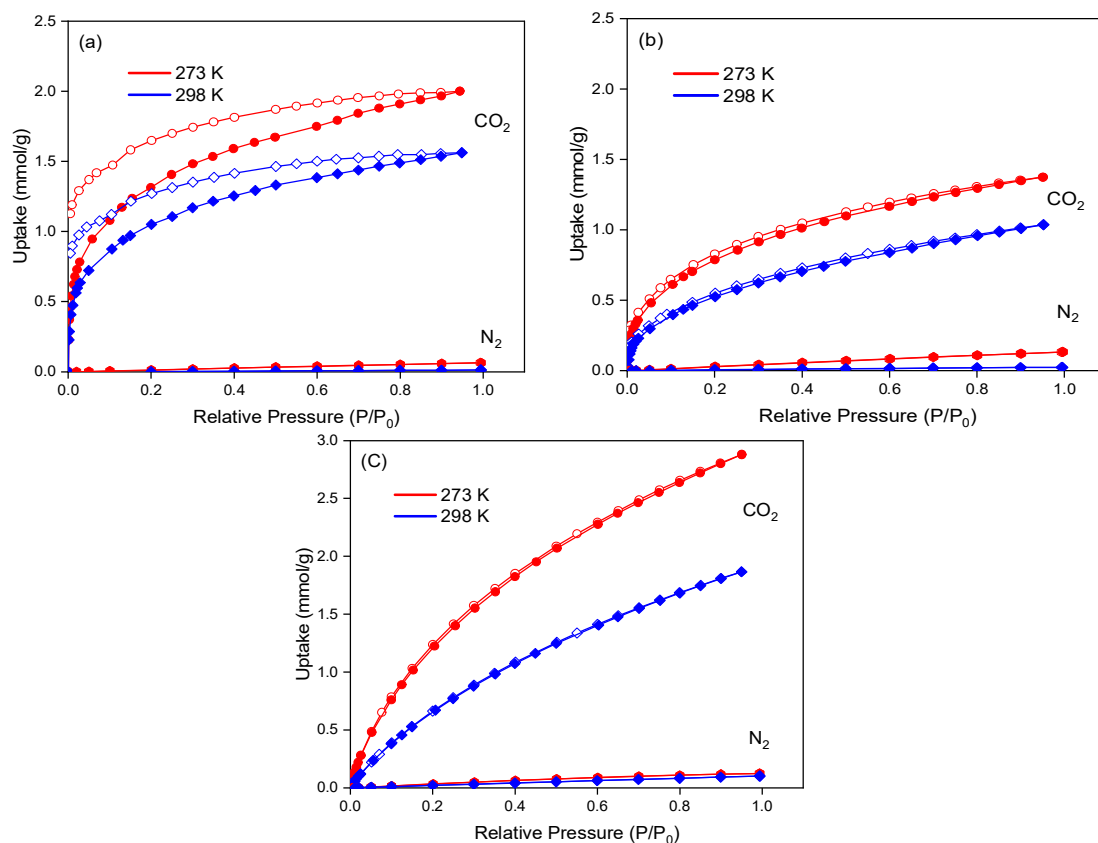


Fig. 15. Gas adsorption isotherms for CO₂ and N₂ for (a) OOTP-8-APTS, (b) OOTP-8-ABTES and (c) OOTP-8, respectively.

An additional observation from Fig. 16 is the effect of temperature on selectivity. While the selectivity of the pristine polymer decreases with increasing temperature, the functionalized polymers exhibit the opposite behavior, with higher selectivity observed at

elevated temperatures. This phenomenon can be attributed to the nature of the adsorption process. In physical adsorption, both capacity and selectivity typically decrease as temperature increases, whereas chemical adsorption is enhanced at higher temperatures.

To further investigate the nature of the adsorption process, the isosteric heat of adsorption (Q_{st}) was measured. The isosteric heat of adsorption provides valuable insights into the energetic interactions between adsorbates and adsorbents, making it a crucial factor in understanding the thermodynamic properties of the materials. This analysis helps confirm whether the adsorption process is predominantly physical or chemical in nature.

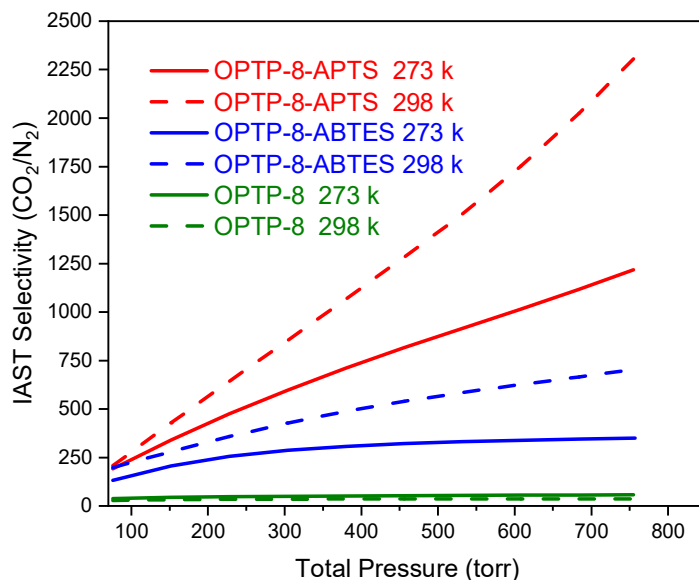


Fig. 16. Selectivity of CO_2 over N_2 adsorption using the ideal adsorbed solution theory (IAST).

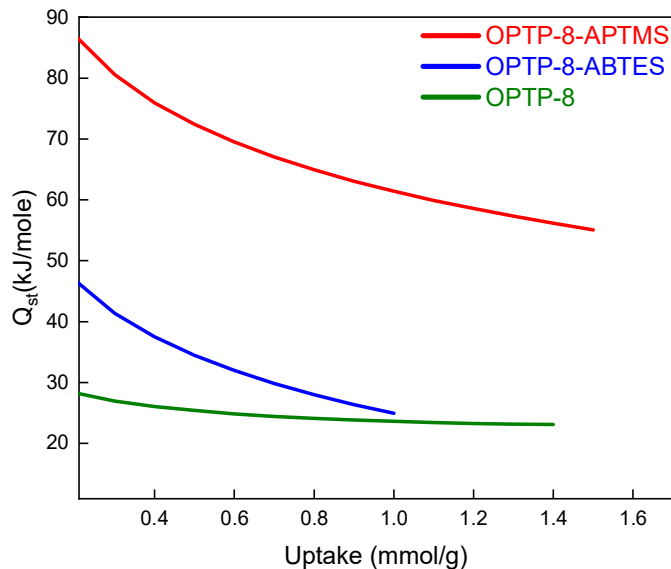


Fig. 17. Isosteric heat of adsorption for CO₂ adsorption.

The average Q_{st} value for CO₂ was 66.35 kJ/mol, 33.48 kJ/mol and 24.66 kJ/mol for OPTP-8-APTS, OPTP-8-ABTES and OPTP-8, respectively. indicating a stronger binding of CO₂ within the polymer framework for functionalized polymer. The calculation was conducted after fitting the desorption curves using Freundlich-Langmuir model. This result suggests that the adsorption process exhibits a favorable chemical binding for CO₂, in the case of functionalized polymer, while the parent polymer shows a physical adsorption behavior. The chemical adsorption is preferred in the case of DAC since it result in higher selectivity and produce higher purity CO₂ which can be directly stored without further purification [81,82].

2.4.4 Thermal and cyclic stability

The thermal stability of the best-performing functionalized polymer (OPTP-8-APTS) and the pristine polymer (OPTP-8) was evaluated using thermogravimetric analysis (TGA), as depicted in Fig. 18. Both polymers initially experience weight loss around 100°C, primarily attributed to the release of water vapor or other gases trapped within the polymer matrix.

Subsequently, both materials begin to decompose at approximately 400°C, indicating a similar onset of thermal degradation. However, the extent of weight loss during thermal decomposition varies significantly between the two materials. The pristine polymer (OPTP-8) exhibits a larger weight loss of 87.7% by the end of the decomposition process, whereas the functionalized polymer (OPTP-8-APTS) shows a reduced weight loss of 64.5%. Unlike the pristine polymer, which disintegrates almost entirely, the functionalized polymer retains approximately 35.5% of its original weight. This remaining mass is primarily composed of silica, directly proportional to the amount incorporation of silane-amine groups into the polymer structure during the functionalization process.

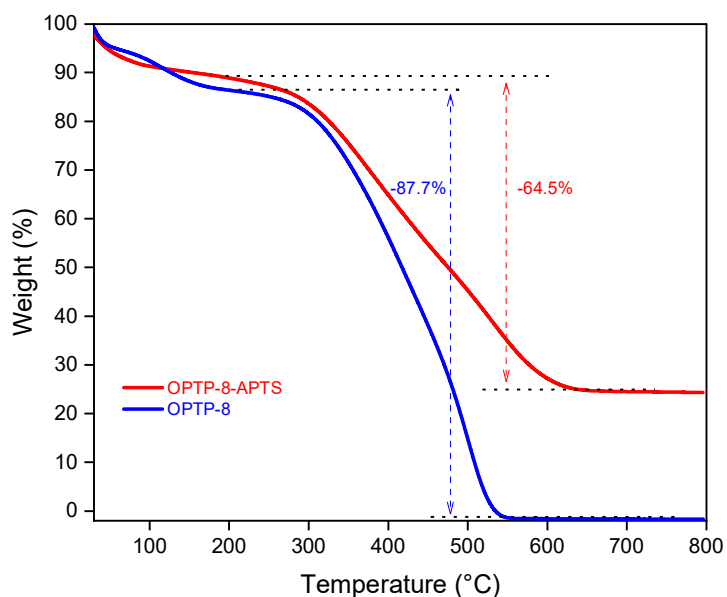


Fig. 18. Thermal stability test of best performing functionalized polymer along with the pristine polymer.

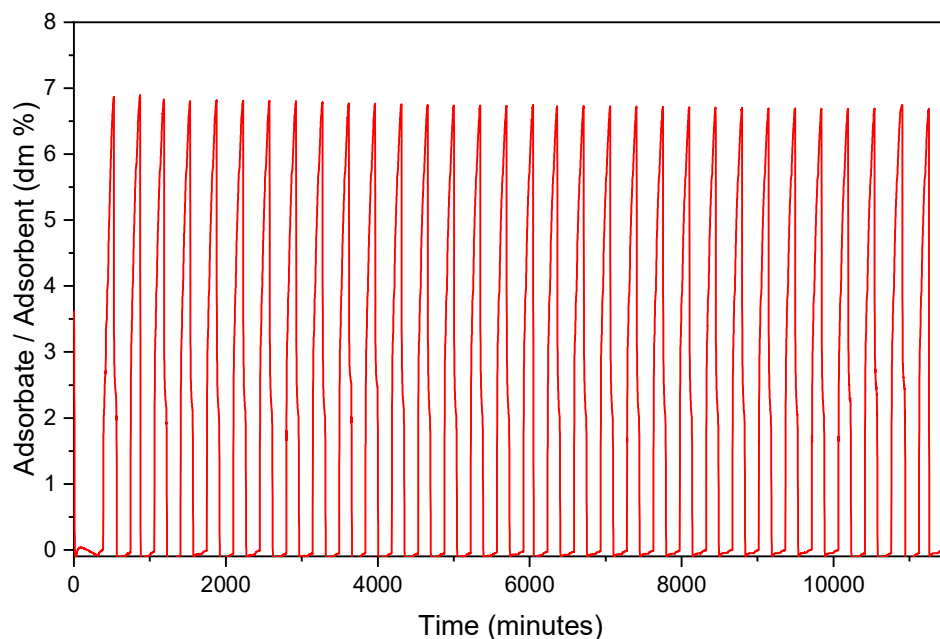


Fig. 19. Cyclic performance of functionalized polymer (OPTP-8-APTS).

Cyclic adsorption and desorption measurements were performed to assess the stability of the functionalized polymer over repeated CO₂ adsorption cycles operating at 298 k and Isotherm mode, as depicted in Fig. 19. The functionalized polymer, OPTP-8-APTS, demonstrated excellent cyclic stability, maintaining consistent adsorption capacity throughout over 32 cycles in 12,000 minutes of testing. The periodic peaks correspond to adsorption and desorption cycles, with minimal loss in capacity observed over time. This indicates that the polymer is able to retain its CO₂ adsorption efficiency across multiple cycles, making it a promising candidate for long-term adsorption applications, such as in DAC or post-combustion CO₂ capture systems.

Table 8. Summary of CO₂ uptake, isosteric heat of adsorption of various porous organic polymers.

POPs	Main function group	BET surface area (m ² /g)	CO ₂ (mmol/g) 1 bar, 273 K	CO ₂ (mmol/g) 1 bar, 298 K	ΔH_{CO_2} (kJ/mol)	Ref.
COF-5	Nonfunctional	1670	1.34	–	–	[83]
PPN-125-DETA	Alkyl amine	229	-	2.05	62	[51]
PPN-80	Alkyl amine	-	-	1.57	72	[84]
MKPOP-4	Hydroxyl	480	1.93	1.32	23.6	[85]
OPTP-8	Hydroxyl	860	2.88	1.86	26.8	This work
OPTP-8-APTS	Alkyl amin	36	2.00	1.56	66.3	This work

Table 8 summarizes a comparison between OPTP-8, OPTP-8-APTS and other polymers from the literature. Although OPTP-8 does not have the highest surface area compared to COF-5, it has higher CO₂ uptake, the phenomenon can be attributed to the hydroxyl group in the polymer framework. The -OH group can interact with CO₂ molecules through hydrogen bonding or van der Waals forces, which capture and stabilize the CO₂ molecules on the surface or within the structure of the polymer. In addition, OPTP-8-APTS shows a comparable CO₂ to other functionalized polymer like PPN-125-DETA, despite having much lower surface area which suggest a window for improvement in the future studies.

CHAPTER 4:

CONCLUSION AND RECOMMENDATION

This thesis aimed to synthesize, optimize, and functionalize phenolic resin-based porous polymers, specifically for CO₂ capture application. The work focused on optimizing the surface area and functionalizing the polymer with amine- containing silanes, which resulted in improved CO₂ adsorption capacities. Throughout the research, several significant findings were made, which contribute to the overall understanding and potential of these materials for practical CO₂ capture. The optimization of the surface area of the pristine polymer (OPTP-8) was achieved using the RSM. The study identified temperature, reaction time, and catalyst amount as the most influential factors affecting the polymer's surface area. Experimental results, supported by ANOVA analysis, demonstrate that interaction between these parameters contributed to maximizing the surface area, with the optimized polymers reaching a surface area of 857.5 cm²/g.

Functionalization of the polymer was carried out using two silane-amine compounds, APTS and ABTES, through covalent bonding. The successful introduction of amine groups onto the polymer's surface was confirmed by various characterization techniques, including FTIR, SEM-EDX, and elemental analysis. FTIR spectra displayed characteristic peaks for amine, silane, and hydroxyl functional group, while EDX mapping revealed a homogeneous distribution of silicon and nitrogen. Confirming the effective functionalization. Elemental analysis further supported the incorporation of amine groups,

showing an increased nitrogen content in the functionalized polymers compared to the pristine material.

The CO₂ adsorption performance of the functionalized polymers was evaluated and compared to the pristine polymer. All samples exhibited Type I isotherms, indicative of monolayer adsorption onto microporous surfaces, with the microporosity of the materials confirmed through DFT analysis. Despite the reduced surface area of the functionalized polymers, the introduction of amine groups resulted in significant enhancement of their CO₂ adsorption capacities. The polymer functionalized with APTS (OPTP-8-APTS) showed the highest CO₂ adsorption capacity at 2 mmol/g, outperforming both the ABTES-functionalized polymer (OPTP-8-ABTES).

Thermal stability was evaluated using thermogravimetric analysis (TGA), which revealed that both the pristine and functionalized polymers began to decompose at approximately 400 °C. The functionalized polymer OPTP-8-APTS, in particular, exhibited significantly better performance, maintaining 35.5% of its weight after thermal degradation. Additionally, cyclic stability tests showed that the functionalized polymers maintained their CO₂ adsorption capacities over multiple cycles, with OPTP-8-APTS retaining its capacity after 32 cycles. The isosteric heat of adsorption (Q_{st}) for CO₂ was calculated to further understand the nature of the adsorption process. The functionalized polymers exhibited a higher heat of adsorption for CO₂, suggesting stronger interactions between the CO₂ molecules and the amine groups on the polymer surface. The selectivity of the functionalized polymers for CO₂ over N₂ was assessed using the Ideal Adsorbed Solution Theory (IAST). Under conditions mimicking DAC, with a CO₂ concentration of 400 ppm, the APTS-functionalized polymer (OPTP-8-APTS) demonstrated significantly higher

selectivity for CO₂ compared to the pristine polymer. Furthermore, the functionalized polymers exhibited a unique behavior where selectivity increased with temperature, suggesting that chemisorption was the dominant mechanism at play.

In conclusion, this study successfully synthesized, optimized, and functionalized phenolic resin-based porous polymers for enhanced CO₂ capture. The functionalized polymers, particularly those modified with APTS, showed improved CO₂ adsorption performance, high thermal stability, and excellent cyclic stability. These findings highlight the potential of these materials for industrial CO₂ capture applications, particularly in DAC and post-combustion capture processes. Future research could focus on scaling up the synthesis process and evaluating the performance of these materials in real-world applications, further contributing to the development of efficient carbon capture technologies.

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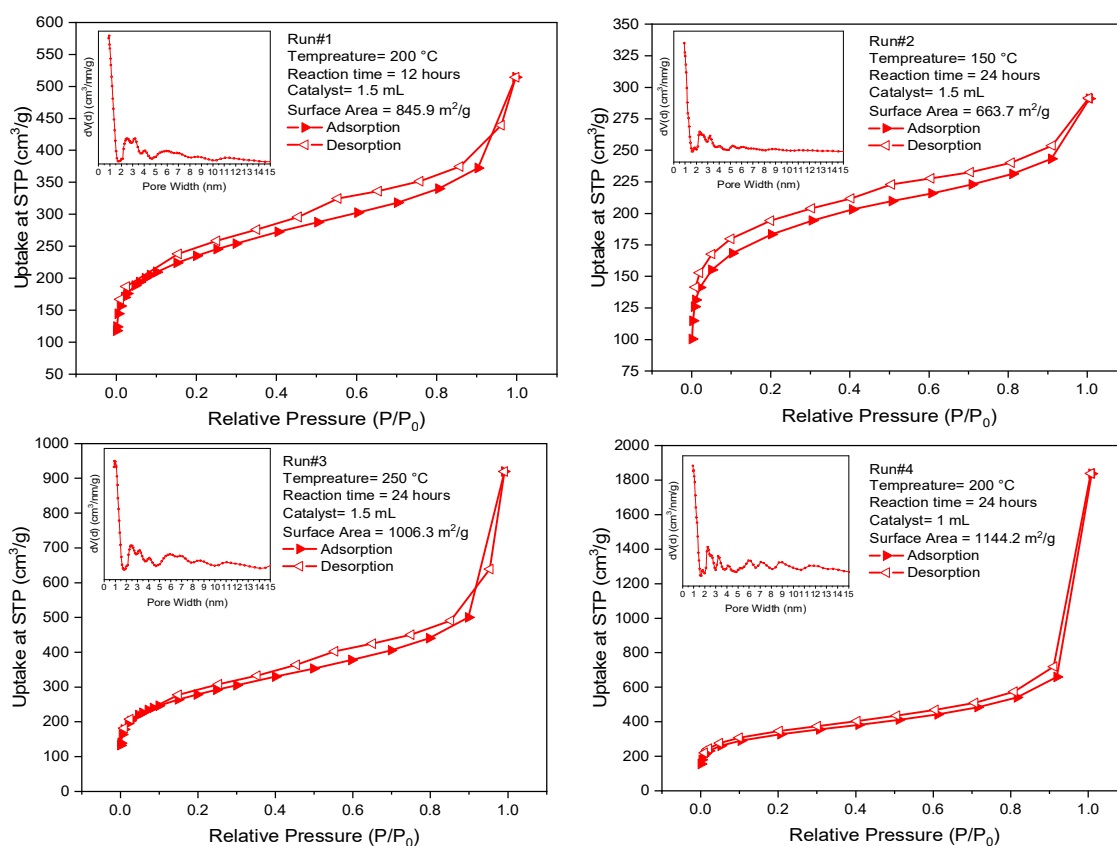
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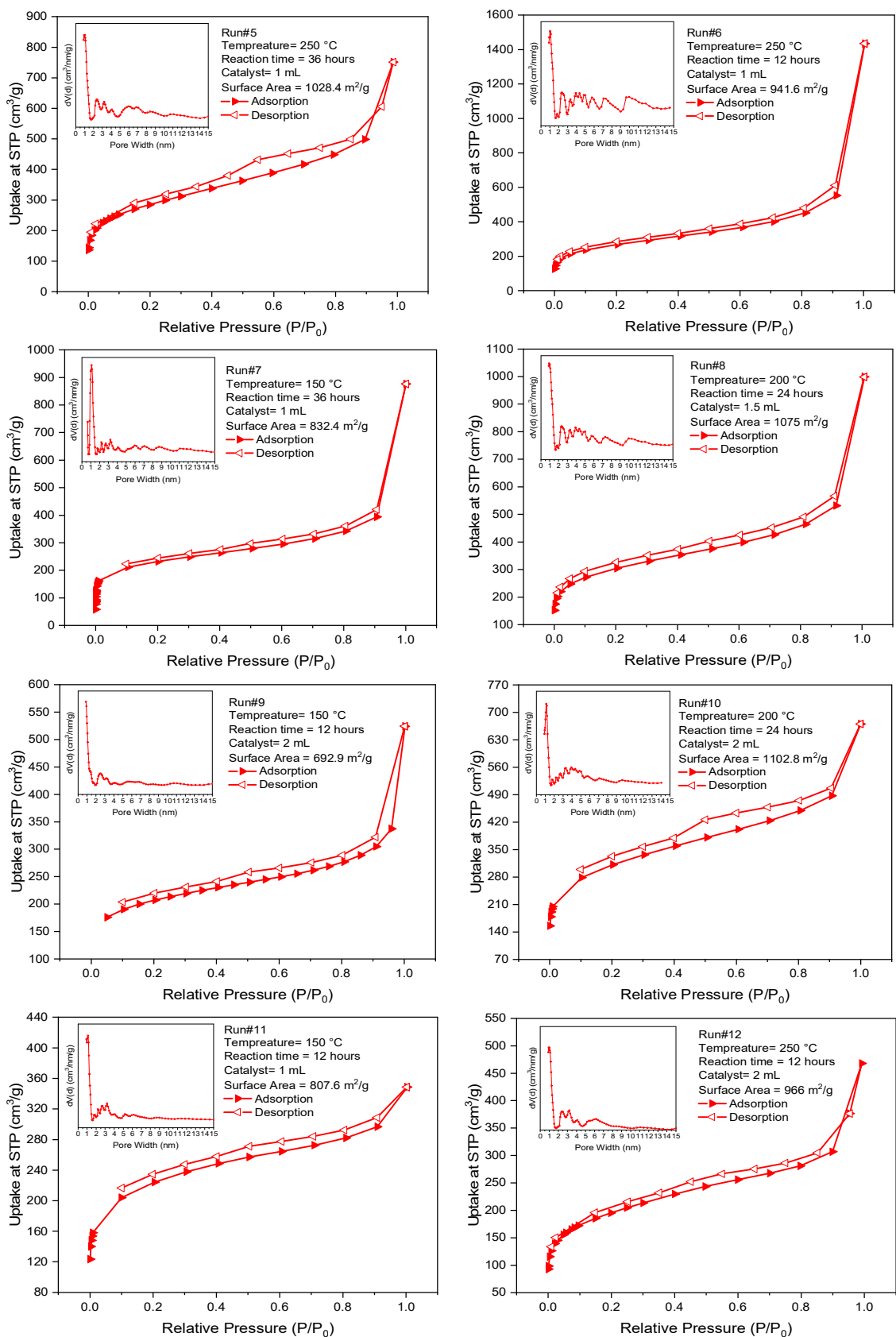
APPENDIX-I

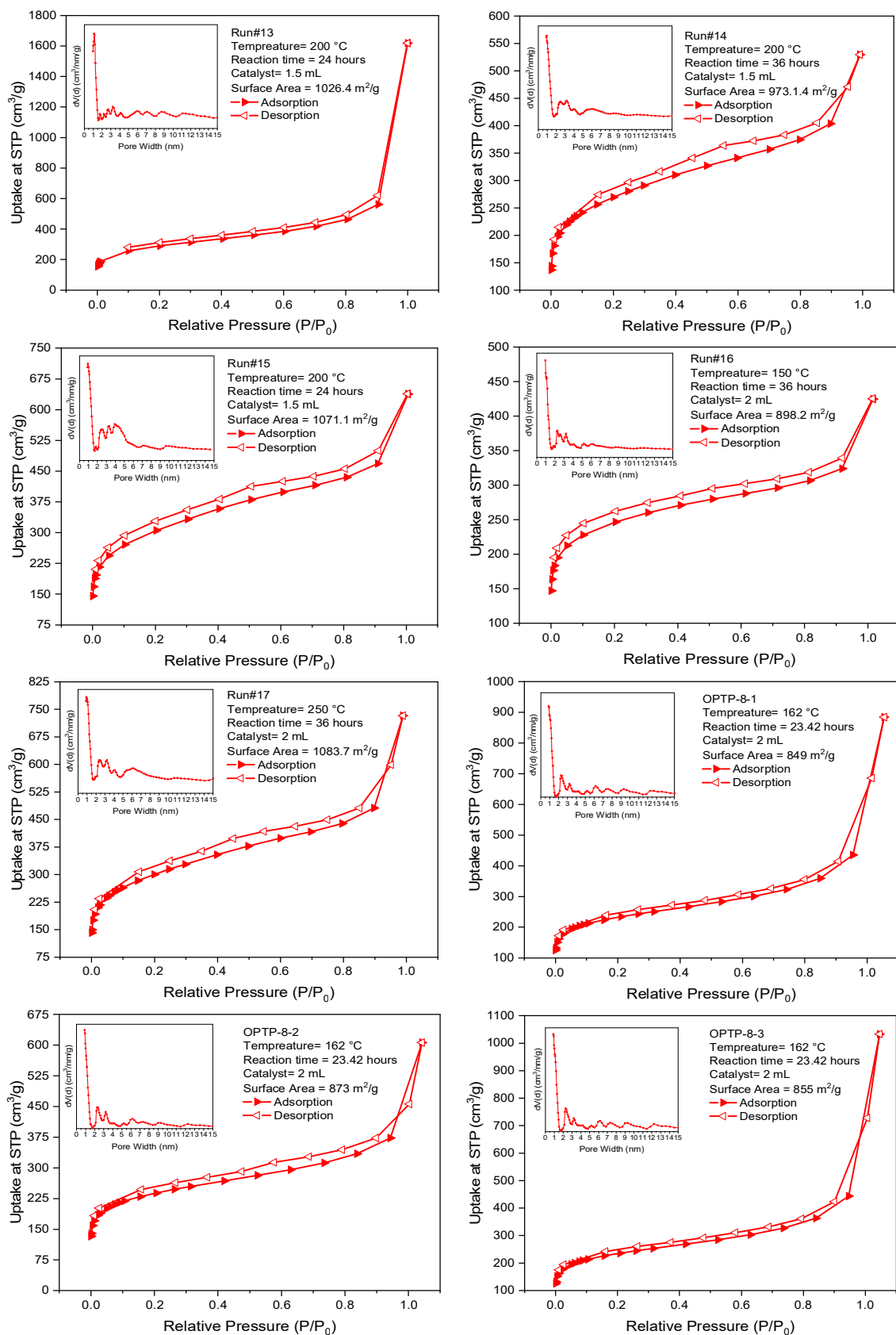
NITROGEN ISOTHERMS USED FOR BET SURFACE AREA CALCULATION & PSD

A. Optimization Section

The nitrogen isotherms were obtained using the method described in characterization section. The calculations of PSD were made using the QSDFT model, assuming (slit/cylinder/sphere) pores, and were performed on the ASiQwin™ software provided by Autosorb™ instrument.

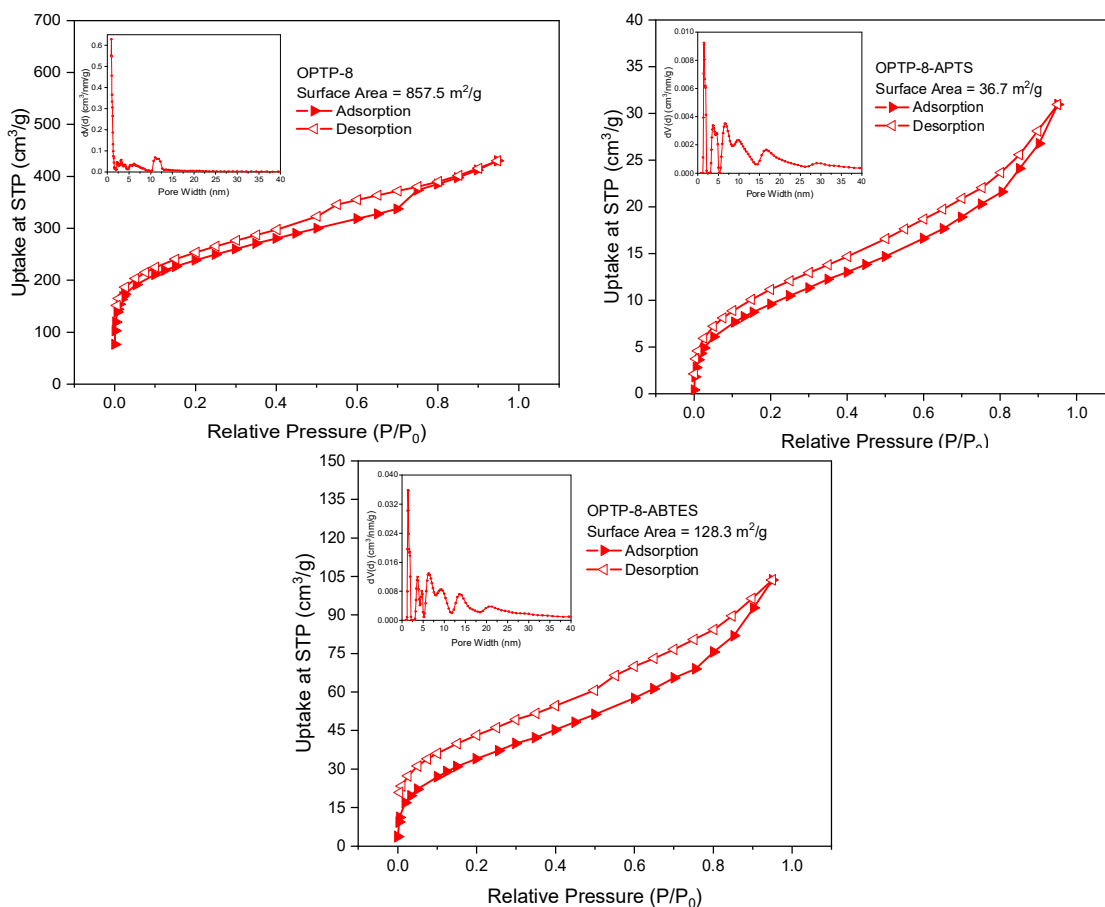






B. Functionalization Section

The nitrogen isotherms were obtained using the method described in characterization section. The calculations of PSD were made using the QSDFT model, assuming (slit/cylinder/sphere) pores, and were performed on the ASiQwin™ software provided by Autosorb™ instrument.



APPENDIX-II

ISOTHERM FITTING MODEL & CALCULATION PROCEDURE

A. Surface Area

The calculation of the surface area was conducted using BET model as follows:

$$\frac{P/P_0}{q_e (1 - P/P_0)} = \frac{1}{q_m C} + \frac{C - 1}{q_m C} \left(\frac{P}{P_0} \right)$$

Where:

- q_e is the specific amount of gas adsorbed at a relative pressure P/P_0 ,
- P is the equilibrium pressure,
- P_0 is the saturation pressure of the adsorbate at the measurement temperature,
- q_m is the monolayer adsorption capacity, and
- C is the BET constant, which is related to the energy of adsorption for the first monolayer.

By plotting the BET equation as:

$$\frac{P/P_0}{q_e (1 - P/P_0)} \text{ vs. } \frac{P}{P_0}$$

a linear relationship is obtained in the relative pressure range $0.05 \leq P/P_0 \leq 0.35$. The slope and intercept of this plot are used to determine q_m , the amount of gas adsorbed at monolayer coverage. The BET constant C can also be extracted from this linear plot.

Once q_m is determined, the surface area S_{BET} , can be calculated using the following equation:

$$S_{BET} = \frac{q_e L \sigma_m}{m}$$

Where:

- L is Avogadro's number ($6.02214076 \times 10^{23}$),
- σ_m is the molecular cross-sectional area of the adsorbate (for nitrogen, it is typically $16.2 \text{ \AA}^2$) and,
- m is the mass of the sample in grams.

B. Isotherm fitting model

The adsorption isotherms for CO₂ and N₂ were primarily modeled using two approaches: the Dual-Site Langmuir model and the Freundlich-Langmuir model. These models were applied to accurately fit the experimental data and describe the adsorption behavior of both gases on the sorbent surface. The fitting parameters obtained from these isotherm models were subsequently utilized to perform critical calculations, such as determining the heat of adsorption and selectivity of the sorbent towards CO₂ over N₂. The heat of adsorption provides insights into the interaction strength between the adsorbate and the adsorbent, while selectivity is essential for evaluating the material's performance in separating CO₂ from N₂ in mixed gas streams.

a. Freundlich-Langmuir

The Freundlich-Langmuir model combines elements of both the Langmuir and Freundlich adsorption isotherms to describe adsorption behavior. This hybrid model is particularly useful for materials with heterogeneous surfaces, where adsorption may not occur uniformly across all sites. The Langmuir model assumes a monolayer adsorption on a homogeneous surface, while the Freundlich model accounts for adsorption on heterogeneous surfaces with varying adsorption energies. By combining these two models, the Freundlich-Langmuir model is able to better capture the adsorption behavior of materials that exhibit both uniform and non-uniform adsorption characteristics, making it well-suited for describing the adsorption of gases like CO₂ and N₂ on complex sorbents. The OriginLab software was used as a fitting tool for both models.

The Freundlich-Langmuir model is described by the following equation:

$$q_e = q_m \frac{b P^c}{1 + b P^c}$$

Where:

- q_e is the amount of adsorbate adsorbed at equilibrium,
- q_m is the monolayer adsorption capacity,
- P is the pressure of the adsorbate,
- b is the Langmuir adsorption constant (1/pressure), which represents the affinity between the adsorbate and the sorbent,
- c is the Freundlich heterogeneity factor, which accounts for the varying adsorption energies on the surface.

b. Dual- Site Langmuir

The Dual-Site Langmuir model is an extension of the Langmuir model, which assumes that the adsorption occurs on two distinct types of adsorption sites, each with its own adsorption energy and capacity. This model is particularly useful for materials with heterogeneous surfaces, where different types of binding sites exist, such as in porous materials or functionalized sorbents. In this model, the total adsorption is considered as a combination of adsorption on two distinct sites, labeled as Site 1 and Site 2. Each site follows the Langmuir adsorption behavior, where adsorption occurs as a monolayer on a fixed number of identical sites. The model can be described by the following equation:

$$q_e = \frac{q_{m1} b_1 P}{1 + b_1 P} + \frac{q_{m2} b_2 P}{1 + b_2 P}$$

Where:

- q_e is the amount of adsorbate adsorbed at equilibrium,
- P is the pressure of the adsorbate,
- q_{m1} and q_{m2} are the maximum adsorption capacity for Site 1 and Site 2, respectively,
- b_1 and b_2 are the Langmuir adsorption constant (1/pressure) for Site1 and Site2, respectively, which represents the affinity between the adsorbate and the sorbent,

C. Enthalpy Heat of Adsorption

The heat of adsorption was calculated using the Clausius-Clapeyron equation, which is a thermodynamic relation that describes how the equilibrium vapor pressure of a substance varies with temperature. In the context of adsorption, it is often used to determine the **heat of adsorption**, which quantifies the energy required to adsorb a molecule onto a surface. This value is crucial for understanding the strength of the interaction between an adsorbate (such as CO₂) and the adsorbent material (such as a porous polymer or solid sorbent).

The Clausius-Clapeyron equation can be expressed as follows for adsorption:

$$\Delta H_{ads}(q_e) = -R \times \ln \left(\frac{P_2}{P_1} \right) \frac{T_1 T_2}{(T_2 - T_1)}$$

- P is the pressure of the adsorbate,
- T is the temperature,
- $\Delta H_{ads}(q_e)$ is the heat of adsorption, represent the energy change during the adsorption process as a function of amount adsorbed,
- R is the universal gas constant (8.314 J/mol. K)

To apply the Clausius-Clapeyron equation to adsorption data, the following steps are typically taken:

1. Adsorption isotherms are measured at several different temperatures, then fitted using any appropriate model (in this study the used isotherms models are mentioned above)
2. For each specific amount of gas adsorbed (q_e), the equilibrium pressure at different temperatures is plotted as $\ln P$ versus $1/T$. This create a linear relationship where the slope is proportional to the heat of adsorption.

3. From the slope of the line obtained in the plot of $\ln P$ versus $1/T$, the heat of adsorption can be calculated using the below equation, steps 2 to 3 are repeated using different value of (q_e) and the heat of adsorption finally reported as function of amount adsorbed.

$$\Delta H_{ads}(q_e) = -R \times Slope$$

D. Ideal Adsorbed Solution Theory (IAST)

The Ideal Adsorbed Solution Theory (IAST) is a theoretical approach developed by Myers and Prausnitz in 1965 to predict the adsorption behavior of gas mixtures based on the adsorption isotherms of individual gases. IAST assumes that the adsorbed phase behaves as an ideal solution, meaning that the interactions between different adsorbate molecules on the adsorbent surface are similar to the interactions between like molecules. This assumption allows IAST to extend single-component adsorption data to predict the adsorption of multi-component gas mixtures, such as CO₂ and N₂.

To determine the selectivity using IAST, single-component adsorption isotherms at a constant temperature must first be obtained for each gas. These isotherms are then fitted to a suitable adsorption model, such as the Dual-Site Langmuir model or the Freundlich-Langmuir model, depending on the behavior of the system. After fitting the isotherms, the spreading pressure (π), a key parameter in IAST that describes the adsorbed phase is equated based on IAST assumption that spreading pressure is the same of both gases in the adsorbed phase, meaning the two gases share the same surface area. This assumption resulted in the following relation for a binary gas mixture system, e.g., CO₂/N₂:

$$\int_0^{P_{CO_2}} \frac{q_{CO_2}}{P} dP = \int_0^{P_{N_2}} \frac{q_{N_2}}{P} dP$$

Where:

- P_i is the partial pressure of component,
- q_i is the adsorption amount of component as a function of total pressure,

To solve the above problem, the mole fractions of components in the adsorption phase are calculated as follows:

$$y_i P_t = x_i P_i$$

Apply this relation to the spreading pressure:

$$\int_0^{\frac{y_{CO_2} P_t}{x_{CO_2}}} \frac{q_{CO_2}}{P} dP = \int_0^{\frac{y_{N_2} P_t}{x_{N_2}}} \frac{q_{N_2}}{P} dP$$

Here, q_i is represented by the pure component isotherm of each gas, obtained by fitting the isotherm, for example if the Freundlich-Langmuir model is used:

$$q_i = q_{m,i} \frac{b_i y_i P^c}{1 + b_i y_i P^c}$$

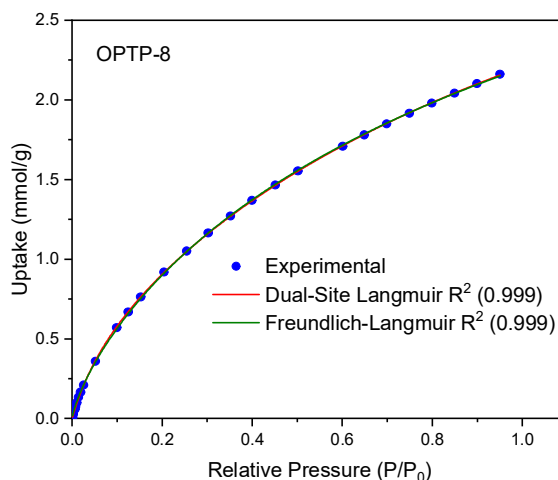
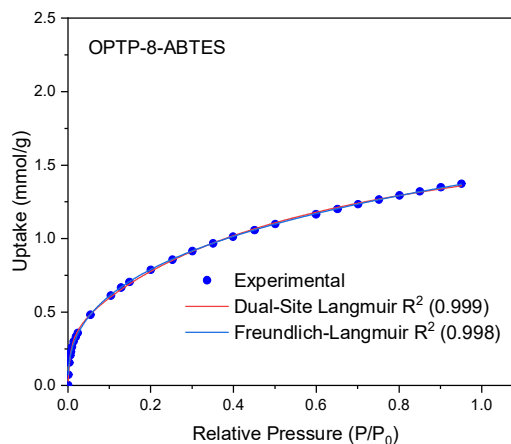
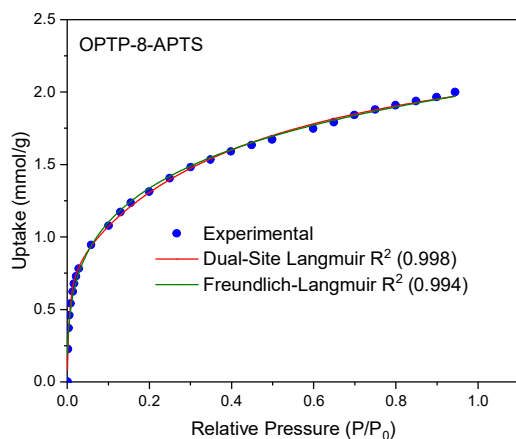
Given P_t, y, q_i, c and b_i , the only unknown variable is x_i , which can be solve using MATLAB or any numerical method software. In this study the tool Graph IAST made by Dautzenberg et al, [78], is used to calculate selectivity which is represented by the following equation:

$$S_{IAST} = \frac{(x_{CO_2}/y_{CO_2})}{(x_{N_2}/y_{N_2})}$$

APPENDIX-III

ISOTHERM FITTING FOR ADSORPTION CURVES USING TWO DIFFERENT MODELS

Prior to the calculation of IAST and heat of adsorption (Q_{st}). The two isotherm modules discussed in APPENDIX-II, Dual-Site Langmuir and Freundlich-Langmuir were used. For all case Dual-Site Langmuir had a higher R^2 value compared to Freundlich-Langmuir but since both had R^2 value approximately one, they both have been used for IAST and Q_{st} calculation.



Vitae

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1. **Abdalla, M. A.**, Zentou, H., Abdulhamid, M. A., Mohammed, M. G., Abdelnaby, M. M., & Abdelaziz, O. Y. (2025). A porous phenolic resin sorbent for enhanced CO₂ capture: Synthesis, optimization, and techno-economic analysis. *Fuel*, 379, 132961. **(Q1, IF:6.7)**
2. Abdelnaby, M. M., Saleh, T. A., Zeama, M., **Abdalla, M. A.**, Ahmed, H. M., & Habib, M. A. (2022). Azo-linked porous organic polymers for selective carbon dioxide capture and metal ion removal. *ACS omega*, 7(17), 14535-14543. **(Q2, IF:4)**
3. EL-Maaty, A. E. A., **Abdalla, M. A.**, Essalhi, M., Abdelnaby, M. M., Mahmoud, M. M., Habib, M. A., ... & Ben-Mansour, R. (2024). Kinetics of Water Adsorption in Metal-Organic Framework (MOF-303) for Adsorption Cooling Application. *Energy Conversion and Management: X*, 24, 100694. **(Q1, IF:7.1)**
4. **Abdalla, M.**, Mohammed, M. G., & Zahid, U. (2024). Design of carbon neutral methanol production via integration of renewable hydrogen and dry reforming process. In *Computer Aided Chemical Engineering* (Vol. 53, pp. 2137-2142). Elsevier. **(Conference)**