

Design and Synthesis of Porous Organic Polymers
for Environmental Remediation

BY

Hassan Ali Amasha

A Thesis Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

May 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Hassan Ali Amasha** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY**.



Dr. Jameel Althagfi
Chairman of Chemistry Department



Prof. Suliman Al-Homidan
Dean of Graduate & Interdisciplinary
Studies

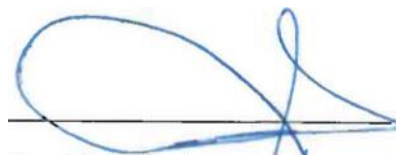
Date



Dr. Othman Al-Hamouz
(Advisor)



Prof. Tawfik Abdo Saleh
(Member)



Dr. Ahmed Al-Harbi
(Member)



© Hassan A. Amasha

2024

Dedication

To my beloved wife Shroog, my son Yazan, dear parents, my brothers & sister

& all my friends for their endless love & support

ACKNOWLEDGMENTS

All praise is to ALLAH Almighty who made it possible for me to accomplish this research work successfully.

First and the most important, I would like to thank my advisor Dr. Othman Al Hamouz for his guidance, support, and patience during this research. His encouragement and insights enabled me to work towards getting desired results and to overcome the problems along the way. I would also like to thank all the amazing committee members, Prof. Tawfik Saleh and Dr. Ahmed Al-Harbi for their interest and valuable suggestions and support for this work by training and offering their lab facilities. I would also like to express my gratitude to all the faculty members of the Chemistry Department at KFUPM. To all of them, I appreciate what they have done to help me in my scholastic and professional growth.

I express my gratitude to the departmental and college administration, Dr. Jameel Althaqfi (Chairman, Department of Chemistry), Prof. Abdulaziz Alsaadi, and Prof. Khalid Alhooshani, for their valuable guidance and administrative assistance.

I acknowledge my Chemistry department staff friends Mr. Mansour Alzaki, Mohammed Alsebaa, Mohammed Al-Ghushairy, Nadir Osman, Sowrirajan Subbaiah and all well-wishers, whom I have not mentioned above and whose best wishes have always encouraged me.

Moreover, I acknowledge the support and encouragement I received from my colleagues at Halliburton, Dr. Saleh Almutairi (Ex Technology manager), Mr. Ayoub Awaji and Dr. Azhar Alhasawi.

Last but not least I would like to thank my family who always supported me throughout my career and helped me in achieving my goals.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	IX
LIST OF FIGURES	X
LIST OF ABBREVIATIONS	XIII
ABSTRACT	XVII
ملخص الرسالة	XVIII
CHAPTER 1 INTRODUCTION	1
1.1 Greenhouse gas effect.....	1
1.2 Carbon capture, and storage technologies	5
1.3 CO ₂ separation technologies	10
1.4 Adsorption	11
1.5 Renewable energy	12
1.6 Nuclear energy	14
1.7 Radioactive Iodine.....	15

CHAPTER 2 LITERATURE REVIEW 18

2.1 Porous organic polymers.18

**CHAPTER 3 MICROWAVE-SYNTHEZIZED HETEROAROMATIC POROUS
ORGANIC POLYMERS FOR CO₂ CAPTURE AND HYDROGEN STORAGE..... 29**

ABSTRACT29

3.1 Introduction30

3.2 Materials and Methods32

3.2.1 Materials32

3.2.2 Characterization.....32

3.2.3 Synthesis of porous organic polymers33

3.2.4 Monte Carlo Simulations35

3.3 Results and Discussion36

3.3.1 Synthesis Strategy36

3.3.2 Structural Characterization36

3.3.3 Sorption Isotherms.....39

3.3.4 Isosteric heat of adsorption (Q_{st}) and selectivity.....41

3.3.5 Molecular level interactions45

3.4 Conclusion.....50

CHAPTER 4 PHENAZINE POROUS POLYMERS FOR RADIOACTIVE IODINE..... 51

Abstract51

4.1 Introduction51

4.2	Experimental section	53
4.2.1	Materials and instruments.....	53
4.2.2	Synthesis of Phenazine based porous polymers.	54
4.2.3	Volatile iodine uptake experiments	54
4.2.4	Solution iodine uptake experiments.....	55
4.3	Results and discussion	55
4.3.1	Characterization of <i>PHP</i> , <i>PHT</i> and <i>PHF</i> porous polymers	56
4.3.2	Adsorption properties of the synthesized polymers.....	59
4.4	Conclusions	66
APPENDIX		67
REFERENCES		71
VITAE		100

LIST OF TABLES

Table 1: Reaction details and porosity information of the synthesized porous polymers.	34
Table 2: Initial slope selectivity of HAF, HAT and HAP toward CO ₂ against CH ₄ and N ₂	43
Table 3: CO ₂ uptake capacity and surface area comparison of synthesized HAF, HAT and HAP polymers with other reported adsorbents	45
Table 4: (a) Pseudo first-order and Pseudo second-order kinetic model parameters of the adsorption of volatile iodine by the porous polymers PHP, PHF and PHT.....	61
Table 5: Langmuir and Freundlich isotherm model parameters for the adsorption of iodine in cyclohexane by PHP, PHT and PHF porous polymers.....	64
Table 6: Pseudo first-order and Pseudo second-order kinetic model parameters of the adsorption of iodine in cyclohexane by the porous polymers PHP, PHF and PHT.	65
Table 7: Langmuir-Freundlich Fitting Data.....	68
Table 8: Theoretical Q _{st} values of the polymers in binary gas mixtures.....	70

LIST OF FIGURES

Figure 1: The effect of greenhouse gases in atmosphere. ^[1]	2
Figure 2: Global greenhouse gas emissions by gas type. ^[2]	3
Figure 3: Top greenhouse gas emitting countries (in gigaton of CO ₂ equivalents: GtCO ₂). ^[3]	4
Figure 4: Worldwide CO ₂ emissions in 2020. ^[7]	6
Figure 5: Current technologies employed to mitigate CO ₂ emissions. ^[4]	8
Figure 6: Several CO ₂ collection technologies currently in use. ^[34]	10
Figure 7: Illustration of CO ₂ separation technologies.	11
Figure 8: Renewable energy technologies.	13
Figure 9: ¹³¹ I decay scheme. ^[43]	16
Figure 10: The development of POP over the last century. ^[50]	19
Figure 11: Microwave-assisted Friedel-Crafts polymerization of porous organic polymers.	34
Figure 12: Structural characterization of synthesized polymers (a) ¹³ C NMR spectrum of the synthesized polymers; (b) FTIR spectra of the synthesized polymers; (c) TGA thermal patterns of the synthesized polymers at rate of 10°C/min.; (d) SEM figure and PXRD patterns of the synthesized polymers within the range of 5-60 (2θ) measured at 2 degrees/min.	38
Figure 13: (a) N ₂ adsorption at 77K of the synthesized polymers exhibiting adsorption (filled circles) and desorption (open circles).; (b) Pore size distribution of the synthesized polymers using NLDFT.; Gas sorption isotherms of the synthesized polymers for (c) CO ₂ (d) CH ₄ (e) N ₂ (f) H ₂ .	41
Figure 14: Isosteric heat of adsorption (Q _{st}) curves for (a) CO ₂ gas, (b) CH ₄ gas, and (c) N ₂ gas.	43

Figure 15: Initial slope selectivity of HAF, HAT and HAP at 273K and 298 K.....	44
Figure 16: Geometry-optimized structures (top) and the Connolly amorphous cells comprising of 30 repeating units (bottom) of the polymers (a) HAF, (b) HAP and (c) HAT. The blue and grey isosurfaces represent the free accessible volumes within the polymers at a probe radius of 1.2 Å.	47
Figure 17: Theoretical adsorption isotherms at 273 K and 298 K of (a) CO ₂ , (b) CH ₄ and (c) N ₂ gases on HAF, HAP and HAT polymers. The adsorption isotherm of H ₂ at 77 K is shown in (d). The inset shows the H ₂ molecules within the HAF polymer.....	48
Figure 18: Theoretical adsorption isotherms of CO ₂ , CH ₄ and N ₂ gases on (a) HAF at 273 K, (b) HAF at 298 K, (c) HAT at 273 K, (d) HAT at 298 K, (e) HAP at 273 K, and (f) HAP at 298 K.....	49
Figure 19: Volatile iodine adsorption experiment setup.....	55
Figure 20: Microwave-assisted polymerization of porous phenazine polymers.	56
Figure 21: (a) Detailed Solid ¹³ C-NMR (CP MAS) spectra of the synthesized polymers PHP, PHT and PHF. (b) FTIR spectra of the synthesized polymers PHP, PHT and PHF. (c) TGA thermograms of the synthesized polymers PHP, PHT and PHF. (d) PXRD patterns of the synthesized polymers PHP, PHT and PHF.	57
Figure 22: N ₂ adsorption/desorption isotherm, and NLDFT pore size distribution curve of the synthesized polymers PHP, PHT and PHF.	58
Figure 23: (a) Effect of time on the adsorption of volatile iodine by the porous polymers PHP, PHT and PHF. (b) Pseudo first-order kinetic model. (c) Pseudo second-order kinetic model. (d) Intraparticle diffusion kinetic model.	60

Figure 24: (a) The effect of initial concentration on the adsorption capacity of PHP, PHT and PHF.	
(b) The Langmuir isotherm model of the adsorption of iodine by PHP, PHT and PHF.	
(c) The Freundlich isotherm model of the adsorption of iodine by PHP, PHT and PHF.	
(d) The difference in color of the iodine solution before and after adsorption by PHP, PHT and PHF after 24 h at different concentrations.....	63
Figure 25: (a) The effect of time on the adsorption capacity of the synthesized polymers PHP, PHT and PHF. (b) Pseudo first-order kinetic model. (c) Pseudo second-order kinetic model.	
(d) The color change of the iodine solution before and after adsorption by the porous polymers PHP, PHT and PHF.....	65
Figure 26: Optimized geometry of the polymer HAF, and the supercells comprising of (a) CO ₂ , (b) CH ₄ and (c) N ₂ gases.....	69
Figure 27: Optimized geometry of the polymer HAP, and the supercells comprising of (a) CO ₂ , (b) CH ₄ and (c) N ₂ gases.....	69
Figure 28: Optimized geometry of the polymer HAT, and the supercells comprising of (a) CO ₂ , (b) CH ₄ and (c) N ₂ gases.....	70

LIST OF ABBREVIATIONS

AC:	Activated Carbon
AHG:	Abdullah Hashim Industrial Gases
BECCS:	Bioenergy with Carbon Capture and Storage
BET:	Brunauer-Emmett-Teller theory
CaL:	Calcium looping
CCMC:	Carbon capture and mineral carbonation
CCS:	Carbon capture and storage
CCU:	Carbon capture and utilization
CCUS:	Carbon capture, utilization, and storage
CH ₄ :	Methane
CLC:	Chemical looping combustion
CMPs:	Conjugated microporous polymers
CO:	Carbon monoxide
CO ₂ :	Carbon dioxide
CPMAS:	Cross-polarization magic angle spinning
DAC:	Direct Air Capture

DACS:	Direct Air Capture and Storage
DACU:	Direct Air Capture and Utilization
DI:	Deionized water
DM:	Dimethoxymethane
DMF:	N, N-dimethylformamide
DSC:	Differential scanning calorimetry
EDX:	Energy dispersive X-ray
F:	Furan
FFV:	Fractional free volume
FTIR:	Fourier transform infrared spectroscopy
GCMC:	Grand Canonical Monte Carlo
GHGs:	Greenhouse gases
H ₂ S:	Hydrogen sulfide
HCPs:	Hyper-Crosslinked Polymers
HSAB:	Hard-Soft Acid-Base
IAEA:	International Atomic Energy Agency
IPCC:	Intergovernmental Panel on Climate Change

IUPAC:	International Union of Pure and Applied Chemistry
KBr:	Potassium Bromide
MeOH:	Methanol
MOFs:	Metal-organic frameworks
N ₂ O:	Nitrous oxide
NH ₄ OH:	Ammonium hydroxide solution
NLDFT:	Non-local density functional theory
NMR:	Nuclear magnetic resonance spectroscopy
NO _x :	Nitrogen Oxides
NPP:	Nuclear power plants
PAFs:	Porous aromatic frameworks
PIMs:	Intrinsic microporosity
POPs:	Porous organic compounds
PY:	Pyrrole
Qst:	Isosteric heat of adsorption
SCF:	Self-consistent field
SEM:	Scanning Electron Microscopy

SO _x :	Sulfur oxides
TGA:	Thermogravimetric analysis
TH:	Thiophene
TMS:	Tetramethyl Silane
TTB:	1,3,5-tris(2-thienyl) benzene
UN:	United Nations
XRD:	X-ray diffraction

ABSTRACT

Full Name : Hassan Ali Hasan Amasha

Thesis Title : Design and Synthesis of Porous Organic Polymers for Environmental
Remediation

Major Field : Chemistry

Date of Degree : May 2024

Environmental remediation is an essential component in the ongoing effort to achieve environmental sustainability and protect human health. With the progress of industry and urbanization, the problems caused by pollution and poisoning of our natural environment have also increased. The consequences of environmental degradation, such as the infiltration of harmful substances into soil and groundwater or the presence of air pollutants in urban atmospheres, have wide-ranging and complex effects. Environmental remediation has arisen as a complete collection of methods and approaches designed to purify and restore ecosystems that have been contaminated by human activity.

This study presents the development of a variety of highly porous polymers with the aim of mitigating or capturing various forms of environmental contamination. These polymers were then characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) and elemental analyzer for structure elucidation, X-ray diffraction (XRD) was used for determination of amorphousity and crystallinity level of the materials. Thermal properties were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Then surface area, pore size analysis and Scanning Electron Microscopy coupled with energy dispersive X-ray (SEM-EDX) for full identification of the surface properties.

ملخص الرسالة

الاسم الكامل: حسان علي حسن عماشه

عنوان الرسالة: تصميم وتحضير البوليمرات العضوية المسامية للمعالجة البيئية

التخصص: الكيمياء

تاريخ الدرجة العلمية: مايو 2024

يعد العلاج البيئي عنصرًا أساسيًا في الجهود المستمرة لتحقيق الاستدامة البيئية وحماية صحة الإنسان. ومع تقدم الصناعة والتحضر، زادت أيضًا المشاكل الناجمة عن تلوث وتسمم بيئتنا الطبيعية. إن عواقب التدهور البيئي، مثل تسرب المواد الضارة إلى التربة والمياه الجوفية أو وجود ملوثات الهواء في الأجواء الحضرية، لها آثار واسعة النطاق ومعقدة. نشأ العلاج البيئي كمجموعة كاملة من الأساليب والأساليب المصممة لتنقية واستعادة النظم البيئية التي تلوثت بسبب النشاط البشري.

تعرض هذه الدراسة تطوير مجموعة متنوعة من البوليمرات عالية المسامية بهدف تخفيف أو التقاط أشكال مختلفة من التلوث البيئي. تم بعد ذلك توصيف هذه البوليمرات باستخدام مطيافية الرنين المغناطيسي النووي (NMR) ، ومطيافية تحويل فورييه للأشعة تحت الحمراء (FTIR) ، ومحلل العناصر لتوضيح البنية، وتم استخدام حيود الأشعة السينية (XRD) لتحديد مستوى عدم التبلور ومستوى البلورة للمواد. تمت دراسة الخواص الحرارية باستخدام تحليل قياس الوزن الحراري (TGA) وقياس السرعات الحرارية بالمسح التفاضلي (DSC). ثم مساحة السطح، وتحليل حجم المسام والمجهر الإلكتروني المسح إلى جانب الأشعة السينية المشتتة للطاقة (SEM-EDX) للتعرف الكامل على خصائص السطح.

CHAPTER 1

INTRODUCTION

Within the complex structure of our planet's ecology, numerous obstacles pose a threat to the fragile equilibrium that supports life. Environmental concerns pose significant threats to our planet's future, ranging from the enormous oceans to the dense rainforest canopies and metropolitan areas. The difficulties encompassing climate change, biodiversity loss, pollution, and resource depletion not only endanger the health of ecosystems but also present significant hazards to human well-being and the stability of society worldwide.

As the global population burgeons and industrialization accelerates, the strain on our environment intensifies. The consequences of human activities are becoming increasingly evident, manifested in rising temperatures, erratic weather patterns, habitat destruction, and the alarming decline of species. These environmental upheavals not only threaten the intricate web of life on Earth but also undermine the very foundations of our civilization.

1.1 Greenhouse gas effect

Greenhouse gases (GHGs) are essential for maintaining the Earth's temperature as they trap heat in the atmosphere, a process referred to as the greenhouse effect. Although this natural process is necessary for sustaining a livable climate, human activities have greatly intensified it by emitting greenhouse gases (GHGs).

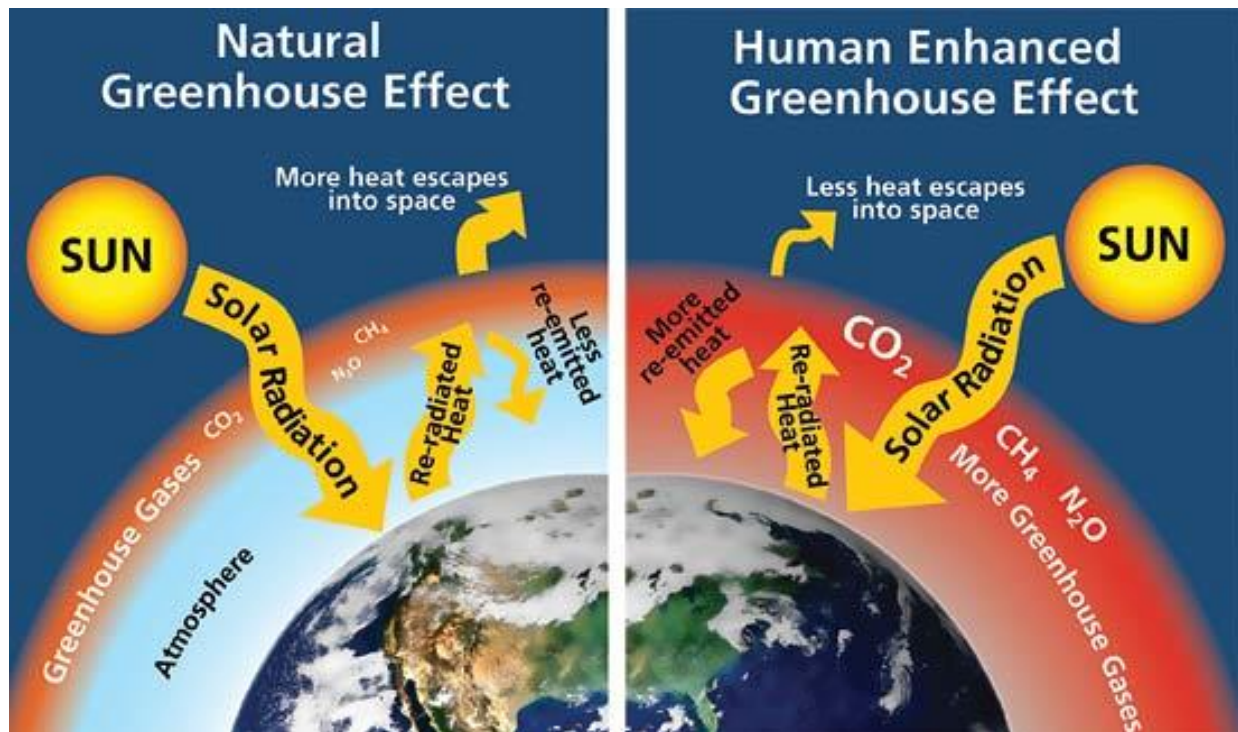


Figure 1: The effect of greenhouse gases in atmosphere.^[1]

Greenhouse gases are produced by both natural processes and human actions. Volcanic eruptions, wildfires, and the decomposition of organic materials are examples of natural sources. Nevertheless, human activities such as the process of burning fossil fuels to generate energy, the clearing of forests, industrial procedures, agriculture, and the management of waste are significant factors in the heightened levels of greenhouse gases (GHGs) in the atmosphere. The primary contributor to greenhouse gas emissions is CO_2 released from fossil fuel combustion. Subsequently, there are releases of methane (CH_4) from livestock farms and landfills, and nitrous oxide (N_2O) emissions from agricultural operations.

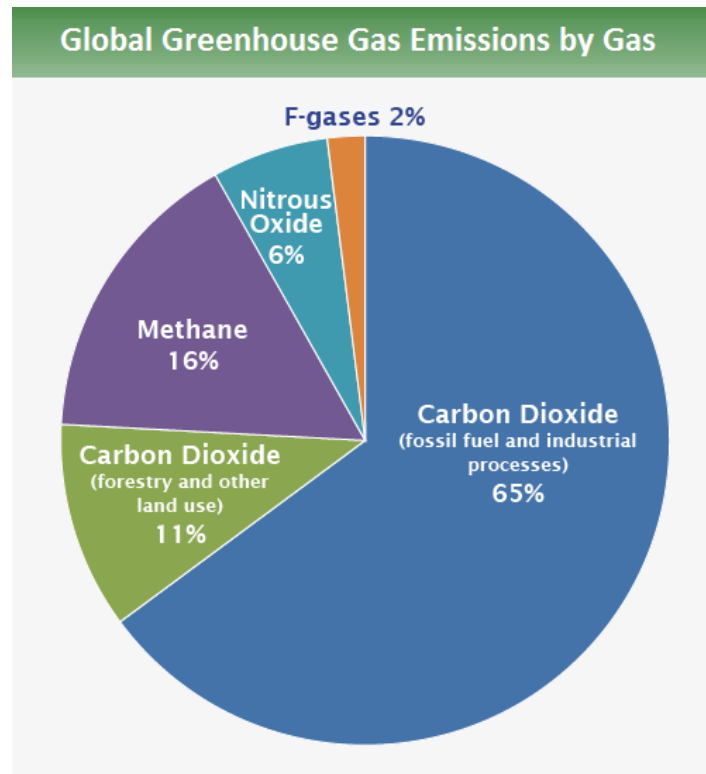


Figure 2: Global greenhouse gas emissions by gas type.^[2]

The buildup of greenhouse gases (GHGs) in the atmospheric environment results in a variety of detrimental impacts on the environment, ecosystems, and human cultures. Increasing temperatures cause the melting of ice caps, which in turn leads to a rise in sea levels and the occurrence of coastal flooding. This poses a significant threat to the millions of individuals residing in low-lying regions. Alterations in meteorological patterns, such as the increased occurrence and severity of heatwaves, droughts, storms, and extreme precipitation events, disturb the efficiency of agricultural production, availability of water resources, and diversity of living organisms. Ocean acidification, resulting from the excessive absorption of carbon dioxide (CO₂), presents a significant peril to marine ecosystems and coral reefs. Furthermore, climate change amplifies pre-existing social disparities, disproportionately impacting marginalized populations and intensifying issues related to poverty, food insecurity, and health hazards.

In 2019, the power generating sector, which relies mainly on fossil fuels, was responsible for 36% of the CO₂ emissions in advanced economies worldwide. This is a decrease from 42% in 2012. Despite coal's declining proportion in primary energy, which reached a 15-year low of 27.2%, it continues to contribute a substantial position in the global energy mix. In 2018, the global coal consumption was divided among the US, India, and China, with shares of 8.4%, 12.0%, and 50.5% correspondingly. In 2018, China accounted for the largest share of global CO₂ emissions at 27.8%, while the United States ranked second with 15.2%.

Fossil fuels have been the primary contributor to CO₂ emissions, accounting for around 65% of worldwide greenhouse gas emissions.

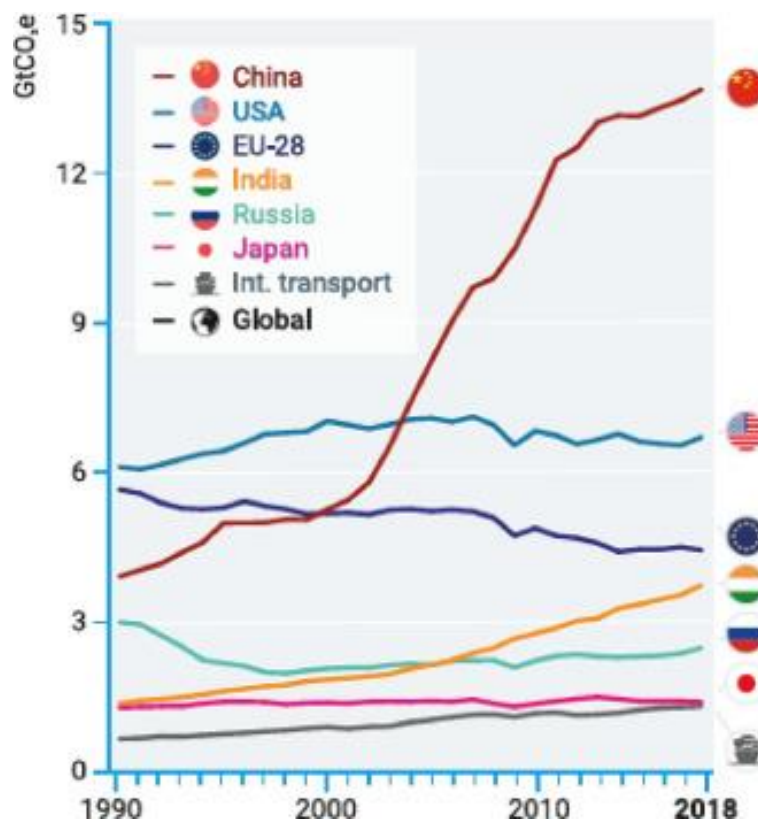


Figure 3: Top greenhouse gas emitting countries (in gigaton of CO₂ equivalents: GtCO₂e).^[3]

Stringent measures are being taken to enforce limitations on CO₂ emissions in response to heightened awareness of environmental issues. The United Nations facilitated the development of the Kyoto Protocol in 1997, an international accord aimed at mitigating greenhouse gas emissions. Consequently, there has been a surge in interest in discovering novel methods to decrease the rates of CO₂ production, along with a considerable focus on the post-treatment of CO₂.

In 2016 the UN established the Paris Agreement which is an internationally recognized and enforceable agreement about climate change. The agreement was ratified by different countries during the UN Climate Change Conference (COP21) in Paris, France. The main goal is to limit the rise in the worldwide mean temperature to a level far below 2°C above the temperature during the pre-industrial era. Additionally, efforts will be made to restrict the rise in temperature to 1.5°C above the levels prior to the industrial era.^[1–13]

1.2 Carbon capture, and storage technologies

Research that prioritizes protecting the Earth's atmosphere from damaging pollutants is highly important. The policy on air protection from dangerous gaseous impurities, such as Sox, Nox CO₂, CO, and Carbon-based substances that are volatile, is mainly influenced through three progressive developments: broadening the range of chemical compounds regulated by global laws to reduce their adverse effect on the climate, efficiently capturing pollutants at their sources of emission, and establishing consistent standards for pollution releases in the industry, energy, and transportation sectors.

Minimizing carbon dioxide (CO₂) emissions from streams of flue gas mixtures is crucial in numerous significant, large-scale technical processes and holds promise in the power sector and environment. It is important to acknowledge remote regions where industrial operations take place, such as power plants that utilize fossil fuels to produce electricity, as well as various industrial

processes including iron and steel mills, cement manufacturing, petrochemical industries, and the process of generating hydrogen by either reforming it by steam methane or gasifying other fuels.

Most recently, global CO₂ emissions from electricity and heat production amounted to over 36.6% (Fig 4). Industrial manufacturing and fuel production accounted for 21.8% of carbon dioxide emissions, while transportation, domestic aviation, and inland waterways contributed 20.1%. Micro-scale non-industrial fixed combustion in buildings accounted for 9.4% of emissions, and other sectors such as emissions generated from industrial processes, agricultural soils, and wastes contributed 12.1%.

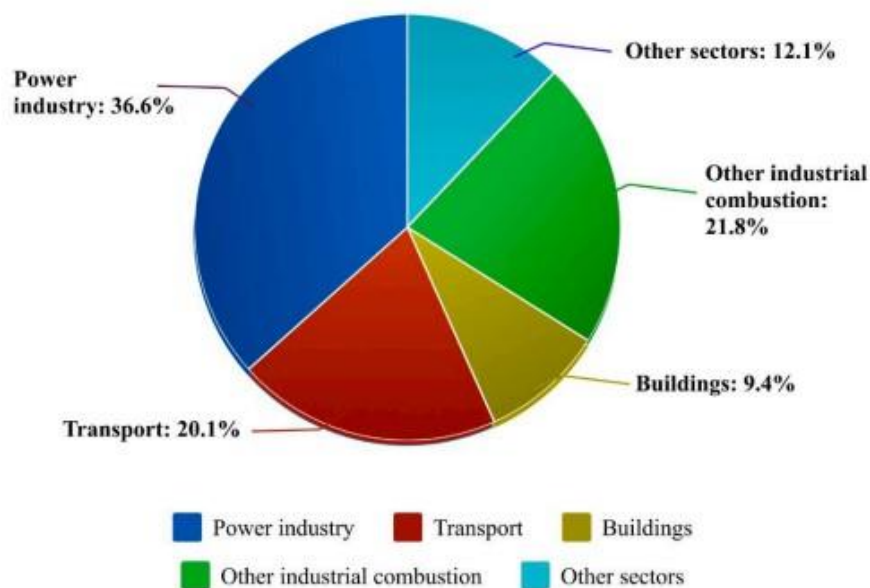


Figure 4: Worldwide CO₂ emissions in 2020.^[7]

Carbon Capture, Utilization, and Storage (CCUS) indicate a variety of approaches that are capable of effectively contributing to achieving climate objectives and act as a substantial means of lowering carbon emissions in industrial sectors worldwide. CCS, or carbon capture and storage, is a widely recognized method to absorb Carbon dioxide from fixed emitted carbon resources and securely conserving it to prevent its escape into the environment. CCS can be further described by

its distinct steps, which include capture, involving Carbon dioxide (CO₂) removal from flue gases; subsequently, transportation; and finally, extended storage that poses no harm to the natural world. This pertains to the direct preservation of carbon dioxide (CO₂) in the oceans, lithosphere, and biosphere. It involves injecting CO₂ into rock formations underground or below the ocean surface to limit its release into the atmosphere and ensure its retention.

After preservation, the place of storage should be regarded as an enclosed receptacle for CO₂, which requires the evaluation of several features of CCS, including detection and surveillance of leaks. Moreover, to CCS, the IPCC emphasizes CCMC as a viable method within the CCS range. The process of carbon capture and mineral carbonation, abbreviated as CCMC, is now undergoing significant advancements.

Another equally significant method, alongside CCS, is bioenergy with carbon capture and storage (BECCS), which entails extracting energy from biomass while concurrently absorbing and storing carbon dioxide. The IPCC Climate Change and Land demonstrate BECCS (Bioenergy with Carbon Capture and Storage) as a highly efficient method for mitigating greenhouse gas emissions related to land utilization. The technology has the capacity to reduce emissions by 0.4–11.3 GtCO₂ annually between 2020 and 2050.

Alternatively, there is competitive technology for carbon capture and storage (CCS) that does not simply store carbon dioxide, but instead repurposes it as a raw substance in manufacturing processes. This technology helps to replace combustible hydrocarbon-based energy sources and synthetic substances and enables the creation of innovative and high-quality items. This process is known as carbon capture and utilization (CCU). Regrettably, it is unfeasible to collect the CO₂

emissions originating from certain sources, namely agricultural waste, domestic and commercial industries, forests, waste produced by municipalities, and particularly transportation.

Therefore, the method called direct air capture (DAC) was developed to retrieve CO₂ that has already been emitted into the atmosphere. When CO₂ is stored and used, it is commonly known as DACS or DACU. Currently, there are two distinct technical methods employed to remove CO₂ from the environment: liquid Direct Air capture and solid Direct Air capture. Presently, there exist 19 functioning direct air capture facilities on a global scale, which are capable of catching more than 0.01 million metric tons of CO₂ annually.

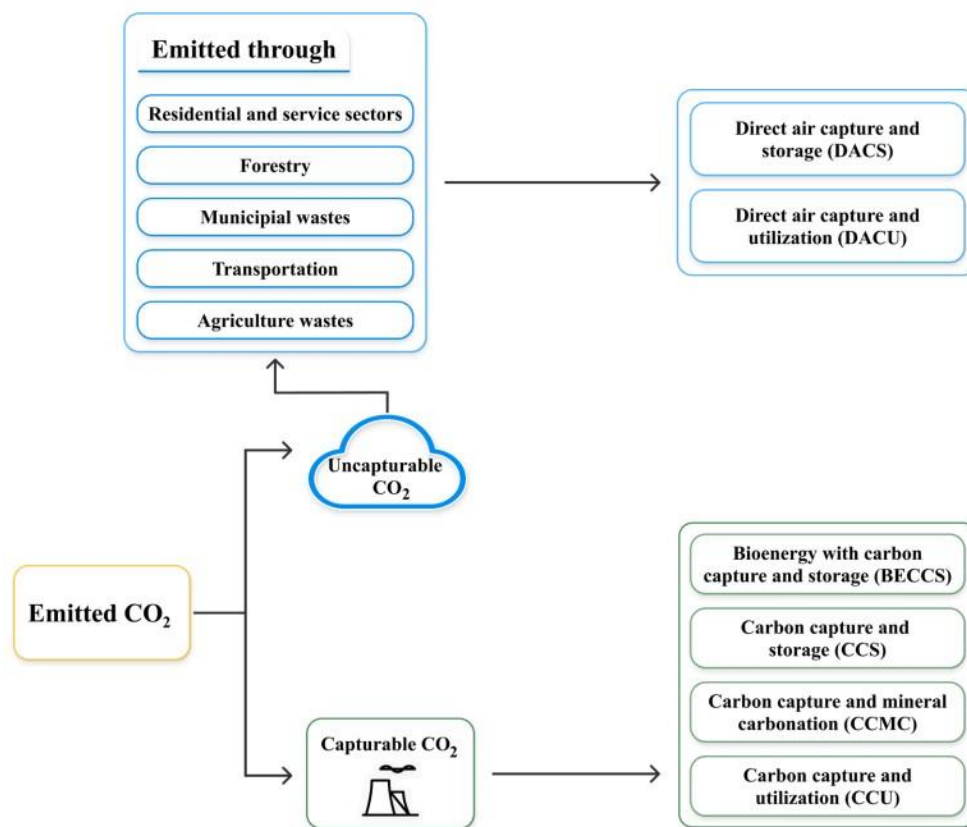


Figure 5: Current technologies employed to mitigate CO₂ emissions.^[4]

CCUS technology offers three primary capture configurations that can be utilized in power plants to retrieve a concentrated amount of CO₂ from fuel burning. The categorization of carbon capture systems encompasses oxy-fuel combustion, pre-combustion capture, and post-combustion capture, as illustrated in figure 6. A different approach, known as capturing from manufacturing process streams, specifically those in the steel, cement, and chemical sectors, is frequently regarded as the fourth option. Furthermore, apart from the aforementioned four methods, there is also a competing process known as Direct Air Capture (DAC) for capturing CO₂ from the earth's atmosphere. In this step, various gas separation technologies, as an instance membrane separation, cryogenic distillation, absorption, adsorption, calcium looping (CaL), and chemical looping combustion (CLC), are employed to isolate carbon dioxide from fossil fuels and/or biomass. These technologies are incorporated within CO₂ capture units and allow the privation of carbon dioxide from other gaseous media. This particular stage of CCS is of utmost importance because of the presence of several additional pollutants in flue gases, including water vapor, CO, CH₄, Sox, and H₂S. These pollutants have the ability to modify the physicochemical properties of the gas stream, such as density and the vapor-liquid phase's equilibrium limit, hence hindering the effectiveness of storage. Therefore, the immediate impact of these contaminants regarding expense, security, and effectiveness of CCS tech is a fundamental factor to address during its economic implementation. The CO₂ capture mechanism is projected to represent between 70 and 80 percent of the total expense of CCS. Consequently, it is essential to produce an extracted stream of gas that has the necessary CO₂ concentration using a very effective technique.^[1,2,14-33]

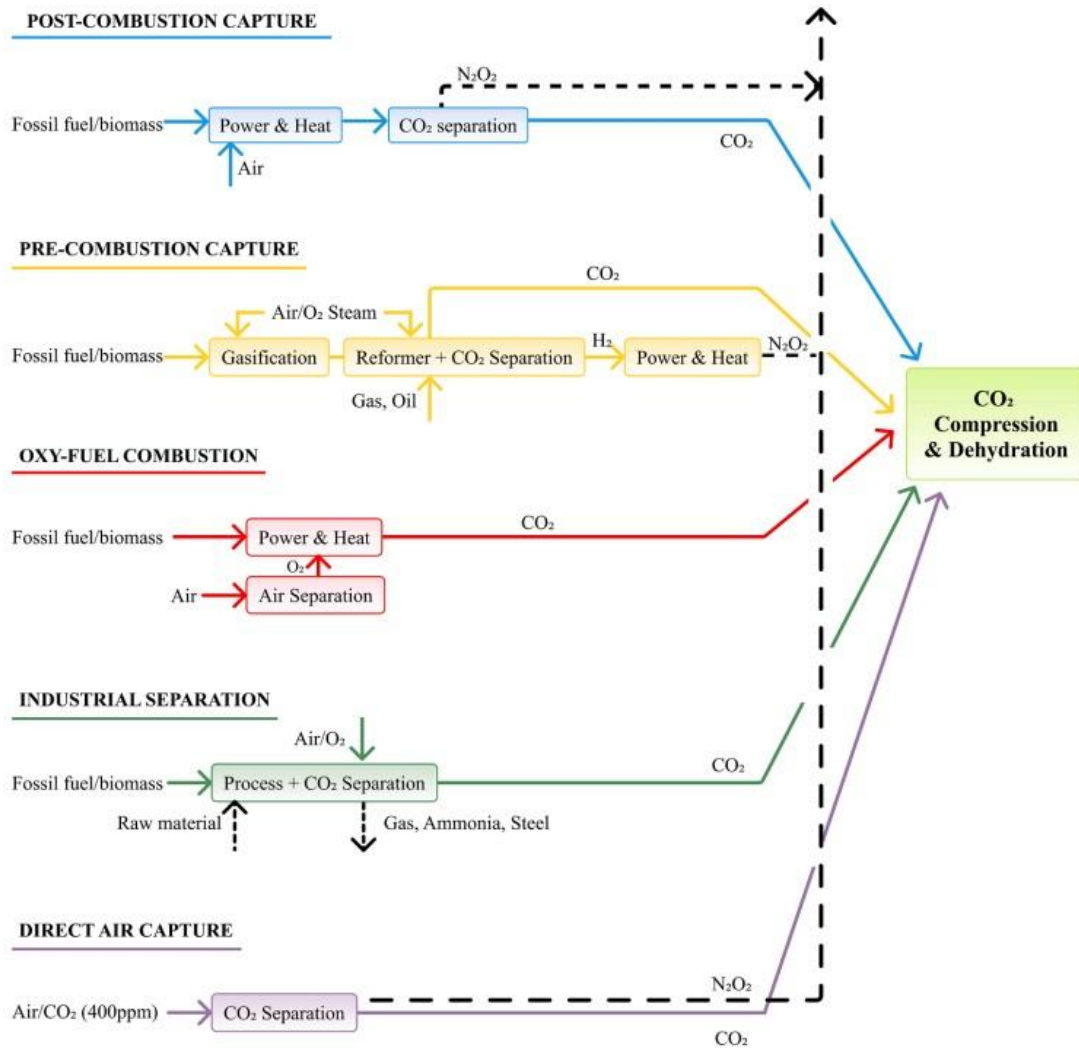


Figure 6: Several CO₂ collection technologies currently in use.^[34]

1.3 CO₂ separation technologies

During every step of the carbon dioxide (CO₂) collection procedure, it is essential to employ suitable methods for separating carbon dioxide (CO₂). The selection of CO₂ segregation method depends upon the specific circumstances that govern how the process will occur, taking into account factors such as the type of fuel utilized, the makeup of the gas requiring treatment, and the partial pressure of CO₂. CO₂ separation technologies encompass a variety of ways used by

industries to separate carbon dioxide from other gases. These methods include basic techniques like physical and chemical absorption and adsorption process, and membranes, as well as more advanced alternatives, in this case chemical looping combustion, calcium looping and cryogenics.^[9,29]

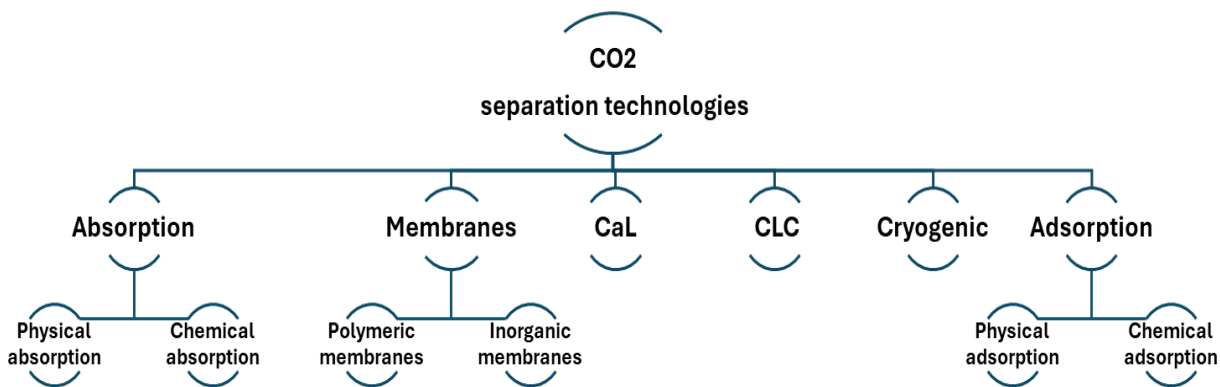


Figure 7: Illustration of CO₂ separation technologies.

1.4 Adsorption

In over a decade, there has been significant research dedicated to studying adsorption as an effective method for removing carbon dioxide (CO₂) from flue gas. This method has shown a significant capacity to capture CO₂ at low temperatures and high pressures, resulting in a final product of high purity. Additionally, adsorption offers the advantage of complete process automation and eliminates the need for numerous unnecessary steps. Currently, the primary obstacles to implementing adsorption on an industrial level are four key factors: efficient and economical production of adsorbents in large quantities, mitigating the decrease in CO₂ adsorption caused by contaminants in the flue gas combination, maintaining and controlling the level of heat of the flue gas at an appropriate scale, and managing the expenses related to frequent replacement of adsorbents.

The primary elements influencing the adsorption of CO₂ by a substance are the level of porosity, which encompasses the growth of micropores and mesopores, and the magnitude of the adsorbent's specific surface area. Moreover, the chemical characteristics of the adsorbent also have an impact. The first factor controls the volume of space in which gas can be adsorbed, while the second factor determines the intensity of the contact forces between molecules of CO₂ and the surface of the solid, which ultimately determines the characteristics of adsorption.^[29]

1.5 Renewable energy

Renewable energy resources are significantly contributing to the future of the world. Energy resources are categorized under three distinct groups: fossil fuels, renewable energies, and nuclear energies. Energy sources that are renewable are resources that can be repeatedly used to produce energy, including biomass energy, geothermal energy, wind energy, solar energy, and others. They are commonly referred to as different energy sources. Household energy needs can be met by renewable energy sources that have the ability to provide energy services while emitting minimum or no pollution into the atmosphere and warming gases. The development of renewable sources systems shall address important challenges such as enhancing energy supply reliability and promoting fuel efficiency, resolving issues related to local energy and water supply, improving the standard of living and employment opportunities for local communities, facilitating sustainable development in remote desert and mountain regions, and fulfilling international agreements on environmental protection. Implementing renewable energy projects in remote regions might generate employment opportunities, hence reducing migration to metropolitan areas. One possible solution to fulfill the energy requirements of rural and small-scale areas in a dependable, cost-effective, and environmentally friendly manner is by harnessing renewable energy in a decentralized fashion.



Figure 8: Renewable energy technologies.

At present, renewable energy sources meet approximately 15 to 20 percent of the global energy demand. Traditional biomass, mostly fuel wood, is the predominant source of supply for cooking and heating purposes, particularly in underdeveloped nations across Africa, Asia, and Latin America. Large hydropower has a significant role in contributing to the worldwide electricity supply, accounting for about 20 percent of it. Currently, geothermal energy, wind energy, solar energy, hydropower, and bioenergy, which are all new renewable energy sources, are providing approximately two percent.

Environmental considerations play a crucial role in the promotion of sustainable development. Activities that consistently harm the environment are not sustainable in the long run due to several causes. These activities have a cumulative negative influence on the environment, which can result in a range of health, ecological, and other issues over time. A significant proportion of the environmental impact on a civilization is linked to the consumption of energy resources. An ideal society pursuing sustainable growth exclusively employs energy resources that have no environmental impact, such as those that do not emit any substances into the environment. Given that every energy resource has an environmental impact, it is logical to propose that certain

concerns about the constraints on sustainable development caused by environmental emissions and their adverse effects can be partially mitigated by enhancing energy efficiency. The relationship between energy efficiency and environmental effect is evident, since higher energy efficiency typically results in reduced resource use and pollution for the same services or products.^[35–39]

1.6 Nuclear energy

Society must confront the fact that it cannot constantly depend on the burning of coal, oil, and gas to meet the majority of its energy requirements. As fossil fuels are phased out, various energy technologies will be evaluated and implemented for specialized purposes. Nevertheless, it can be contended that the technology of nuclear fission is the only established means of energy with the capacity to supply the immense quantities of energy necessary to support contemporary industrialized nations in a secure, cost-effective, and dependable manner, while also being environmentally and resource-wise sustainable in the long run. Therefore, nuclear fission must have a significant part in the essential restructuring of the energy-supply system in the 21st century. During the initial stage of this imperative worldwide energy transition, the primary focus should be on transitioning a significant portion of the world's electricity generation capacity from fossil fuels to nuclear fission. This can feasibly be accomplished within a few decades, as has previously been accomplished in France throughout the 1970s and 1980s. An energy shift of this nature would have a major impact on reducing global carbon dioxide emissions, as well as mitigating the release of other significant greenhouse gases such as methane. Developed countries should assume the forefront position in this change.

Currently, there are over 400 nuclear reactors operating in 30 nations worldwide, together generating a total electric capacity of 380 GW. Annually, these reactors generate approximately 2410 terawatt-hours of electricity, accounting for almost 11% of the global power production. The

International Atomic Energy Agency (IAEA) predicts that the global capacity of nuclear power plants (NPP) would range from 385 to 632 gigawatts (GW) by the year 2030.

A major concern associated with nuclear power is the production of radioactive waste. This waste remains perilous for extended periods of time and necessitates meticulous handling and disposal to avert environmental pollution.^[40–42]

1.7 Radioactive Iodine

Nuclear energy is a prominent contributor to the global electricity supply. It offers significant benefits in terms of cleanliness, security, and cheaper overall running expenses compared to nearly all fossil fuels. The primary challenges encountered by nuclear energy are operational safety and the management of radioactive waste. The off-gas flow that is emitted during the reprocessing of spent nuclear fuels and in the event of severe accidents at nuclear facilities comprises a range of radioactive elements, including ^{137}Cs , ^{90}Sr , ^{129}I , ^{131}I , ^{85}Kr , and others.

The presence of iodine contamination, specifically from nuclear and medical waste (^{129}I and ^{131}I), is a significant concern for both human health and the ecosystem. This is because iodine has the capacity to accumulate in soil, streams, and specific tissues, particularly the thyroid gland, among others. Radioactive iodine is a significant contaminant in nuclear incidents like the Fukushima and Chernobyl nuclear power plant catastrophes, as well as in the routine disposal of radioactive waste from electricity producing plants. ^{131}I is a transient isotope that normally decays within 8.02 days, while ^{129}I is a long-lasting isotope that takes around 1.57×10^7 years to decay. Both isotopes ^{129}I and ^{131}I are notable for their emission of beta particles and mild gamma radiation. Isotopes such as these can easily disperse across water or the environment. It can directly harm the ecosystem; however, they are additionally capable of being consumed through polluted food or water, leading to higher rates of thyroid cancer and hypothyroidism.

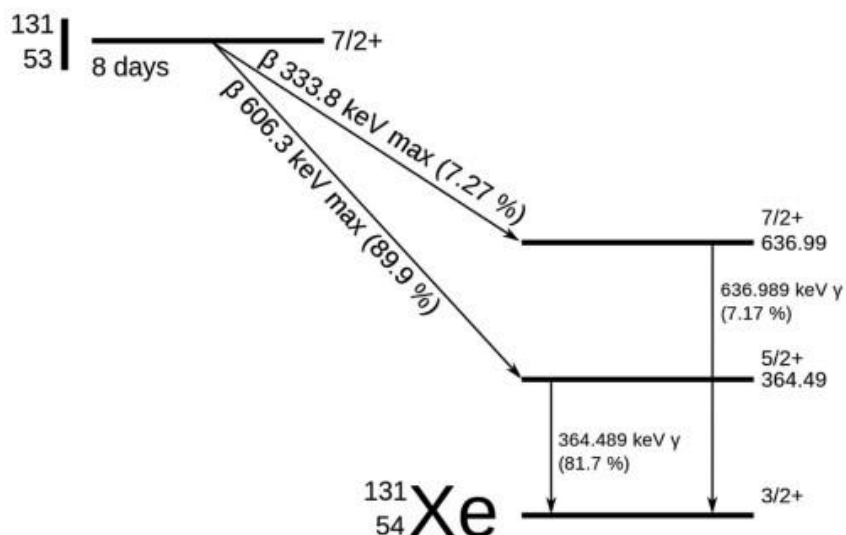


Figure 9: ^{131}I decay scheme.^[43]

Hence, it is imperative to capture radioactive iodine from nuclear waste prior to its initial discharge into the environment in order to guarantee the secure utilization of nuclear energy. The process of solid adsorbent adsorption is widely acknowledged as a highly efficient approach due to its ability to hold a large amount of substances, its affordability, and its straightforward procedure. Currently, there are several solid adsorbents available for absorbing radioactive iodine, such as porous organic compounds (POPs), hyper-crosslinked polymers (HCPs), activated carbon (AC), silver-based materials, and metal-organic frameworks (MOFs).

Activated carbon is an attractive option for removing iodine since it is inexpensive and has a well-developed pore structure. However, its potential to absorb iodine is very modest. Silver-based materials exhibit exceptional physical properties and demonstrate favorable results for capturing iodine. Nevertheless, its high cost and limited ability to be recycled have impeded its widespread use. MOFs and POPs have garnered interest due to their porous nature and significant specific surface area. Nevertheless, the unstable character of iodine is attributed to its acidic and oxidizing

properties. Therefore, it is crucial to create an adsorbent that is inexpensive, can be reused, and has a high adsorption capacity.^[40,42–49]

These environmental hazards were the ignition spark that motivated us to investigate and synthesize a new material like POP's, which is currently demonstrating its capability and effectiveness as environmental remediation.

CHAPTER 2

LITERATURE REVIEW

Environmental remediation is a critical process aimed at restoring and revitalizing ecosystems that have been adversely affected by human activities. As the global population continues to grow, so does the impact on the environment. Pollution, deforestation, industrial activities, and other human interventions have led to the degradation of air, water, and soil quality, posing significant threats to biodiversity and human health. In response to these challenges, environmental remediation emerges as a vital solution to mitigate and reverse the damage inflicted upon our planet.

2.1 Porous organic polymers.

Porous organic polymers (POPs) are a class of covalent organic porous materials characterized by their significant porosity and composition of light elements such as boron, carbon, hydrogen, nitrogen, and oxygen. Such substances are held together by strong covalent bonds. Their intricate composition and advantageous characteristics, such as physical, and chemical stability, excellent thermal, substantial surface area, expansive pores, and favorable resistance to various solvents, make them highly promising for a broad range of applications. These applications include but are not limited to gas adsorption and separation, supercapacitors, sensors, heterogeneous catalysts, water treatment, drug delivery, optoelectronic devices, and environmental remediation. Up to now, there have been reports on five typical (POPs), which are polymer of intrinsic microporosity (PIMs), conjugated microporous polymers (CMPs), covalent organic frameworks (COFs), hyper-crosslinked polymers (HCPs), and porous aromatic frameworks (PAFs).

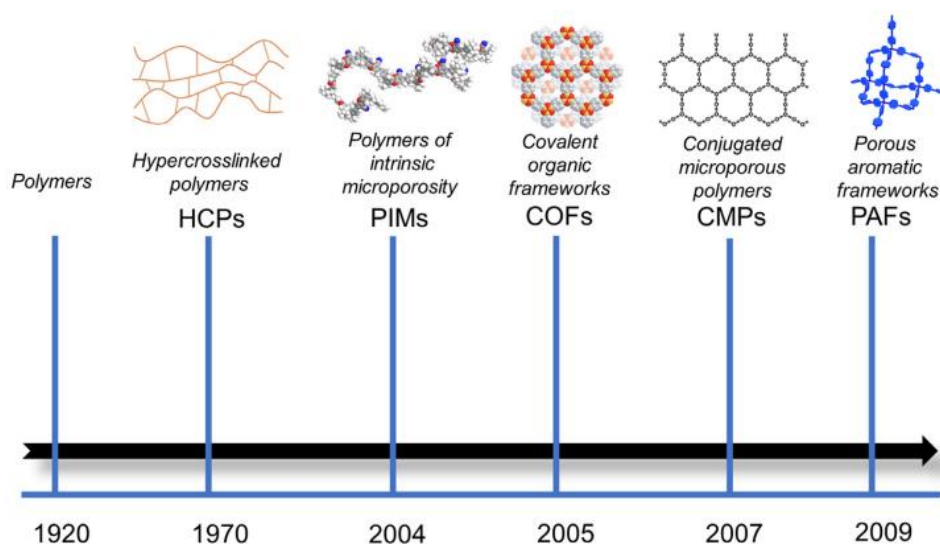


Figure 10: The development of POP over the last century.^[50]

Over the years, several synthetic methods for producing POPs have been developed, such as the Suzuki cross coupling reaction, Friedel–Crafts reaction, Sonogashira–Hagihara reaction, condensation, Yamamoto reaction, cyclotrimerization, and others.

The majority of these synthetic approaches frequently encounter certain unavoidable issues. For instance, several procedures necessitate the use of costly and oxygen-sensitive noble metal catalysts such as palladium (Pd), hence hindering their widespread implementation. However, most of these substances are subject to one or more of the following limitations: challenging operating circumstances, stringent synthesis conditions, extended reaction time, purification process complexities, and limited repeatability. Considerable endeavors have been undertaken to produce (POPs) by the Friedel–Crafts process. This strategy offers a multitude of benefits that surpass those of other strategies. The material is easily manageable and functions under gentle synthesis circumstances, necessitating a low reaction temperature. It utilizes cost-effective ingredients and yields high quantities of POPs with suitable surface areas. Moreover, the POPs synthesized using this approach exhibit competitive performance in diverse domains. As to the

International Union of Pure and Applied Chemistry (IUPAC), porous materials could be listed in three categories depending on the sizes of their pores: microporous (less than 2 nanometers), mesoporous (2 to 50 nanometers), and macroporous (more than 50 nanometers). The porosity is closely correlated with their capacity for absorption. Researchers frequently utilize the N₂ absorption instrument to analyze the surface areas and pore size distributions of their polymer substances. Regardless of whether their pore size is mostly dispersed on the micro or meso scale, their surface area typically falls within the range of 100 to 5500 m² g⁻¹. However, the performance of these objects is not solely determined by their surface area; their pore size distributions also significantly influence their efficiency. The size of the pores distributions of these polymers are primarily influenced by their both exterior and interior morphologies. Additionally, the presence of homogeneous holes in the structures of polymers allows for effective permeability and release, thereby maximizing their potential applications in various fields such as biology, energy, catalysis, absorption, and separation.^[50–56]

Bien Tan group^[57] in 2011, they suggested a novel approach that entails connecting rigid building pieces using an external cross-linker through a process similar to knitting. They employed a modest one-step Friedel-Crafts reaction, utilizing an inexpensive cross-linker, with common aromatic compounds such as 1,3,5-triphenylbenzene, biphenyl, benzene, of low functionality. This resulted in the production of economically viable microporous polymers with highly elevated surface areas. The only byproduct generated in this process was methanol. In this single-step cross-linking method, Dimethoxymethane was employed as an external cross-linker to chemically react with different aromatic monomers.

Later on Bien group's in 2012, succeeded to fabricate a series of polymers using one-step Friedel-Crafts reaction, the compound formaldehyde dimethyl acetal was employed as an external cross-

linker, along with other aromatic monomers (pyrrole, furan, and thiophene), which can undergo direct crosslinking to produce the highly porous networks., 1,2-dichloroethane and ferric chloride were used as solvent and catalyst respectively, the mixture was subjected to heating at a temperature of 45 °C for a duration of 5 hours, followed by further heating at a temperature of 80 °C for a duration of 19 hours. In all cases, a solid precipitate rapidly formed from the reaction mixture. The result showed a surface area between 726 m² g⁻¹ and 437 m² g⁻¹ for the developed materials^[58]

Daqiang Yuan (2015)^[59], managed to synthesize a group of permeable hyper-cross-linked polymers, characterized by their exceptional physiochemical stability, have been efficiently developed and synthesized without the need for a template. The Friedel–Crafts alkylation reactions were conducted using biphenyl, benzene, and 1,3,5-triphenylbenzene as co-condensing rigid aromatic building blocks, together with 1,3,5-tris(bromomethyl)benzene or 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene as cross-linkers. These reactions were catalyzed by anhydrous AlCl₃ or FeCl₃, one of the microporous polymers that reach up to 1783 m² g⁻¹ surface area.

Sudipta K. Kundu and Asim Bhaumik, 2016^[60] an innovative approach has been devised to synthesize hyper-cross-linked microporous copolymers, namely HMC-1, HMC-2, and HMC-3. This method involves the use of thiophene and 2,4,6-tri(thiophen-2-yl)-1,3,5-triazine monomers in varying molar ratios, in the presence of anhydrous FeCl₃. Using solvothermal conditions at a temperature of 150 °C, the reaction was conducted in chloroform. These polymers are characterized by their high porosity and durability, demonstrating exceptional BET surface areas and super microporosity. The inclusion of thiophene and triazine moieties in the copolymer grid enhances the presence of electron-donating nitrogen (N) and sulfur (S) sites in the porous

frameworks. Therefore, these permeable polymers exhibited effective absorption of Lewis acidic CO₂ molecules and demonstrated favorable selectivity for CO₂/N₂ adsorption. An observed maximum CO₂ absorption of 14.2 mmol g⁻¹ has been recorded at a temperature of 273 K and a pressure of 3 bar.

J.H. and Y.-N. L group^[61] in 2018, described a simple and efficient technique for synthesizing a range of NPCs using triazine-based porous organic polymers. The NPCs that have been produced exhibit a customizable porosity structure and a high level of N-doping, achieved by manipulating carbonization temperature and the polymer precursors. The carbon material, called NPC-4-600, has a BET surface area of 1518 m²/g, a pore volume of 1.11 cm³/g, an ultra-micropore volume of 0.20 cm³/g, and a nitrogen content of 9.71 wt %. It demonstrates a high CO₂ adsorption capacity of 207 mg/g and a CO₂/N₂ selectivity of 34.5 at a temperature of 273 K and a pressure of 1.0 bar.

Jianhan Huang^[62], in 2020, A novel class of amino-functionalized porphyrin-based porous organic polymers (POPs) was synthesized using the Friedel–Craft acylation reaction and Schiff-base reaction. Both the amino-functionalized agent and the stiff cross-linking bridges for the polymerization process were made of melamine. The polymers that were obtained displayed a significant specific surface area of 587 m² g⁻¹ and a substantial pore volume of 0.46 cm³ g⁻¹. These polymers also contained a substantial amount of imine, amino, and triazine functionalities, accounting for 42.08 wt. %. At a temperature of 273 K and a pressure of 1.0 bar, the carbon dioxide (CO₂) uptake was measured to be 172 mg g⁻¹.

In 2020, Othman Charles S. Al Hamouz^[63], A unique microporous polymer with crosslinked structure was created using enhanced acid-catalyzed Friedel-Crafts polycondensation reaction. The synthesis used aniline and pyrrole, with p-formaldehyde serving as the external crosslinker,

with the use of catalysis, the result POP exhibited a significantly high crosslinked network joined by strong bonds.

Later in the same year, Al Hamouz group^[64], effectively utilized an acid-catalyzed polycondensation reaction to create a novel microporous organic polymer, using pyrrole and melamine which cross-linked via p-formaldehyde, his POP has great selectivity toward CO₂ and H₂S.

Furthermore, in 2022, Mariolino Carta group^[65] addressed the design, synthesis, and characterization of a range of hyper-cross-linked polymers with intrinsic microporosity (PIMs). These polymers have a high capacity for CO₂ absorption and demonstrate favorable selectivity ratios for CO₂/N₂ and CO₂/CH₄. These properties make them a strong contender for applications in carbon capture and biogas upgrading, the initial hydrocarbon polymers were modified by including functional groups such as -NO₂, -NH₂, and -HSO₃, in order to adjust their ability to selectively adsorb CO₂ against nitrogen and methane.

Later, Giorgio Gatti group^[54] synthesized hyper-cross-linked polymers by optimizing the Friedel-Crafts reaction methodology, as a result a remarkable decrease in catalyst amount achieved. The HCPs showed SSABET of 905 m²/g and total pore volume of ≈ 1.12 cm³/g. The CO₂ uptake was 2.55 mmol/g at 273 K and 1 bar. High pressure measurements at 298 K yielded in the uptake of 7.33 mmol/g of CO₂ at 24 bar and 3.84 mmol/g of CH₄ at 42 bar.

POPs provide various advantageous characteristics as effective carbon capture materials. (1) Porous Organic Polymers (POPs) are synthesized using rigid monomers, leading to the formation of permanent porosity within the polymer structure. (2) Various bonding methods and crosslinking reactions can be employed to create POPs with diverse topological structures and adjustable pore

characteristics. (3) The cross-linking of lighter elements is utilized in the construction of POPs, resulting in polymers with a high capacity for CO₂ adsorption. (4) The presence of covalent bonds in POPs contributes to their favorable physiochemical stability. By employing this approach, it becomes possible to develop and manufacture specialized porous organic polymers (POPs) that possess distinct performance characteristics and pore architectures, thereby catering to the specific requirements of applications such as CO₂ collection, energy storage, catalysis, and others^[66,67]

The pursuit of these difficulties necessitates the advancement of a distinct array of materials possessing exceptional qualities. Solid sorbent materials are being recognized as a promising approach for addressing environmental remediation challenges, particularly due to their ability to physically adsorb carbon dioxide and water pollutants. Numerous studies have documented the exceptional physical, chemical, and mechanical properties of porous Organic Polymers (POPs). These materials possess substantial surface areas, structural versatility, and the potential for incorporating diverse functional groups^[68–70].

The field of nuclear safety has spurred advancements in various scientific disciplines. One significant area of concern is the presence of dissolved and volatile radionuclides in nuclear and medical waste streams, which are considered important pollutants deserving increased attention. Among these radionuclides, radioactive iodine is particularly noteworthy due to its long lifespan and severe detrimental effects on human health. Consequently, there is a pressing need to develop highly efficient materials capable of capturing dissolved and volatile radioactive iodine. Porous Organic Polymers offer a promising solution through physical adsorption, as they possess a high adsorption capacity, large surface area, and excellent efficiency in absorbing liquids and gases, as well as removing certain contaminants^[71].

The presence of volatile radionuclides, specifically iodine isotopes ^{131}I and ^{129}I , poses significant risks to both the environment and human metabolic systems. Hence, Porous organic polymers (POPs) have shown significant promise as effective choices for the reversible trapping of volatile iodine, due to their inherent porosity and strong chemical and thermal stability. A Synthesis of viologen-based has been conducted by mixing Dichloroethylene and 4,4'-bipyridinium in 1,2-dichloroethane with anhydrous ferric chloride as a catalysis^[72].

The synthesis of a functional porous organic polymer (P-TzTz) was achieved by the hydrothermal technique, employing BTT-CHO and DTO as reactants, with no catalyst. The amorphous polymer produced in Guoe Cheng study possesses a significant number of sulfur and nitrogen heteroatoms inside its π -conjugated structure. This polymer demonstrates remarkable ability to reversibly capture iodine, with a high absorption capacity of 326 wt.% for volatile iodine and an adsorption capacity of 494.09 mg g⁻¹^[73].

In 2020, Tawfik A. Saleh and Al Hamouz^[74], have synthesized a novel thiophenol-thiophene polymer for mercury removal form liquid hydrocarbons and wastewater via Friedel-Crafts polycondensation reaction, the polymer composed of thiophenol and thiophene shown remarkable efficacy in eliminating methylmercury from a hydrocarbon mixture consisting of decane and toluene.

Further in 2021, Jianhan Huang^[75], reported the synthesis of thiophene and furan -modified hyper-crosslinked polymers. These polymers were synthesized by subjecting chloromethylated polystyrene to two-step Friedel-Crafts alkylation processes. The resulting polymers exhibited a surface area of up to 574 m² g⁻¹.

Porous polymers have garnered significant research interest due to their structural versatility and wide-ranging applications, such as chemical catalysis, gas separation and storage, energy storage, pollutant removal, and irradiative iodine adsorption. This is attributed to their ability to combine the advantageous properties of porous materials and polymers. Porous polymers have traditionally been synthesized using the utilization of inflexible tiny molecules as fundamental constituents. The development of a broad range of porous polymers has been facilitated by the structural diversity of organic frameworks and the availability of various connection methods^[76].

A newly developed porous organic polymer (CTF-CAR) has been created using a catalyst-free Schiff-base polymerization method. The polymer incorporates thiophenes as the auxiliary group and carbazole as the electron-rich core unit, CTF-CAR has a high capacity for absorbing iodine vapor and rhodamine B due to its strong ability to donate electrons and its many binding sites for heteroatoms. The absorption capacities for iodine vapor and rhodamine B are 2.86 g g⁻¹ and 199.7 mg g⁻¹, respectively^[77].

Most recently in 2023 Chun Zhang group^[78], developed a porous triptycene polymer utilizing Tröger's base as linker and the triptycene as connector. The polymer in three dimensions demonstrates a significant surface area of 1528 m² g⁻¹, with supreme thermal stability. TB-PTN showed a high CO₂ uptake of 22.3 wt % (273 K, 1 bar) and outstanding iodine vapor adsorption (240 wt %).

Later on, Haijun Tan^[79], presented a very efficient synthesis of a porous organic polymer (PTZ-TPC-MA) with an abundance of electrons. This polymer was generated using a Schiff base polycondensation reaction between an aldehyde monomer and melamine (MA), resulting in a significant yield and a straightforward process. The iodine vapor adsorption capacity can reach up

to 198.1 wt%, and it exhibits a removal rate of 79.8% for iodine from a hexane solution. Furthermore, the tests on recyclability have also verified its exceptional capacity for reuse. The material exhibited superior capacity for capturing gaseous iodine and iodine in solution.

Bikram Mondal and Gopal Das^[80], In order to accomplish the reversible adsorption of iodine using a porous material, they have successfully created a very durable porous organic polymer called POF-1. This was achieved through the condensation of 2,2'-bithiophene-5,5'-dicarboxaldehyde and tris(4-aminophenyl) methane using microwave irradiation. The porous amorphous polymer possesses sulfur heteroatom and imine sorption sites, rendering it highly effective for absorbing iodine. It exhibits a remarkable iodine absorption capacity of 4.25 g g⁻¹ in volatile iodine and an adsorption capacity of 141.0 mg/L in an iodine cyclohexane solution.

Arunachalam^[81], accomplished the creation of a cross-linked tripodal receptor polymer (TPP) by performing a Friedel-Crafts polymerization procedure between a tren-based tripodal receptor (L) and tris-(1,3,5-bromomethyl)-2,4,6-trimethyl benzene (CL) as the cross-linker. It has been shown that the cross-linked tripodal polymer functions as a novel adsorbent, effectively capturing iodine vapor and dissolved iodine from water by harnessing the synergistic combination of host-guest interactions facilitated by tripodal receptors and the porosity of cross-linked polymers. This polymer had a notable ability to catch iodine vapor, with a capacity of 2.47 g g⁻¹ at a temperature of 80 °C. Additionally, it displayed an amazing iodine adsorption per unit BET surface area of 86 wt. / (m² /g).

Baiwang Sun^[82], have successfully synthesized three two-dimensional porous organic polymers, namely POP-PDTE, POP-PDTK, and POP-PDTB, by employing a Schiff base condensation procedure to introduce piperazine functional groups. This reaction can be efficiently carried out at

ambient temperature and is well-suited for industrial-scale manufacturing. The numerous functional components efficiently provide robust host-guest interactions for collecting I₂ molecules. These three materials demonstrate exceptional ability to adsorb iodine and can be easily recycled when exposed to iodine vapor, iodine n-hexane solution, and iodine aqueous solution.

Samanta S^[83], a sequence of POPs containing amide groups was initiated using cis, cis-1,3,5-cyclohexanetricarbonyl chloride through nucleophilic substitution, marking the first instance of this process. The POPs exhibited irregular particle-like structures and demonstrated thermal stability up to 310 °C for BD-POP. The polymers formed in their original form were amorphous and had skeleton rich in nitrogen and oxygen heteroatoms, leading to exceptional absorption of iodine. The POPs absorbed iodine through a noncovalent interaction, similar to a host-guest interaction.

Nuclear reactions are increasingly significant in energy and medicinal therapy applications. The production and proper handling of radioactive waste pose significant operational difficulties. Ensuring the appropriate handling and containment of nuclear waste is crucial when evaluating the use of nuclear energy for different purposes. Special precautions must be taken when dealing with volatile radioactive wastes, such as the radioisotopes of iodine (¹²⁹I/¹³¹I), during the reprocessing of used nuclear fuel. Iodine exists in off-gas streams in the form of either molecular iodine (I₂) or organic iodides. ¹²⁹I exhibits lower radioactivity compared to ¹³¹I, although possesses an exceptionally protracted half-life. Both substances are extremely poisonous, and their almost complete removal from gas emissions necessitates the use of iodine filters filled with effective adsorbents. Hence, it is imperative to create materials that possess effective capabilities for capturing and storing iodine vapor^[84].

CHAPTER 3

Microwave-Synthesized Heteroaromatic Porous Organic Polymers for CO₂ Capture and Hydrogen Storage

ABSTRACT

In this paper, three porous organic polymers (POPs) were synthesized by microwave-assisted Friedel-Crafts polymerization reaction of 1,3,5-tris(2-thienyl) benzene (TTB) with furan (HAF), thiophene (HAT), and pyrrole (HAP) in the presence of dimethoxymethane using anhydrous iron (III) chloride as a catalyst. The polymers displayed inherent porosity, with BET surface areas ranging from 528 to 634 m² /g. These polymers exhibited high CO₂ adsorption capacity, with values of 2.61, 2.17, and 2.37 mmol/g at 273 K and 1 atm, as well as strong affinity, with Q_{st} values of 43-48 kJ/mol. The polymers showed hydrogen storage of 3.3-5.3 mmol/g (0.66-1.06 wt.%) at 77K, and 1 atm. The polymers showed Initial slope selectivity for CO₂/N₂: 34-61 at 273 K and 1 atm, and 23-57 at 298 K and 1 atm. Whereas, the polymers showed initial slope selectivity for CO₂/CH₄: 5-9 at 273K and 4-7 at 298 K and 1 atm. Grand Canonical Monte Carlo (GCMC) simulations revealed that the polymers exhibit matching electronic properties with CO₂ molecules and achieve excellent selectivity in accordance with the hard-soft acid-base (HSAB) theory. These findings demonstrate the potential of these polymers for CO₂ capture and clean energy applications.

3.1 Introduction

Concerns regarding the emission of carbon dioxide (CO₂) have been much more prevalent in public awareness over the last several years due to the potential consequences that might result in several environmental and climate-related issues, one of which being global warming. In particular, the CO₂ levels reached a record-breaking 414 ppm in 2021 and it is predicted that if continued to depend on burning fossil fuels as predominant energy source, it will climb to 800 ppm during the following century ^[58]. Therefore, several approaches and techniques have been identified to mitigate the effects of CO₂ given the significant ramifications for the environment and human health. These strategies include finding new methods for CO₂ separation and reducing new CO₂ emissions and investigating ways to improve energy efficiency in order to reduce total energy usage ^[85]. Liquid amine scrubbers are a commonly used technique to chemically capture CO₂ by forming carbamate compounds. This method reduces and adsorbs CO₂ well, but it has sustainability problems as well. These include high energy consumption, limited operating life, corrosion, amine loss from evaporation, and high regeneration costs ^[86]. An alternate strategy for capturing and storing CO₂ is chemical adsorption of solid adsorbents such solid amines, hydroxides, and alkali metals. These materials have a poor degree of selectivity and significant energy needs for 3 regenerations ^[87]. To address concerns related to low adsorption capacity and energy consumption, experts have shifted their focus to the physical adsorption of CO₂ via a range of materials. For instance, porous aromatic frameworks (PAFs) ^[88], covalent organic frameworks (COFs) ^[89], metalorganic frameworks (MOFs) ^[90,91], MCM-41 silica ^[92], self-assembled iron-containing mordenite monoliths ^[93], and porous organic polymers (POPs) ^[94,95] have been used as potent physisorbents to capture CO₂. All three adsorbents, MOFs, COFs, and POPs can provide high CO₂ affinity. In this direction, POPs are preferred among them because of their simple

synthesis and structural flexibility. Unlike other adsorbents, porous polymers can possibly be tailored to show a high level of selectivity for CO₂. They also have great resistance to contaminants, quick adsorption kinetics, enhanced CO₂ adsorption, and, most importantly, cost-effectiveness due to reduced manufacturing and regeneration costs ^[96–98]. The recent interest in synthesizing of POPs has increased significantly. These polymers can be made by a variety of techniques, including the Suzuki coupling ^[99], Sonogashira-Hagihara ^[100], oxidation coupling ^[101], and non-metal catalyzed reactions ^[102]. Most of these approaches were conventionally used in solvothermal processes. However, these conventional techniques are marked by complicated steps in which the reaction mixture receives a heterogeneous input of external energy from the vessel walls ^[103]. To address these concerns, there has been considerable attention towards microwave-assisted polymerization because of its capacity to reduce synthesis time, its simplicity, and its effective transmission of energy to reactants in comparison to traditional solvothermal processes. Microwave-assisted synthesis provides a method that is both efficient and environmentally friendly, ensuring uniform energy distribution throughout the reaction container by molecular vibrations ^[104]. When POPs were prepared utilizing a Microwave-assisted technique with different 4 monomers, considerable improvements in CO₂ capture efficiency were noticed ^[105], underlining the need for new POPs designed for CO₂. Hence, the goal of this effort is to use Friedel-Crafts alkylation with microwave assistance to synthesize new porous organic polymers (POPs). Specifically, dimethoxymethane was used as a cross-linking agent coupled with 1,3,5-tris(2-thienyl) benzene (TTB) and other monomers, including furan, thiophene, and pyrrole by using anhydrous iron (III) chloride. These monomers were chosen because of their increased chemical stability and abundance of CO₂ adsorption sites ^[58]. A comprehensive analysis was conducted to evaluate the effectiveness of the synthesized polymers, utilizing various techniques including

NMR, FTIR, TGA, XRD and SEM. A detailed assessment of the adsorption capabilities of the synthesized polymers was achieved through the systematic measurement of their gas adsorption capacity.

3.2 Materials and Methods

3.2.1 Materials

All reagents and chemicals were used in their original condition, with no extra purification. The products that were purchased from Sigma Aldrich were furan (99% purity), thiophene (99% purity), dimethoxymethane (DM) (98% purity), anhydrous iron chloride (III) (FeCl_3 , 99.99% purity) and 1,3,5-tris(2-thienyl) benzene (TTB) (97% purity). Ammonia solution (35% w/w) and pyrrole (98% purity) were obtained from Alfa Aesar, and pyrrole was promptly distilled at 140°C under a nitrogen gas flow before usage. To conduct gas sorption evaluations, AHG Industrial Co. LTD, Saudi Arabia supplied nitrogen, methane, hydrogen, and CO_2 gases with the purity of 99.99 %.

3.2.2 Characterization

The Bruker 400 MHz spectrometer was employed to measure the natural abundance solid-state ^{13}C NMR at a frequency of around 125.65 MHz (11.74T) in ambient conditions. For this, the sample was compressed onto a 4 mm zirconium oxide rotor. A pulse delay of 5 s and a magic angle spinning rate of 14 kHz were implemented in conjunction with high-power decoupling and CPMAS which stands for cross-polarization magic angle spinning. ^{13}C chemical shifts were calibrated with reference to tetramethyl silane (TMS), aligning them based on the high-frequency isotropic peak of solid adamantane at 29.5 ppm. The FTIR spectra was collected by employing KBr in Thermo Scientific Nicolet iS10 spectrometer with wavelength range of 4000 to 500 cm^{-1} .

An STA 429 thermal analyzer made by Netzsch-Geratebau was used to perform thermal gravimetric analysis (TGA). The polymers were heated to 700 °C at a steady rate of 10 °C/min under air environment. XRD profiles were generated at a scan rate of 2°/min using a Rigaku Ultima IV fitted with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Using a scanning electron microscopy (SEM) (Thermo Fisher Quattro S), the micrographs of the polymers were captured. An energy dispersive X-ray analyzer (EDX, Oxford Inc.) was used to confirm the composition of elements in the polymers. A secondary electron mode was used, with a 10 mm working distance and an increasing voltage of 5 kV. The specimens were evenly distributed onto double-sided sticky tape and then covered with a thin coating of gold for a duration of 30 s prior to examination. A Micromeritics 3-Flex was utilized for low-pressure gas adsorption studies. At 77 K, isotherms were measured in a liquid nitrogen bath, while at 273 K and 298 K, isotherms were acquired using a chiller. Additionally, the data is included in the Supplementary Information section.

3.2.3 Synthesis of porous organic polymers

In a typical experiment, 1,3,5-tris(2-thienyl) benzene (TTB), dimethoxymethane (DM), furan (F), and anhydrous iron chloride (III) (FeCl_3) were introduced into a 100 ml Teflon reactor (easy-prep) containing 40 ml of 1,2-dichloroethane. Subsequently, the reaction vessels were sealed and placed in a MARSTTM 6 Synthesis microwave reactor. The temperature profile was set as follows: the temperature was increased gradually (ramping for 15 min.) from room temperature to 60 °C and held for 10 min., followed by increasing the temperature to 90 °C (ramping for 15 min.) and held for 20 min. Upon completion of the reaction, the reaction vessel was allowed to cool to room temperature. The resulting black solid (HAF) underwent washing with methanol, ammonia, distilled water, concentrated Nitric acid and finally washed for 24 h with methanol followed by filtration and drying under vacuum at 80 °C for 24 h. A similar procedure was adopted for the

reaction of 1,3,5-tris(2-thienyl) benzene (TTB) with thiophene (TH) and pyrrole (PY) to produce HAT and HAP polymers, respectively (Figure 11). The reaction details of the synthesized polymers are shown in Table 1.

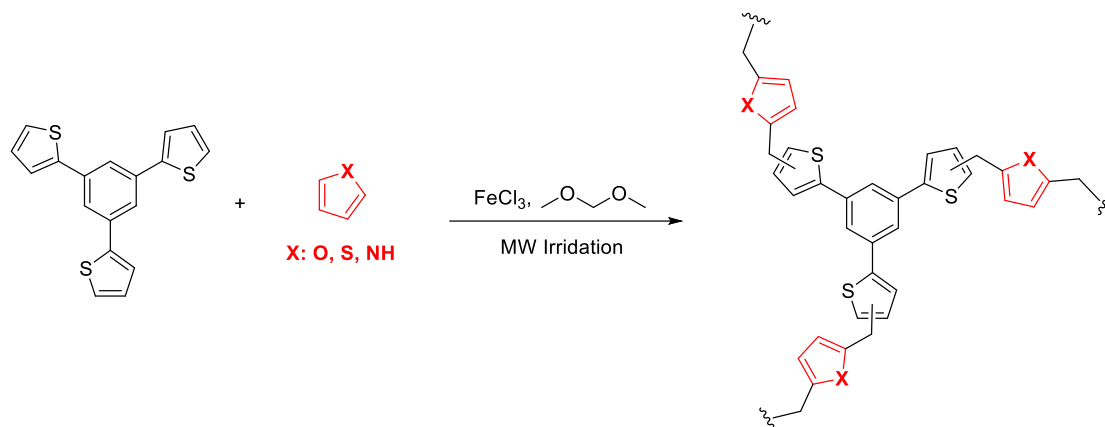


Figure 11: Microwave-assisted Friedel-Crafts polymerization of porous organic polymers.

Table 1: Reaction details and porosity information of the synthesized porous polymers.

Polymer	TTB mol (g)	DM mol (g)	F mol (g)	TH mol (g)	PY mol (g)	FeCl ₃ mol (g)	BET (m ² /g)	Elemental analysis					Yield %* (g)
								C Calc. (Exp.)	N Calc. (Exp.)	S Calc. (Exp.)	S/C Calc. (Exp)	N/C Calc. (Exp)	
HAF	0.005 (1.62)	0.03 (2.28)	0.015 (1.02)	-	-	0.06 (9.73)	634	70.19 (57.84)	0 (0.78)	17.03 (14.77)	0.24 (0.26)	0 (0.01)	66.66 (3.28)
HAT	0.003 (1)	0.018 (1.37)	-	0.009 (0.76)	-	0.036 (5.84)	528	64.67 (53.53)	0 (0.74)	31.37 (21.91)	0.49 (0.41)	0 (0.01)	73.16 (2.29)
HAP	0.003 (1)	0.018 (1.37)	-	-	0.009 (0.60)	0.036 (5.84)	539	70.55 (53.58)	7.48 (4.75)	17.12 (12.38)	0.24 (0.23)	0.11 (0.09)	83.50 (2.48)

3.2.4 Monte Carlo Simulations

Molecular dynamics simulations were conducted to corroborate the experimental findings, and to probe the selectivity of the polymers to the gases CO₂, CH₄ and N₂. The polymer units were built and optimized on the “Forcite” Module of Materials Studio simulation software ^[106], using the COMPASS II forcefield ^[107], and a self-consistent field (SCF) convergence threshold of 1.0×10^{-5} Ha. Due to the simplicity, robustness, and the high probability of yielding accurate results at low cost, the SMART optimization algorithm was selected ^[108]. The maximum force tolerance and energy tolerance were set at 1.0×10^{-3} kcal/mol Å⁻¹ and 1.0×10^{-5} kcal/mol, respectively. Using the “Locate” taskbar on the “Sorption” Module, the lowest energy and most probable adsorption centers of the gases on the polymers were predicted, while the adsorption capacities were modeled using the principle of the Grand Canonical Monte Carlo (GCMC) simulation at 273 K and 298 K, respectively ^[98,109–111]. The adsorption isotherms were fitted using the Langmuir equation depicted as:

$$y = \frac{abx}{1 + bx}$$

Where, a and b represent the gas uptake limit in mmol/g, and the adsorption constant at MPa⁻¹, respectively. The gas uptake in mmol/g was calculated from the average gas loading per cell from the isotherms using the equation:

$$\text{Gas uptake} \left(\frac{\text{mmol}}{\text{g}} \right) = \frac{\text{Average loading per cell}}{M_r \left(\frac{\text{g}}{\text{mol}} \right)} \times 1000$$

Where, M_r represent the molecular weight of the polymers in the simulation supercell.

3.3 Results and Discussion

3.3.1 Synthesis Strategy

The Friedel–Crafts alkylation polymerization process was employed as the synthetic strategy for developing new CO₂-philic, microporous polymers. Because of their strong affinity for CO₂, rigidity to produce porous polymers, chemical and thermal stability, 1,3,5-tris(2-thienyl) benzene, furan, thiophene, and pyrrole are significant heteroaromatic monomers that are used to synthesize porous polymers [58,86]. To initiate the polymerization process for synthesizing furan-based polymer, furan and TTB were dissolved in 1,2-dichloroethane in Teflon reactor. Dimethoxymethane (DM), a cross-linking agent in excess, was also added along with anhydrous FeCl₃ catalyst, selected due to its high Lewis acidity [112], then the reaction vessel was sealed and placed in a MARS™ 6 Synthesis microwave reactor for enhanced and homogenous thermal distribution by microwave irradiation to insure the incorporation of monomers in the polymeric structure via the desired molar quantities.

3.3.2 Structural Characterization

The addition of monomers and their associated connections within the structure, or the structural knowledge of synthesized polymers HAF, HAT and HAP, was achieved by a combination of CPMAS ¹³C NMR and FTIR spectroscopies. The ¹³C NMR spectra showed significant resonance signals for the synthesized polymers, as seen in Fig. 12a. The peaks observed at around 35 ppm can be attributed to the methylene linkages present between the TTB and the used monomers, namely furan, thiophene, and pyrrole for HAF, HAT and HAP, respectively [113]. The peaks at 110-140 ppm correspond to the aromatic -C=C- carbon between the monomers and TTB. The aromatic carbons associated with pyrrole, furan, and thiophene monomers comprised the peaks located between 140 and 153 ppm. The existence of the

functional groups in the synthesized polymers was verified by the FTIR spectra, which are shown in Fig. 12b. The methylene linkages of the synthesized polymers exhibited a band at 2920 cm⁻¹, which was ascribed to their -CH₂- stretching vibration. The peaks observed at 3400 cm⁻¹, 1070 cm⁻¹ and 830 cm⁻¹ were attributed to the presence of -NH-, -C-S-C- and -C-O- rings of the pyrrole, thiophene and furan, respectively. After establishing the structure, the focus shifted to evaluating the thermal stability (Fig. 12c) of the synthesized polymers. When HAF, HAT, and HAP were exposed to air flow, their thermal gravimetric (TGA) curves showed that their weight slowly decreased before 250 °C. This suggested that these porous materials are thermally stable. The initial weight loss below 150 °C was attributed to the solvent molecules that were confined inside the pores. The peak above 300°C indicated the initial thermal degradation of the methylene cross-linkages ^[64]. Around 450°C, all the polymers underwent complete degradation, resulting in the formation of NO_x, SO_x and CO₂ gas molecules. These findings are in agreement with the data that was previously published ^[114] on porous organic materials, which demonstrated that the strong cross-linkages that exist between the structures are responsible for the better thermal resistance of the polymers. Fig. 12d provides the findings of porous polymer obtained from powder X-ray diffraction. The synthesized polymers exhibited the amorphous nature in the XRD patterns, since there were no discernible peaks indicating crystallinity. SEM micrographs were obtained after examining the morphological features of the synthesized polymers HAF, HAT, and HAP. The SEM pictures in Fig. 12d revealed that all the polymers had a spherical form with a porous nature. Elemental analysis results shown in Table 1 of the synthesized polymers reveal difference between the calculated and the experimental values which is typical for porous organic polymers, but to our pleasure the ratio between S/C and N/C was similar to the targeted

synthesis molar ratios which confirms the advantage of microwave irradiation as a facile method for the synthesis of porous polymeric materials with confined molecular structures ^[115].

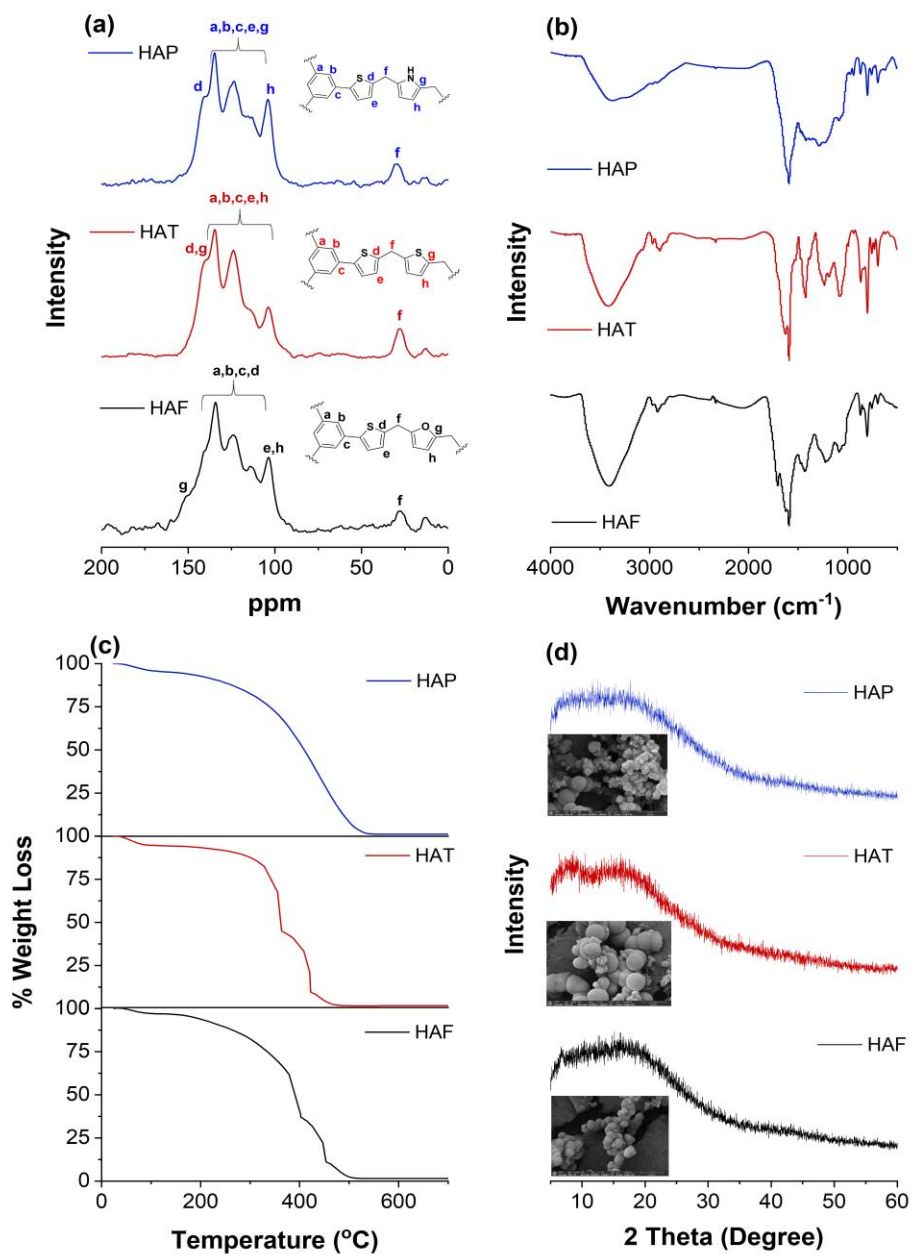


Figure 12: Structural characterization of synthesized polymers (a) ¹³C NMR spectrum of the synthesized polymers; (b) FTIR spectra of the synthesized polymers; (c) TGA thermal patterns of the synthesized polymers at rate of 10°C/min.; (d) SEM figure and PXRD patterns of the synthesized polymers within the range of 5-60 (2θ) measured at 2 degrees/min.

3.3.3 Sorption Isotherms

The nitrogen isotherms at 77 K, seen in Fig. 13a, were examined to determine the BET surface area and the related NLDFT (non-localized density functional theory) pore size distributions in the microporous region. An isotherm with a significant Type II behavior was formed by the synthetic polymers, HAF, HAT, and HAP. This isotherm exhibited a distinctive sharp uptake at $P/P^0 > 0.9$, whereas a Type I isotherm exhibited a steep uptake at $P/P^0 > 0.1$. Both micropores and mesopores were present in these categories, which indicated their presence. A progressive adsorption in the region of $0.2 < P/P^0 < 0.8$ was indicative of the mesoporous structure of the material. According to the results of the NLDFT technique presented in Fig. 13b, these synthetic polymers were discovered to be mostly micro- and meso-porous, and their pore diameters were in the range of 5 nm. The synthesized polymers exhibited significant surface areas, as determined by the BET method. Specifically, the surface areas for HAF, HAT, and HAP were measured to be $634 \text{ m}^2/\text{g}$, $528 \text{ m}^2/\text{g}$, and $539 \text{ m}^2/\text{g}$, respectively. The pore volume measurements for HAF, HAT, and HAP polymers were determined as $0.396 \text{ cm}^3/\text{g}$, $0.285 \text{ cm}^3/\text{g}$ and $0.341 \text{ cm}^3/\text{g}$, respectively. The increased pore volume and higher surface area of the HAF and HAP polymers in comparison to the HAT polymer resulted in greater N_2 absorption capacity. This indicates that a polymer with a greater pore volume and larger surface area offers a greater number of active sites for gas adsorption ^[59,62,63]. The persistent porosity and improved thermal stability of the produced polymers motivated us to investigate the CO_2 , CH_4 , N_2 , and H_2 adsorption characteristics. After confirming that the synthesized polymers had high surface areas and improved thermal stability, the next step was determining its superior ability to capture CO_2 compared to other gases present in natural gas streams. For this purpose, CO_2 , CH_4 and N_2 gas adsorption was conducted at 273 K and 298 K for HAF, HAT and HAP

polymers, as depicted in Fig. 13(c-e). As evidenced by 13 all the isotherms, reversible adsorption and desorption occurred; this indicated that the gas adsorbs onto the polymer backbone in a physical manner, distinct from the formation of any chemical bonds. From Fig. 13c, at 273 K, it can be elucidated that the synthesized polymers HAF, HAT and HAP showed CO₂ uptake capacity of 2.61 mmol/g, 1.48 mmol/g, and 2.37 mmol/g, respectively. Similar CO₂ uptake observations were found at 298 K for these polymers and the obtained values were 1.48 mmol/g, 1.22 mmol/g, and 1.45 mmol/g for HAF, HAT and HAP polymers, respectively. Notably, increased CO₂ uptake by HAF was correlative with a greater micropore volume of 0.152 cm³ /g compared to HAT and HAP with a micropore volume of 0.122 and 0.133 cm³ /g, respectively. The polymers exhibited a greater potential for CO₂ adsorption compared to the observed CH₄ (Fig. 13d), suggesting that they provided stronger affinity to CO₂. Likewise, N₂ adsorption results for these polymers were acquired at 273 K and 298 K, as illustrated in Fig. 13e. Hence, it can be elucidated that these synthetic polymers exhibited higher selectivity towards CO₂, as evidenced by their limited adsorption outputs of CH₄ and N₂. To a greater and more friendly future with a greener fuel, the adsorption of H₂ at 77 K was conducted to explore the capability of the polymers to store hydrogen. As shown in Fig. 13f, the uptake capacity of HAF, HAT and HAP were 5.32 mmol/g, 3.33 mmol/g and 3.74 mmol/g, respectively. From Fig. 13f, it was observed that HAF polymer displayed the highest H₂ adsorption because of the larger surface area, and higher micropore volume which resulted in a greater amount of space for H₂ to be adsorbed. These findings are consistent with those found for other porous materials, including COFs ^[116,117] and POPs ^[118].

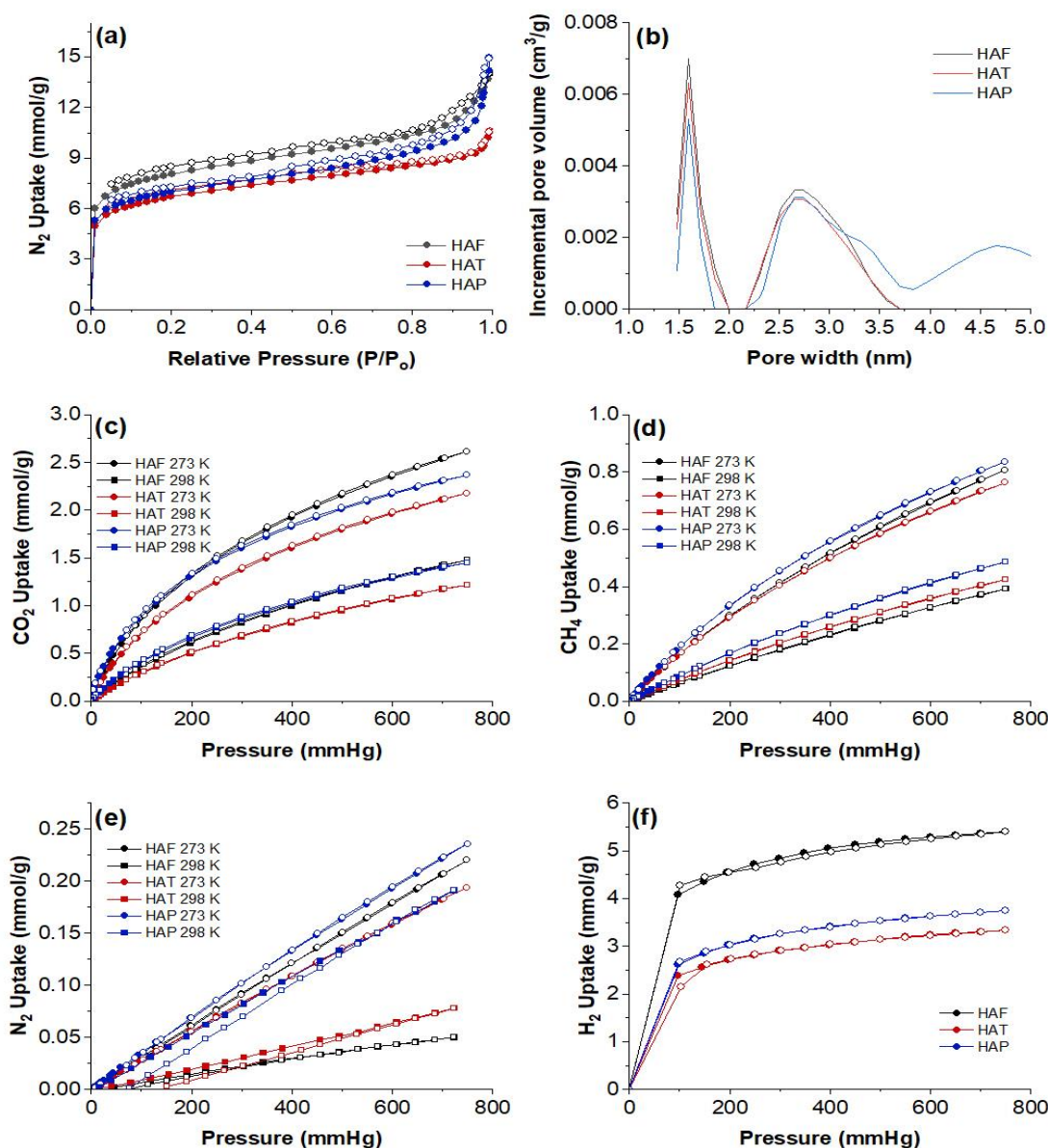


Figure 13: (a) N₂ adsorption at 77K of the synthesized polymers exhibiting adsorption (filled circles) and desorption (open circles).; (b) Pore size distribution of the synthesized polymers using NLDFT.; Gas sorption isotherms of the synthesized polymers for (c) CO₂ (d) CH₄ (e) N₂ (f) H₂.

3.3.4 Isosteric heat of adsorption (Q_{st}) and selectivity

To understand the affinity of the adsorbents with distinct guest molecules, the Q_{st} for the adsorption of CO₂, CH₄, and N₂ were determined. The Langmuir-Freundlich isotherm model was applied on the adsorption experimental data at 273 K and 298 K (Supplementary data Q_{st}). The energy dependent interaction between the polymers and CO₂ molecules is illustrated in

Fig. 14a, where the interaction decreases with increasing surface coverage. The estimated onset Qst outcomes for CO₂ for HAF, HAT, and HAP were 44 kJ/mol, 43 kJ/mol, and 48 kJ/mol, respectively, indicating a physisorption interaction ^[119–121]. The higher Qst value of HAP in comparison to HAF and HAT could be explained by the presence of nitrogen atoms present in the pyrrole moieties which have stronger binding affinity to CO₂ compared to oxygen and sulfur. In comparison to similar materials like HM11 (29.3 kJ/mol) ^[86], PAF-1 (15.6 kJ/mol) ^[122], and M2 (33.6 kJ/mol) ^[98], the Qst values of the synthesized polymers were quite high which shows strong binding affinity between the polymers with CO₂ (supplementary information). Fig. 14b revealed that the synthesized polymers exhibited a similar trend to CO₂ in terms of CH₄ observations, although with lower Qst values due to the nonpolar structure of CH₄ caused it to have lower Qst values than CO₂ ^[123]. The synthesized polymers, HAF, HAT, and HAP showed Qst values of 27.8 kJ/mol, 24.4 kJ/mol, and 23.5 kJ/mol, respectively, which is beneficial for natural gas purification and shows higher selectivity toward CO₂. (supplementary information). The significant Qst values observed for CO₂ indicated a strong affinity for binding between the polymers and CO₂. In contrast, the Qst values obtained for CH₄ were lower, suggesting that the polymers had a reduced ability to bind to CH₄ ^[86]. Similarly, the Qst value of the polymers was determined to assess their affinity to N₂ gas molecules. The results are shown in Fig. 14c, indicating that the HAF polymer had 16.5 kJ/mol (Qst value) higher than HAT and HAP with values of 12.3 and 5.1 kJ/mol (supplementary information). The decline followed by a rise in adsorption energies as surface coverage increases demonstrated the presence of adsorbent sites with same energy interactions with the gas molecules ^[124]. Whereas, in HAT and HAP the Qst curve showed a decrease in the binding energy with the increasing surface coverage.

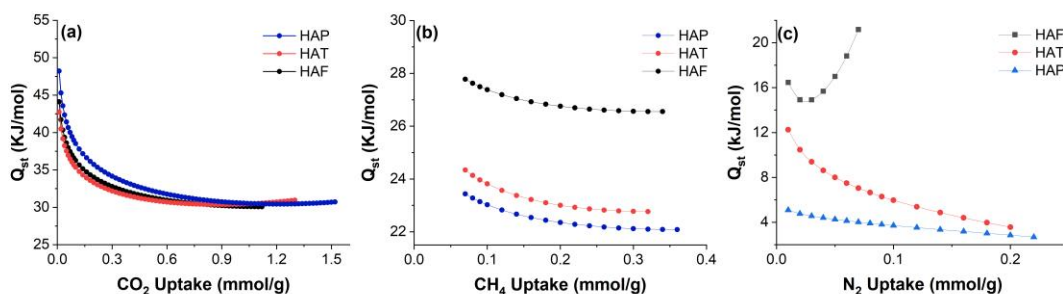


Figure 14: Isothermic heat of adsorption (Q_{st}) curves for (a) CO_2 gas, (b) CH_4 gas, and (c) N_2 gas.

To study the effect of Q_{st} on selectivity, Initial slope selectivity was applied on the adsorption data as shown in Fig. 15 (Table 2). Interesting results were obtained, the selectivity values indicate that HAP at 273 K showed higher selectivity of CO_2/N_2 : 61.71 compared to HAF and HAT with values of 37 and 34, respectively, which is reflected by the higher Q_{st} value for CO_2 and lower Q_{st} value for N_2 . Whereas, at 298 K the selectivity was controlled by the higher surface area obtained by HAF with a selectivity of CO_2/N_2 : 57.85 compared to HAT and HAP with values of 35.86 and 23.26, respectively. A similar trend was observed for the selectivity of CO_2/CH_4 . Table 3 shows the storage and CO_2 capture capabilities of the porous polymers in comparison to reported materials in the literature.

Table 2: Initial slope selectivity of HAF, HAT and HAP toward CO_2 against CH_4 and N_2 .

Polymer	Gas Selectivity			
	CO_2/N_2	CO_2/N_2	CO_2/CH_4	CO_2/CH_4
	273 K	298K	273K	298 K
HAF	37.87	57.85	7.28	6.53
HAT	34.13	35.86	5.63	4.11
HAP	61.71	23.26	9.02	5.75

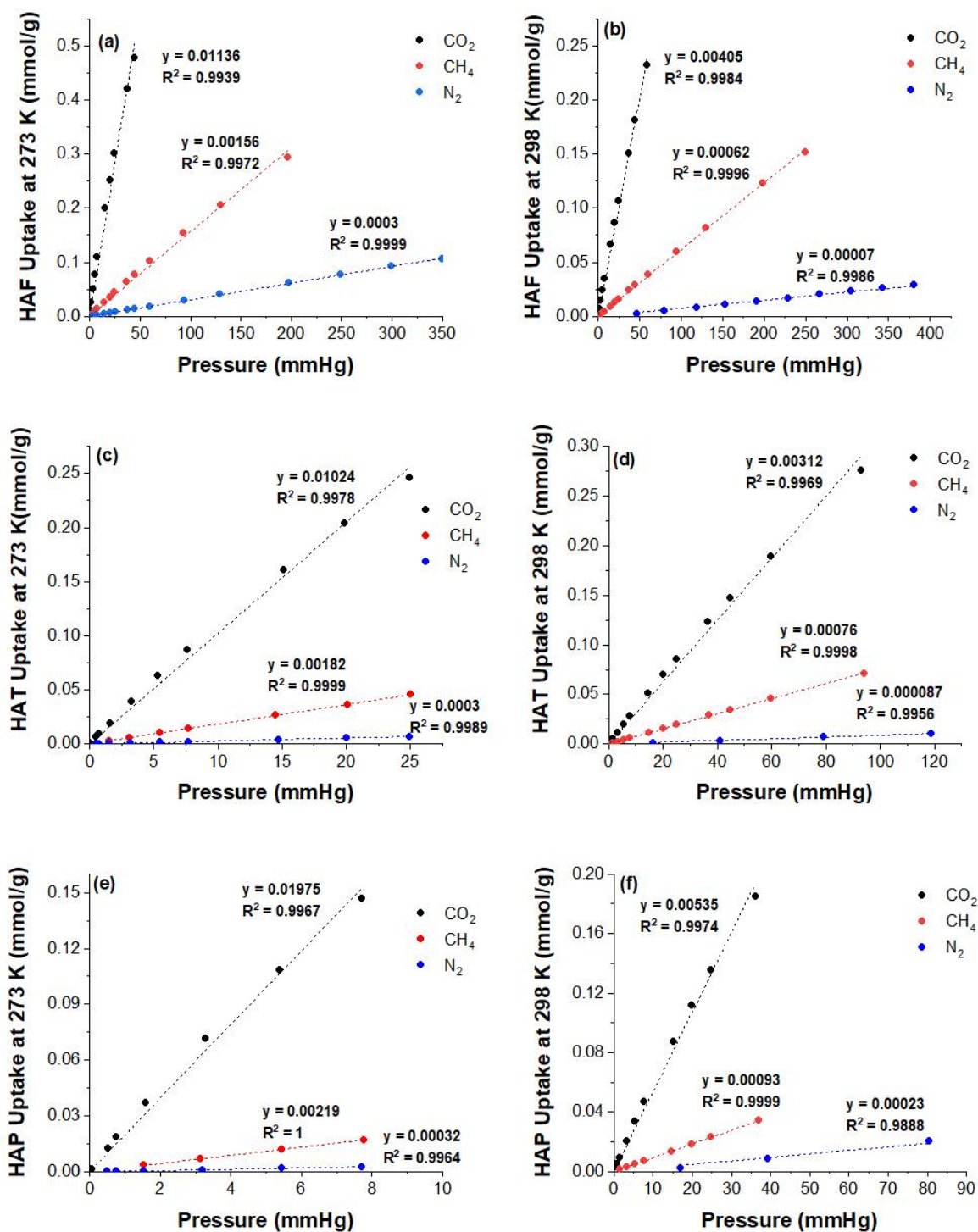


Figure 15: Initial slope selectivity of HAF, HAT and HAP at 273K and 298 K.

Table 3: CO₂ uptake capacity and surface area comparison of synthesized HAF, HAT and HAP polymers with other reported adsorbents

Adsorbent name	Surface area m ² /g	CO ₂ uptake capacity mmol/g		H ₂ uptake mmol/g(wt.%)	Selectivity (298K)		Reference
		273 K	298K		CO ₂ /CH ₄	CO ₂ /N ₂	
HAF	634	2.61	1.48	5.32 (1.06)	7	58	Current study
HAT	528	2.17	1.22	3.33 (0.66)	4	36	
HAP	539	2.37	1.45	3.74 (0.75)	6	23	
M1	575	1.85	1.24	2.94 (0.6)	9	43	[98]
M2	389	2.10	1.41	3.88 (0.8)			
BTAP-3	420	1.58	1.41	-	8	32	[125]
TAP1	474	2.2	1.4	5.25 (1.05)	9	91	[126]
SN@CMP-1	89	2.1	1.32	-	4.6	22.6	[127]
MOPs	100	1.79	-	-	10.2	55	[128]
POF	735	2.7	1.71	-	9.7	37	[129]
PAF-20	702	1.16	-	0.89 (0.079)	-	-	[130]
C2M1-A1	609	1.45	-	3.6 (0.72)	-	-	[59]
BIPLP-1	380	2.5	1.75	-	5	26	[131]

3.3.5 Molecular level interactions

The optimized geometries of the polymers HAF, HAP and HAT and the corresponding geometry optimized supercells showing the Connolly isosurfaces are presented in Fig. 16. Amorphous cells packed with 30 repeating units of the polymers and having lattice dimensions if $30 \times 30 \times 30$ Å were built and structurally relaxed to the minima on the Forcite module. The

cells were subjected to NPT and NVT dynamics simulations each for a duration of 1000 ps for equilibration at a timestep of 1.0×10^{-3} ps. During the simulations, the pressure and temperature of the system were controlled using the Berendsen barostat and the Nose-Hoover thermostat, respectively. The initial velocities of the polymers were randomly set by the Boltzmann distribution, while the Ewald 19 summation method was used to control the long-range coulombic interactions. Lastly, the Lennard Jones attractive/repulsive interactions were estimated within a cut-off range of 18.5 Å, including the long-range corrections. All the polymers exhibited closely-packed geometries with high tendency for intra-molecular $\pi - \pi$ interactions, resulting in high porosity as evidenced by the blue grey isosurfaces which represent the free accessible volumes within the polymers. The HAF, HAP and HAT polymers demonstrated high potential for gas permeability with Connolly surface areas in the order of 8600, 7900 and 7400 Å² at 298 K, respectively. Similarly, the HAF exhibited a superior percentage free volume with a calculated fractional free volume (FFV) of 0.521, in contrast to HAP and HAT with the values of 0.469 and 0.438, respectively. These values indicate the inherent structural features of the polymers and depict their strong potential for gas permeation and separation.

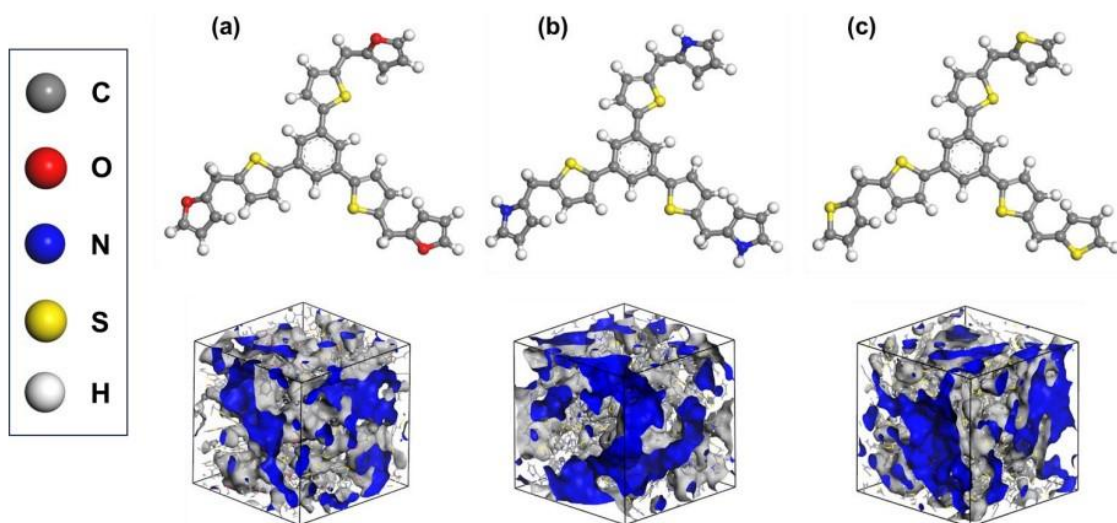


Figure 16: Geometry-optimized structures (top) and the Connolly amorphous cells comprising of 30 repeating units (bottom) of the polymers (a) HAF, (b) HAP and (c) HAT. The blue and grey isosurfaces represent the free accessible volumes within the polymers at a probe radius of 1.2 Å.

The interaction and permeation of single component gases (CO_2 , CH_4 and N_2) on the polymer units at temperatures of 273 and 298 K, and pressure up to 760 mmHg were simulated in supercells with lattice dimensions $30 \times 30 \times 50 \text{ Å}$ as presented in Fig. 26–28 (appendix). The corresponding Langmuir-fitted theoretical sorption isotherms are presented in Fig. 17. The polymers demonstrated excellent affinity towards CO_2 molecules (Fig. 17a) compared to CH_4 (Fig. 17b) and N_2 (Fig. 17c) molecules at 273 and 298 K. This can be attributed to the strong quadrupolar effect of CO_2 which is absent in CH_4 and N_2 . Moreover, the HAF and HAP polymers due to stronger Lewis's acid/base attractions exhibited higher uptake capacity of 3.05 and 3.02 mmol/g at 273 K, and 1.45 and 1.40 mmol/g at 298 K, respectively. The HAT polymer in contrast exhibited weaker attractions resulting in lower uptake limits of 2.55 and 1.15 mmol/g at 273 and 298 K, respectively. Fewer interaction sites were predicted for N_2 gas on the polymers resulting in significantly lower uptake, in agreement with the experimental findings. Hence, theoretical Q_{st} values of 42.5, 41.0 and 46.4 kJ/mol were calculated for CO_2 on HAF, HAT and HAP, while values of 25.6, 20.2 and 19.8 kJ/mol were predicted for CH_4 and 5.20, 4.10 and 1.73 kJ/mol for N_2 gases, respectively. Q_{st}

values below 20 kJ/mol often indicate physisorption, while values greater than 40 kJ/mol suggest strong chemisorption ^[110]. The calculated Q_{st} values in the present study implies both physisorption and chemisorption on the studied gases. Similarly, the polymers demonstrate excellent potential for the cryogenic H_2 storage (Fig. 17d) due to the strong physisorption to H_2 molecules via the polymer heteroatoms, achieving uptake capacities of 6.35, 5.25 and 5.56 mmol/g at 77 K for HAF, HAP and HAT, respectively.

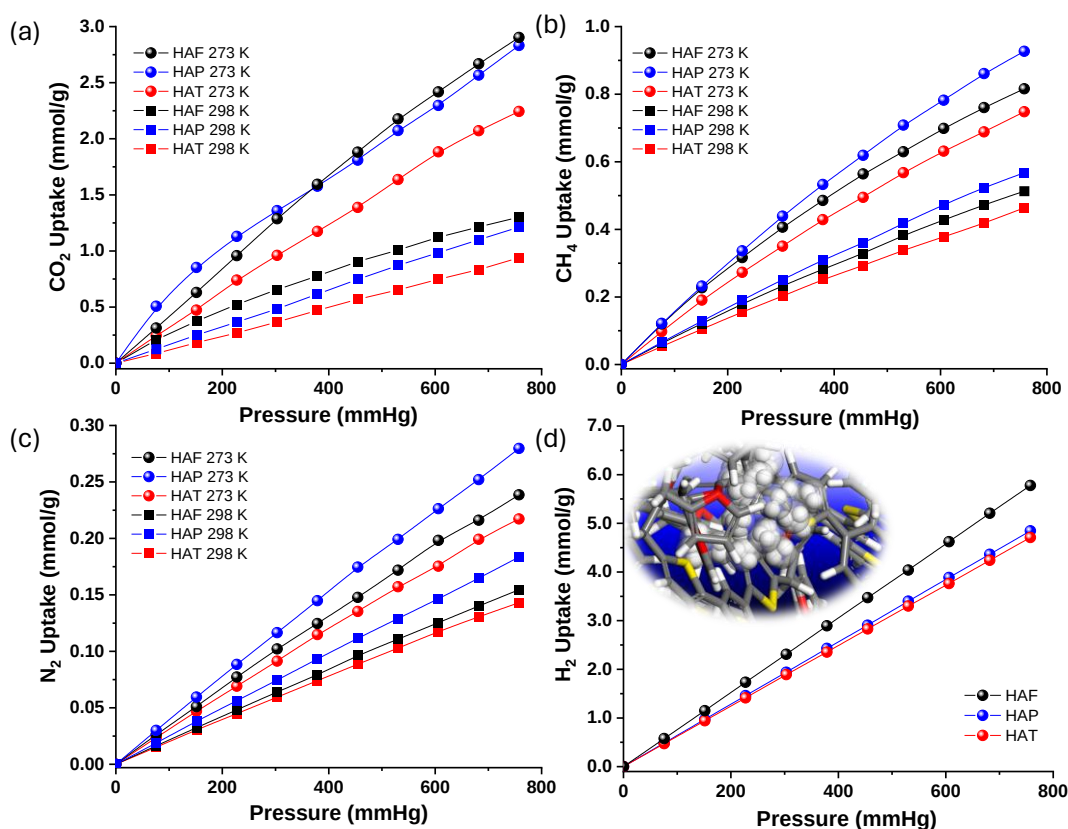


Figure 17: Theoretical adsorption isotherms at 273 K and 298 K of (a) CO_2 , (b) CH_4 and (c) N_2 gases on HAF, HAP and HAT polymers. The adsorption isotherm of H_2 at 77 K is shown in (d). The inset shows the H_2 molecules within the HAF polymer.

Lastly, the selectivity of the polymers in binary mixtures of CO_2/CH_4 and CO_2/N_2 at 273 and 298 K was explored, and the predicted sorption isotherms are presented in Fig. 18. The polymers demonstrated remarkable selectivity to CO_2 in all mixtures and temperatures due to the match in

electronic properties, and in accordance with the hard-soft acid-base (HSAB) principle ^[132]. The corresponding Qst values presented in Table 8 agree with the experimental results and affirm the selectivity of the synthetic polymers to CO₂ over CH₄ and N₂, making them potential candidates for natural gas purification.

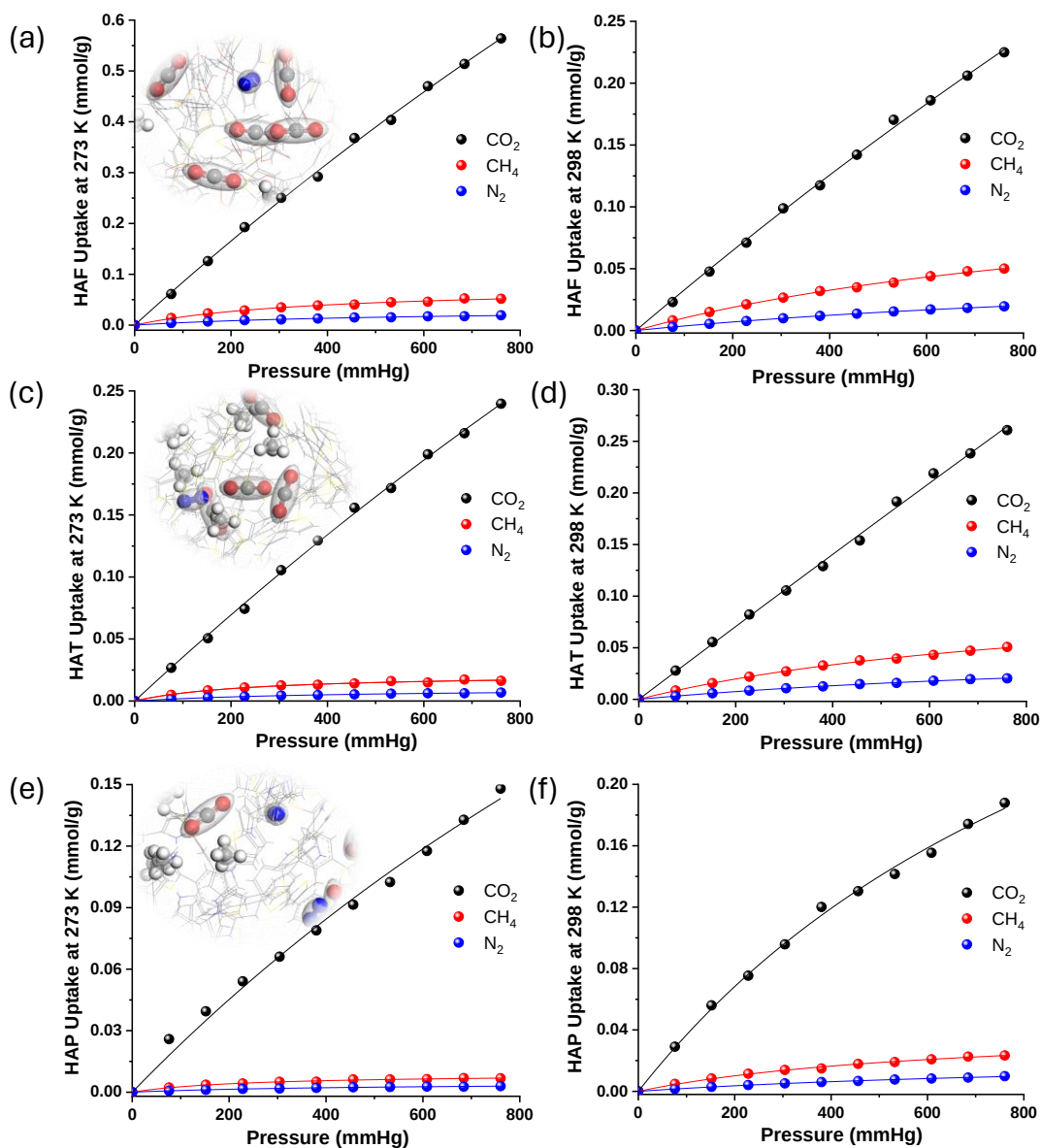


Figure 18: Theoretical adsorption isotherms of CO₂, CH₄ and N₂ gases on (a) HAF at 273 K, (b) HAF at 298 K, (c) HAT at 273 K, (d) HAT at 298 K, (e) HAP at 273 K, and (f) HAP at 298 K.

3.4 Conclusion

Herein, we successfully synthesized three porous polymers HAF, HAT and HAP via microwave assisted Friedel-Crafts polymerization. The structural characteristics demonstrated the confirmation of polymer synthesis, resulting in improved thermal stability up to 300 °C and porosity. The BET analysis revealed that the HAF polymer possessed the highest surface area of 634 m² /g compared to HAT and HAP. The polymers showed preference toward CO₂ adsorption over CH₄ and N₂. The molar values of CO₂ adsorption at 273 K are 2.61, 2.17, and 2.37 mmol/g, and at 298 K, the values are 1.48, 1.22, and 1.45 mmol/g for HAF, HAT, and HAP polymers respectively. Molecular dynamics predictions were in excellent agreement with the experimental findings and demonstrated the efficacy of microwave heating in rapidly synthesizing and tailoring porous polymers with outstanding characteristics. This work highlights the interplay between surface area and binding affinity that is revealed by the higher uptake and lower selectivity of HAF and the lower uptake and higher selectivity of HAP. The combination of heteroaromatic moieties shows the interplay of functionality and porosity in adsorption and selectivity of the polymers produced and making them very promising for the separation and capture of CO₂ and applying these polymers in clean energy storage.

CHAPTER 4

Phenazine Porous polymers for Radioactive Iodine Capture

Abstract

The removal of radioactive iodine from different environments enables the use of nuclear energy in a sustainable and efficient way. In this study we report the synthesis of three novel porous polymers via microwave assisted Friedel crafts polymerization of phenazine with pyrrole (PHP), Thiophene (PHT) and furan (PHF) with dimethoxymethane as a linker and iron (III) chloride as a catalyst. The polymers showed permanent porosity with surface areas of 137-330 m²/g and good thermal stability. The efficiency of the synthesized porous polymers in the removal of volatile iodine reached 885- 1005 mg/g capacity whereas the removal capacities reached 202-222 mg/g in cyclohexane solution. Their excellent removal capabilities accompanied with their rigid and stable structures makes them an excellent choice for the removal of radioactive iodine waste.

4.1 Introduction

Energy being a main source for the development of human civilization, it is essential to find sustainable energy solutions to meet the global energy demand for progress without harming the environment. Both developing and developed nations must have access to reliable energy sources. As a visible growth in energy demand is seen with passing years, exploring all accessible energy sources is fundamentally required to meet the same. Hence nuclear energy is envisioned to play a vital role for a long-term sustainable energy security and numerous nuclear power plants (NPPs) are built and operated worldwide for the purpose ^[133]. The amount of radioactivity released from a NPP is very much regulated to be within the safety levels set by the nuclear regulatory agencies, very well up to the normal background levels. Both ¹²⁹I and ¹³¹I are the most important

radioisotopes produced by the fission of uranium atoms in a nuclear reactor ^[134]. ¹³¹I being short lived ($T_{1/2} = 8$ days) as compared to ¹²⁹I ($T_{1/2} = 15.7$ million-year), decays out rapidly if formed and release during the normal operation of the NPP. Both the isotopes ¹²⁹I and ¹³¹I are prominent beta and weak gamma emitters ^[135]. Iodine that is radioactive can enter the body by inhalation or ingestion pathways. It dissolves in water and hence moves easily from the atmosphere and can enter humans and other living organisms through various ingestion pathways ^[136]. Also, ¹³¹I is extensively used in nuclear medicine due to its short half-life and beta emission properties ^[137]. Iodine is particularly helpful for identifying and treating thyroid issues due to its tendency to concentrate in thyroid glands ^[138]. If radioactive iodine is accidentally released into the environment, it could enter the grass->cow->cow milk pathway and raise the thyroid dose for those who drink milk, especially newborns and young children ^[139].

It is essential to synthesis materials with excellent adsorption capacities and reusability for iodine adsorption. Several materials have been reported for iodine adsorption, including activated carbon ^[140], graphene ^[141], metal organic framework (MOF) ^[142,143], zeolites ^[144], covalent organic polymer ^[145,146], silver-mordenite ^[147–150] aerogels ^[151], etc. Ag-based solid materials have been commonly used for iodine adsorption. However, the interaction between iodine and silver is strong and irreversible ^[147,152]. Porous organic polymers (POP) have lately surpassed these Ag-based materials due to their quick recycling and low consumption of energy. Physical adsorption of iodine follows several driving forces ^[153], such as 1) coordinatively unsaturated sites on the materials can absorb iodine 2) Iodine can adsorb on the basic sites via acid-base interaction 3) π electron system in the organic moiety can influence the adsorption of iodine 4) The heteroatoms (N, S, or O) present in the moiety also influence the iodine adsorption capacity. POPs with a range of compositions and tunable pore sizes are of tremendous interest due to their outstanding gas

adsorption performance ^[154]. POPs with heteroatoms have garnered significant interest due to their nitrogen-rich moiety and strong affinity for iodine adsorption. However, POPs have not yet been thoroughly investigated for iodine adsorption ^[155].

In this study, a series of novel porous polymers with rigid structure and functionality were synthesized via microwave-assisted Friedel-Crafts alkylation. This POP exhibits high surface areas and excellent thermal and chemical stability. The porous polymers with high functionality showed to be efficient in the removal of iodine in the gaseous and solution.

4.2 Experimental section

4.2.1 Materials and instruments

Phenazine (98% purity), N, N-dimethylformamide (DMF, 99% purity), were purchased from Acros organic. Pyrrole (98% purity, pyrrole was distilled under vacuum before use), thiophene (99% purity), furan (98% purity), dimethoxymethane (98% purity), were purchased from Alfa Aesar. Anhydrous iron (III) chloride (97% purity) was purchased from Sigma Aldrich. Methanol (MeOH; $\geq 99.9\%$ purity) was acquired from Merck while ammonium hydroxide solution (NH₄OH; 28–30 w/w%) was obtained from Fisher Scientific.

Solid NMR ¹³C-NMR CPMAS was conducted on a Bruker 400 MHz spectrometer. FTIR spectra were conducted on a PerkinElmer 16F PC FTIR spectrometer. Thermal gravimetric analysis was conducted on a QMS 403 C Aëolos with STA 449 F1 Jupiter. Surface area analyzer and pore size distribution were carried out on a Micrometric Tristar II Plus. Powder X-ray diffraction patterns were carried out on a Rigaku MiniFlex II X-ray diffractometer. Reactions were conducted in Teflon sealed easyprep vials on a MARS 6 Microwave system.

4.2.2 Synthesis of Phenazine based porous polymers.

In a typical experiment ^[86], Facile microwave synthesis was carried out by dissolving phenazine (1.8g, 0.01 mol) in 50 ml of DMF in a microwave vessel (Easyprep). Pyrrole (2.01g, 0.03 mol) and dimethoxymethane (4.6g, 0.01 mol) were then added to the mixture and stirred until a homogenous solution was obtained. Anhydrous FeCl₃ (9.7g, 0.06 mol) were dissolved in the mixture. The solution was flushed with N₂ to insure inert environment. The vessel was sealed and placed in the microwave oven and heated at 90°C for 30 min. After the solution was cooled down, the solid material was collected by filtration. To remove the excess FeCl₃, the solid product was washed with MeOH, ammonia solution, DI water and finally washed with MeOH. The solid was dried at 70°C under vacuum for overnight to yield 5.8 g of polymer PHP. in a similar experiment thiophene and furan was used instead of pyrrole to yield PHT (5.0 g) and PHF (5.0 g), respectively.

4.2.3 Volatile iodine uptake experiments

In a typical adsorption experiment ^[156,157], volatile iodine capture was conducted in a sealed beaker filled with iodine vapor at 348 K and 1 atm., as shown in Fig. 19. The amount of iodine captured was measured by the weight difference before and after adsorption. In a typical procedure, a 5 ml open vial containing 20 mg of polymer was inserted in a sealed container containing iodine at 348 K and 1 atm. for a certain amount of time, once the experiment completed the weight of polymer was measured. the uptake of iodine by the porous polymer was calculated as follow:

$$\% \text{ wt.} = \frac{(m_f - m_i)}{m_i} \times 100\% \quad (1)$$

where, % wt. represents the % removal of iodine vapor, and mf is the mass of polymer after adsorption (mg), mi is the mass of polymer before adsorption (mg).

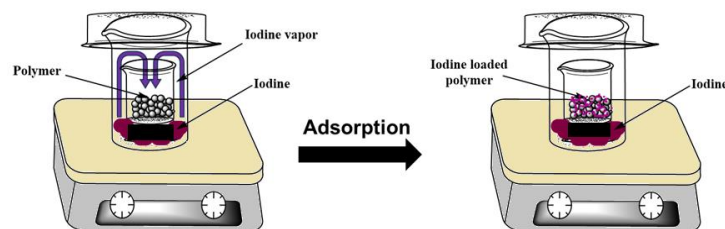


Figure 19: Volatile iodine adsorption experiment setup.

4.2.4 Solution iodine uptake experiments

In a typical experiment ^[73], a 5 ml solution of iodine in cyclohexane of a certain concentration (1000, 750, 500 and 250 mg/L) was added 20 mg of polymer and stirred for a certain amount of time. Finally, the solution was filtered and the amount of iodine in the filtrate was measured by UV-adsorption. The adsorption capacity of the polymer was calculated as follows:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (2)$$

Where, q_e is the adsorption capacity (mg/g), C_o is the initial concentration of iodine, C_e is the equilibrium concentration of iodine after adsorption, V is the volume of the solution (L), m is the mass of polymer(g).

4.3 Results and discussion

Three novel porous polymers (PHP, PHT and PHF) were synthesized by microwave-assisted polymerization of phenazine with pyrrole, furan and thiophene. Dimethoxymethane was used as a linker and anhydrous iron (III) chloride as a catalyst by Friedel-crafts alkylation. The polymers were designed to assure efficient adsorption of iodine, the aromatic moieties were chosen to form permanent porous structures with good binding sites equipped with heteroatoms that possess high electronegativities and lone pairs of electrons as shown in figure 20.

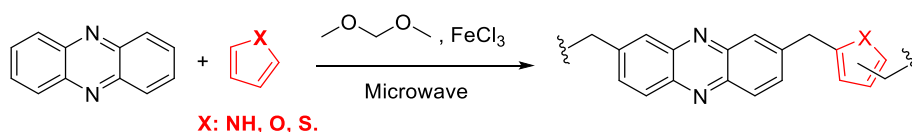


Figure 20: Microwave-assisted polymerization of porous phenazine polymers.

4.3.1 Characterization of *PHP*, *PHT* and *PHF* porous polymers

To elucidate the structure and thermal stability of the synthesized polymers, we used a combination of solid state ^{13}C NMR (CP MAS), Fourier Infrared spectroscopy (FTIR), powder X-ray Diffraction (PXRD) and thermogravimetric analysis (TGA) as shown in Fig. 21. The NMR spectra in Fig. 21a shows the detailed assignment of NMR peaks to the designated polymers. A characteristic peak $\sim 30\text{--}50$ ppm was assigned to the methylene linkage between the aromatic moieties of phenazine with pyrrole, furan and thiophene. The peaks $\sim 100\text{--}160$ ppm are characteristic to the aromatic carbons of the phenazine, pyrrole, thiophene and furan ^[54,58]. The NMR spectra confirm the structure and the formation of the designed polymers. The FTIR spectra shown in Fig. 21b, an absorption band $\sim 2980\text{ cm}^{-1}$ is characteristic to the methylene bridge ($-\text{CH}_2-$) between the aromatic moieties. An absorption band $\sim 1600\text{--}1700\text{ cm}^{-1}$ is characteristic to the aromatic $-\text{C}=\text{C}-$ and $-\text{C}=\text{N}-$ stretching vibrations of the aromatic moieties. An absorption band $\sim 1500\text{ cm}^{-1}$ is characteristic to $-\text{C}=\text{C}-$ stretching vibrations of the aromatic moieties of furan and thiophene, whereas an absorption band $\sim 1400\text{ cm}^{-1}$ is characteristic to the pyrrole $-\text{C}=\text{C}-$ stretching vibration, an adsorption band $\sim 700\text{ cm}^{-1}$ is characteristic to the $-\text{C}-\text{S}-\text{C}-$ stretching vibration of the thiophene aromatic moiety. An absorption band $\sim 1000\text{--}1100\text{ cm}^{-1}$ is characteristic to the $-\text{C}-\text{O}-$ and $-\text{C}-\text{N}-$ stretching vibrations of furan and, phenazine and pyrrole moieties, respectively ^[158,159]. Thermogravimetric analysis of the polymers revealed that the polymers are highly stable, where PHP and PHT began thermal degradation $\sim 320^\circ\text{C}$ whereas, PHF began thermal degradation $\sim 220^\circ\text{C}$ as shown in Fig. 21c, which is due to the rigid aromatic structure of

the polymers. Fig. 21d shows the PXRD patterns of the synthesized polymers; the patterns reveal that the synthesized polymers are amorphous in nature ^[160].

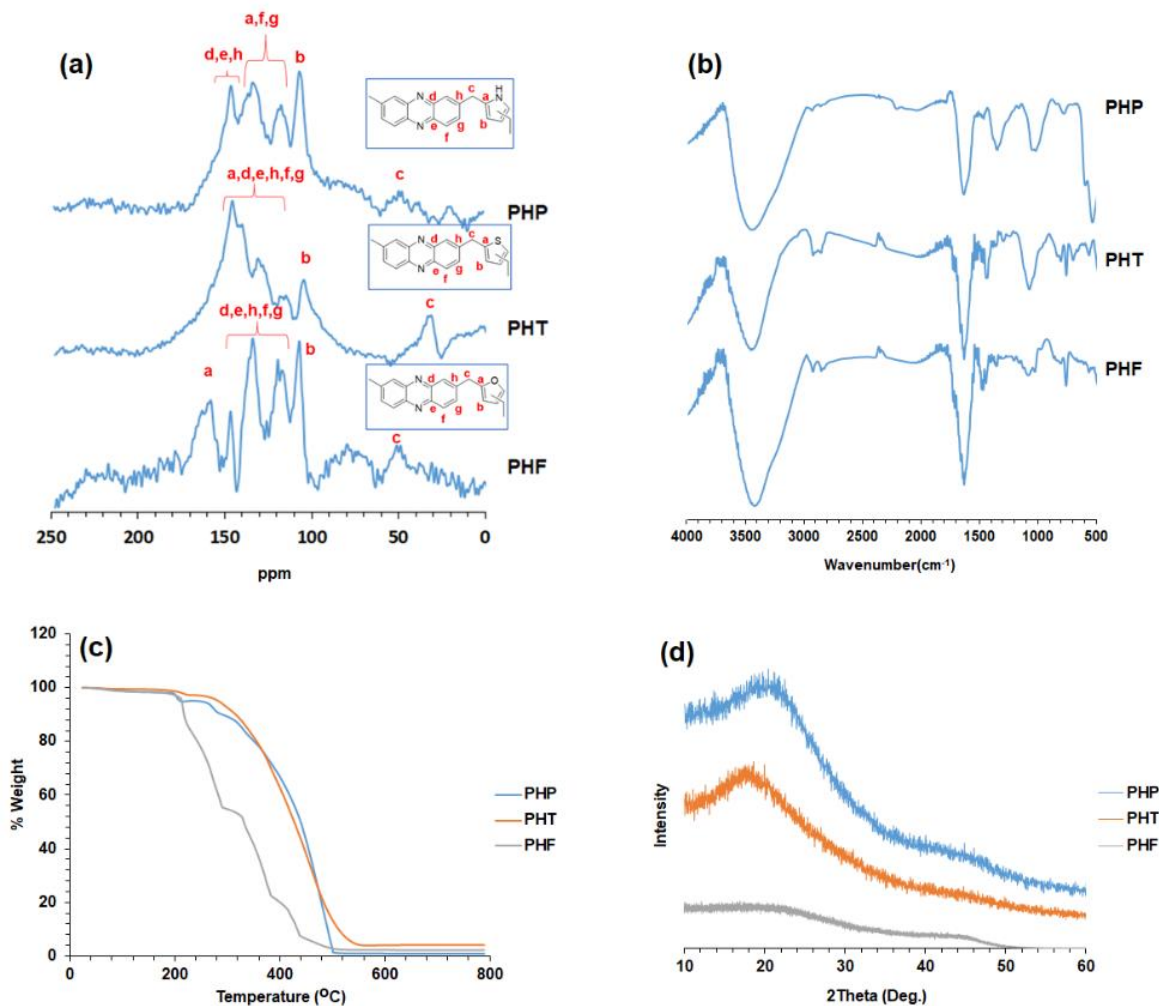


Figure 21: (a) Detailed Solid ^{13}C -NMR (CP MAS) spectra of the synthesized polymers PHP, PHT and PHF. (b) FTIR spectra of the synthesized polymers PHP, PHT and PHF. (c) TGA thermograms of the synthesized polymers PHP, PHT and PHF. (d) PXRD patterns of the synthesized polymers PHP, PHT and PHF.

The porosity of the synthesized polymers was assessed at 77K by N₂ adsorption/desorption isotherms and are represented in Fig. 22. The Fig. reveals that the synthesized polymers are permanently porous with BET surface areas of 330 m²/g for PHP, 280 m²/g for PHT and 137 m²/g for PHF. The adsorption isotherms reveal a sharp uptake at a relative low pressure ($P/P_o < 0.1$) indicating the microporous nature of the polymers. At a high relative pressure ($P/P_o > 0.9$), the isotherms reveal a phenomenon of interparticle condensation of N₂ which is a result due to the formation of macropores between the polymer particles. The NLDFT pore size distribution reveal micropores of 1.5 nm and mesopores of 2-4 nm [64,161].

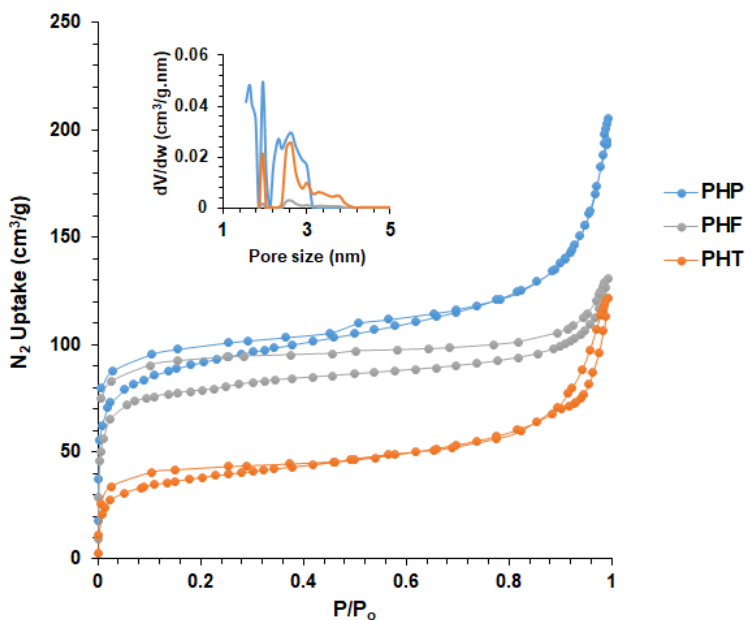


Figure 22: N₂ adsorption/desorption isotherm, and NLDFT pore size distribution curve of the synthesized polymers PHP, PHT and PHF.

4.3.2 Adsorption properties of the synthesized polymers

4.3.2.1 Adsorption of Volatile Iodine

The adsorption of volatile iodine by the synthesized porous polymers is shown in Fig. 23 and table 4. As shown in Fig. 23a the polymers exhibited a sharp increase in the % removal reaching saturation within 3 h, which after that the % removal begins to slowly increase indicating that the adsorption sites have been occupied by iodine molecules. The presence of functional groups accompanied with the porous nature of the polymers revealed their excellent removal capabilities reaching an uptake capacity of 100 % in the case of PHT. To comprehend the mechanistic and kinetic properties of the synthesized polymers, the experimental results were investigated by three kinetic models: Langmuir, Freundlich and intraparticle diffusion models. Fig. 23b shows the application of the pseudo first-order kinetic model on the experimental adsorption results. The linear equation is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - kt \quad (3)$$

where, q_e the adsorption capacity at equilibrium (mg/g), q_t represents the adsorption capacity at time t , k is the rate constant, and t represents the time (h) ^[162,163].

The models reveal that the adsorption of volatile iodine fits well with the linear kinetic model with regression values of $R^2 > 0.9880$. which indicates that the adsorption of volatile iodine is physisorption in nature. Whereas, applying the pseudo second-order kinetic model which is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (4)$$

Reveals that the experimental data with regression values of $R^2 < 0.9736$, indicating that the data doesn't fit the kinetic model ^[164]. The experimental data has also been applied to understand the mechanism of the adsorption by the intraparticle diffusion model. The rate determining step can be either controlled by film diffusion or intraparticle diffusion, or both. From the data applied to the model shown in fig. 23d, the rate determining step is controlled by film diffusion where iodine gas molecules are adsorbed on the surface and pores of the porous polymers followed by equilibrium ^[165].

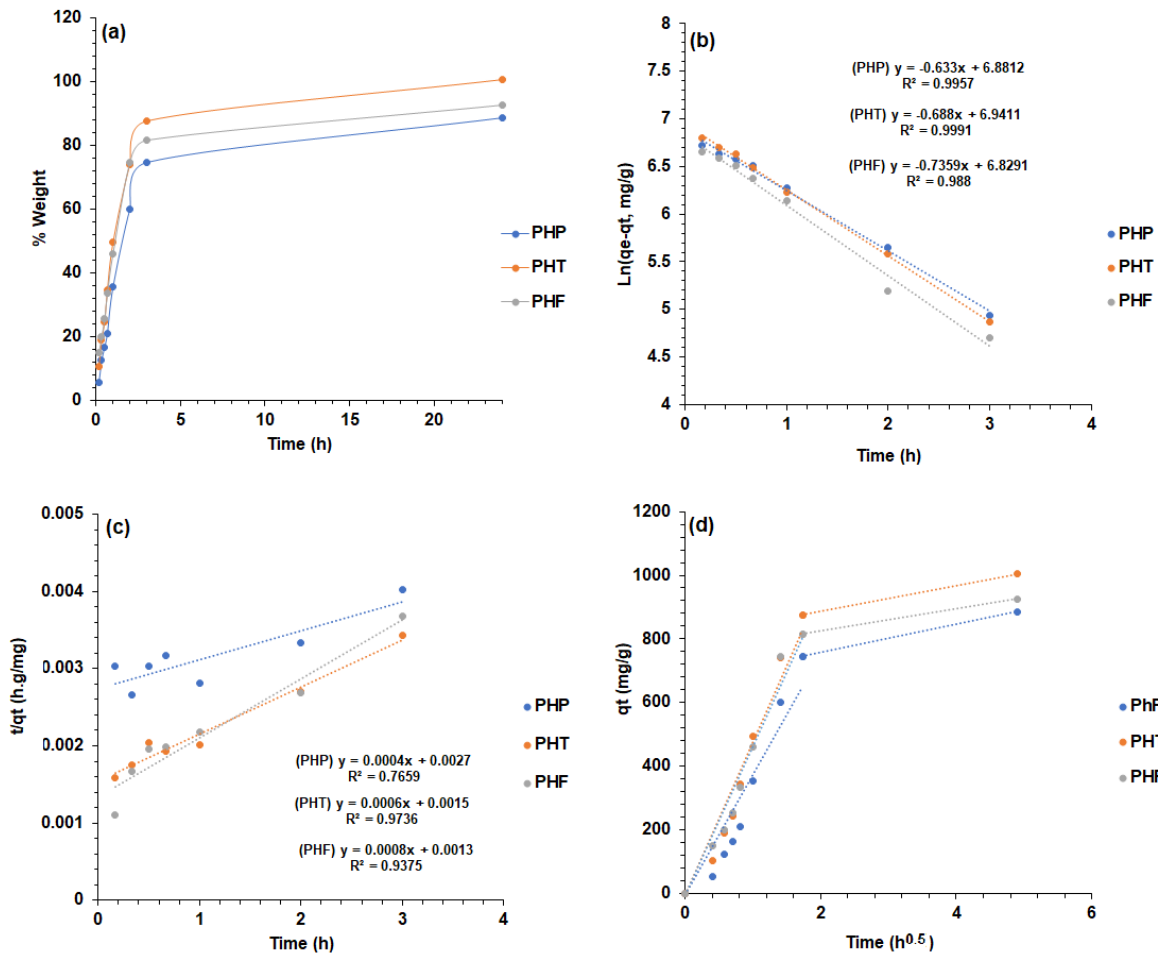


Figure 23: (a) Effect of time on the adsorption of volatile iodine by the porous polymers PHP, PHT and PHF. (b) Pseudo first-order kinetic model. (c) Pseudo second-order kinetic model. (d) Intraparticle diffusion kinetic model.

Table 4: (a) Pseudo first-order and Pseudo second-order kinetic model parameters of the adsorption of volatile iodine by the porous polymers PHP, PHF and PHT.

		Constants			
Model	Polymer	$q_{e(\text{exp})}$	$q_{e(\text{calc.})}$	k	R^2
Pseudo first-order	<i>PHP</i>	885.0	974.0	0.6330	0.9957
	<i>PHT</i>	1005	1034	0.6880	0.9991
	<i>PHF</i>	925.0	924.0	0.7360	0.9880
		$q_{e(\text{exp})}$	$q_{e(\text{calc.})}$	k	R^2
Pseudo second-order	<i>PHP</i>	885.0	2500	5.930×10^{-5}	0.7659
	<i>PHT</i>	1005	1667	2.390×10^{-4}	0.9736
	<i>PHF</i>	925.0	1250	4.920×10^{-4}	0.9375

4.3.2.2 Adsorption of iodine from cyclohexane solution

The adsorption of iodine was also investigated in solution, where the polymers showed their capability to adsorb iodine dissolved in cyclohexane. The capability of the polymers could be attributed to the high concentration of functional groups present in their structures. The adsorption of iodine in cyclohexane were studied under different concentrations (1000, 750, 500 and 250 mg/l) at 298 K. the experiments were conducted by measuring the capacity of the polymers to adsorb iodine within 24 h and the results are shown in Fig.24 As shown in fig.24a the adsorption capacity increases as the concentration increases with a maximum of 223 mg/g for PHT, 202 mg/g for PHP and 207 mg/g for PHF. Langmuir and Freundlich isotherm models were applied to the experimental data to comprehend the nature of the adsorption process. The Langmuir isotherm model (Fig.24b) which describes the homogeneous nature of the adsorption, where each iodine molecule can be adsorbed by only one adsorption site. The linear equation of the Langmuir isotherm model can be expressed as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (5)$$

where C_e is the concentration of iodine after adsorption (mg/L), b is the Langmuir model constant and q_m is the adsorption capacity at full coverage of the adsorption sites in the polymer (mg/g) ^[166]. The Freundlich isotherm model shown in fig.24c describes the heterogeneous nature of the adsorption process where it assumes that more than one iodine molecule can be adsorbed by one adsorption site. The linear equation of the isotherm model can be expressed as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

where n and k_f represent the Freundlich model constants ^[167]. From figures 24b, 24c and table 5, the experimental data of the adsorption of iodine by PHP, PHF and PHT fitted the Freundlich isotherm model better than the Langmuir model implying that the adsorption process is heterogeneous in nature. The n isotherm constant values of the Freundlich model are above unity indicating that the adsorption process is favorable in nature.

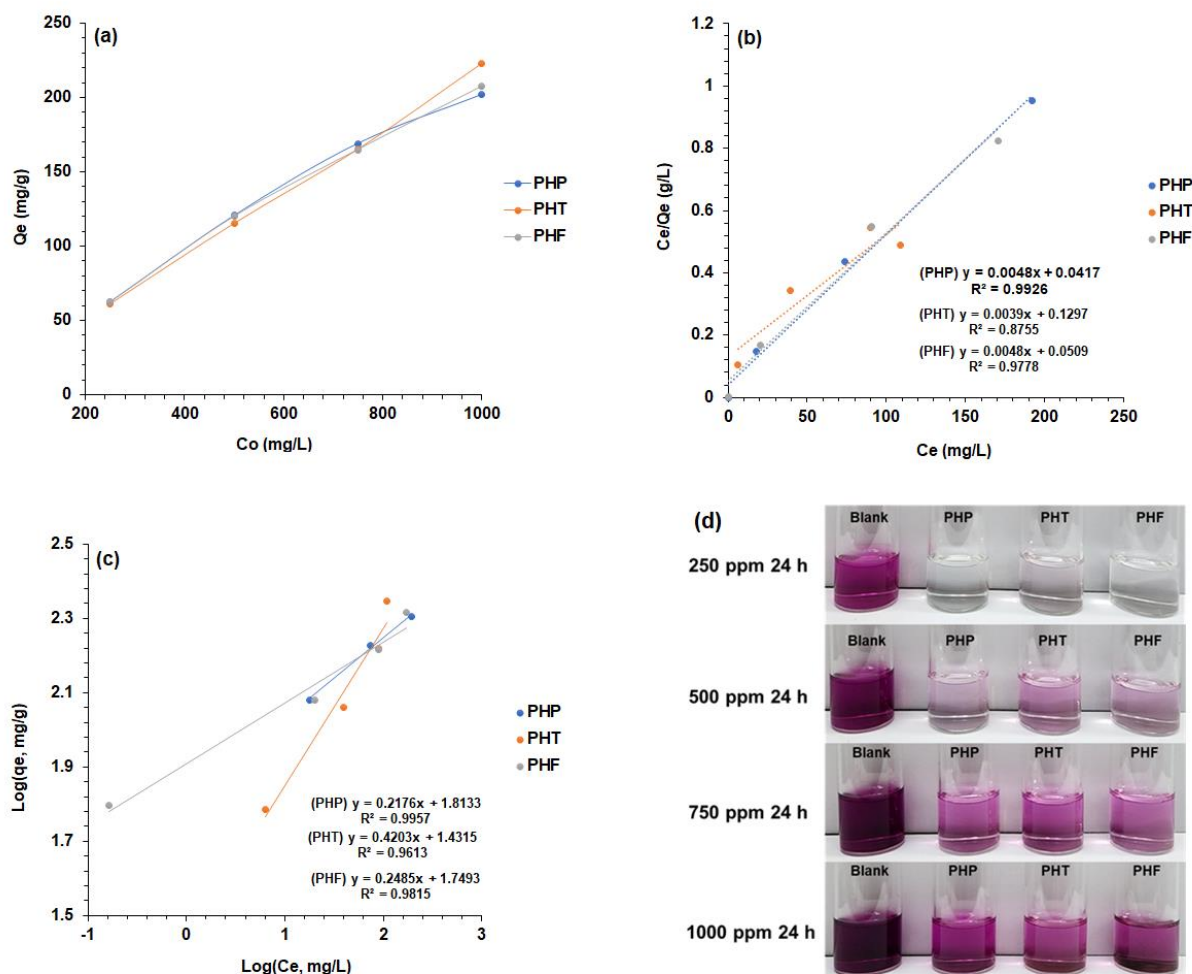


Figure 24: (a) The effect of initial concentration on the adsorption capacity of PHP, PHT and PHF. (b) The Langmuir isotherm model of the adsorption of iodine by PHP, PHT and PHF. (c) The Freundlich isotherm model of the adsorption of iodine by PHP, PHT and PHF. (d) The difference in color of the iodine solution before and after adsorption by PHP, PHT and PHF after 24 h at different concentrations.

Table 5: Langmuir and Freundlich isotherm model parameters for the adsorption of iodine in cyclohexane by PHP, PHT and PHF porous polymers

Model	Polymer	Constants			
		$q_{e(\text{exp})}$	$q_{m(\text{calc.})}$	b	R^2
Langmuir	PHP	202.0	208.3	0.0120	0.9926
	PHT	222.0	256.4	0.0300	0.8755
	PHF	207.0	208.3	0.0940	0.9778
Freundlich		n	k_f	R^2	
		PHP	4.595	65.16	0.9957
		PHT	2.379	27.01	0.9613
		PHF	4.024	56.14	0.9815

Fig. 25 and table 6, shows the experimental data fitting to two kinetic models; pseudo first-order and Pseudo second-order kinetic models, Fig. 25a reveals that the adsorption capacity of the polymers PHP, PHT and PHF increases sharply within 4 hours followed by slow increase in the adsorption capacity which is due to the decrease in the adsorption sites in the synthesized polymers. Fig. 25b and 25c shows that the data fits the pseudo-second-order kinetic model with regression values of $R^2 > 0.9900$, which assumes that the adsorption process is chemisorption in nature ^[168]. Interestingly as can be seen between the adsorption of iodine as volatile and solution the nature of the adsorption changes from physisorption to chemisorption which indicates that the adsorption is controlled by porosity and functionality in the adsorption of vapor iodine molecules, whereas in the solution part the adsorption is mainly controlled by the presence of functional groups and their capability to bind with iodine molecules dissolved in cyclohexane.

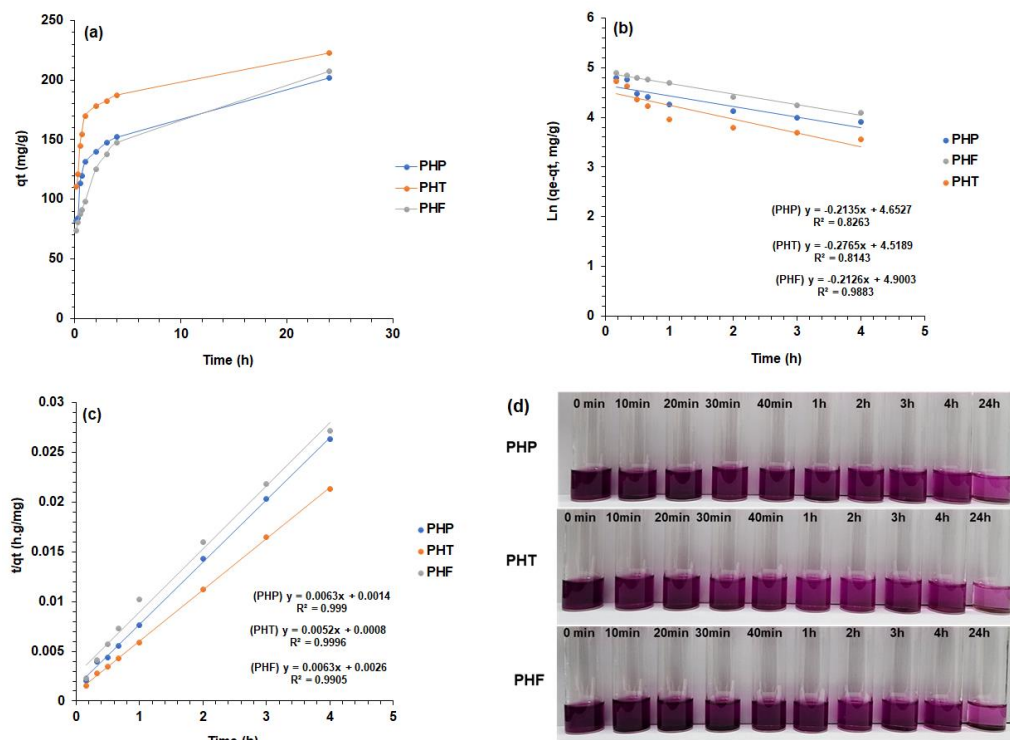


Figure 25: (a) The effect of time on the adsorption capacity of the synthesized polymers PHP, PHT and PHF. (b) Pseudo first-order kinetic model. (c) Pseudo second-order kinetic model. (d) The color change of the iodine solution before and after adsorption by the porous polymers PHP, PHT and PHF.

Table 6: Pseudo first-order and Pseudo second-order kinetic model parameters of the adsorption of iodine in cyclohexane by the porous polymers PHP, PHF and PHT.

Model	Polymer	Constants			
		$q_e(\text{exp})$	$q_e(\text{calc.})$	k	R^2
Pseudo first-order	PHP	201.9	104.9	0.2135	0.8263
	PHT	222.7	91.73	0.2765	0.8143
	PHF	207.3	134.3	0.2126	0.9883
Pseudo second-order		$q_e(\text{exp})$	$q_e(\text{calc.})$	k	R^2
		201.9	158.7	0.0284	0.990
		222.7	192.3	0.0338	0.9996
	PHF	207.3	158.7	0.0153	0.9905

4.4 Conclusions

Three novel porous polymers PHP, PHT and PHF were synthesized by microwave assisted Freidel crafts alkylation. The structure of the synthesized polymers was confirmed by solid state ^{13}C -NMR CP MAS, FTIR and their thermal stability was investigated by TGA. The polymers were amorphous in nature and permanently porous with surface areas 137-330 m^2/g . The porous polymers showed their capability to adsorb iodine in gas phase and solution phase which shows their efficacy in the removal of iodine. The efficacy of the polymers was investigated by pseudo first-order and second-order kinetic models and showed that the adsorption in the gas phase to be controlled by physisorption whereas, in the solution phase to be controlled by chemisorption. These conclusions show that incorporating porosity and functionality enables the porous polymers to work efficiently under different environments. Also, it provides sufficient potential for the use of these porous polymers as an adsorbent for the removal of radioactive iodine release from nuclear reactors.

Appendix

Microwave-Synthesized Heteroaromatic Porous Organic Polymers for CO₂ Capture and Hydrogen Storage

(Supplementary Information)

Isosteric heat of adsorption (Q_{st})

The Isosteric heat of adsorption (Q_{st}) at zero coverage is an essential parameter to study the strength of adsorption between the adsorbate and the adsorbent under study. To obtain the Q_{st} value through Clausius-Clapeyron approach ^[169], the single gas isotherm at two different temperature, 273 K and 298 K, was fitted to a Langmuir-Freundlich Model:

$$q(P) = \frac{q \cdot (k \cdot P)^n}{1 + (k \cdot P)^n} \quad (1)$$

Where q(P) is the adsorbed quantity of adsorbate (mmol/g), P is the pressure (kPa), q is the maximum adsorption (mmol/g), k is the affinity constant, and n is the constant of heterogeneity.

The Isosteric heat of adsorption (Q_{st}) is calculated through the following equation:

$$Q_{st} = -R \cdot \ln \left(\frac{p_2}{p_1} \right) \cdot \frac{T_1 \cdot T_2}{(T_2 - T_1)} \quad (2)$$

Table 7: Langmuir-Freundlich Fitting Data

Gas	Polymer	Temperature (K)	q	k	n	R ²
CO ₂	HAF	273	5.08111	0.0104582	0.824273	0.999942
		298	3.78901	0.0060405	0.902347	0.999998
	HAT	273	4.14734	0.0109767	0.836024	0.999949
		298	3.0579	0.00633002	0.913002	0.999983
	HAP	273	4.23998	0.0131969	0.763284	0.999947
		298	3.26439	0.00758038	0.852077	0.999997
CH ₄	HAF	273	2.4794	0.00463534	0.955347	0.999999
		298	1.88463	0.00262476	1.00097	0.999991
	HAT	273	2.19495	0.00591355	0.935308	0.999986
		298	1.66124	0.00337356	0.984972	0.999994
	HAP	273	2.19495	0.00591355	0.935308	0.999986
		298	1.77468	0.00368094	0.97787	0.999993
N ₂	HAF	273	3.02522	0.000789507	1.00292	0.999996
		298	0.1349	0.00667604	1.21837	1.00003
	HAT	273	1.58355	0.0014119	1.00729	0.999991
		298	2.17889	0.000531707	1.11012	0.994046
	HAP	273	2.20734	0.00116463	0.988156	0.999994
		298	3.86462	0.000539743	1.00184	0.999869

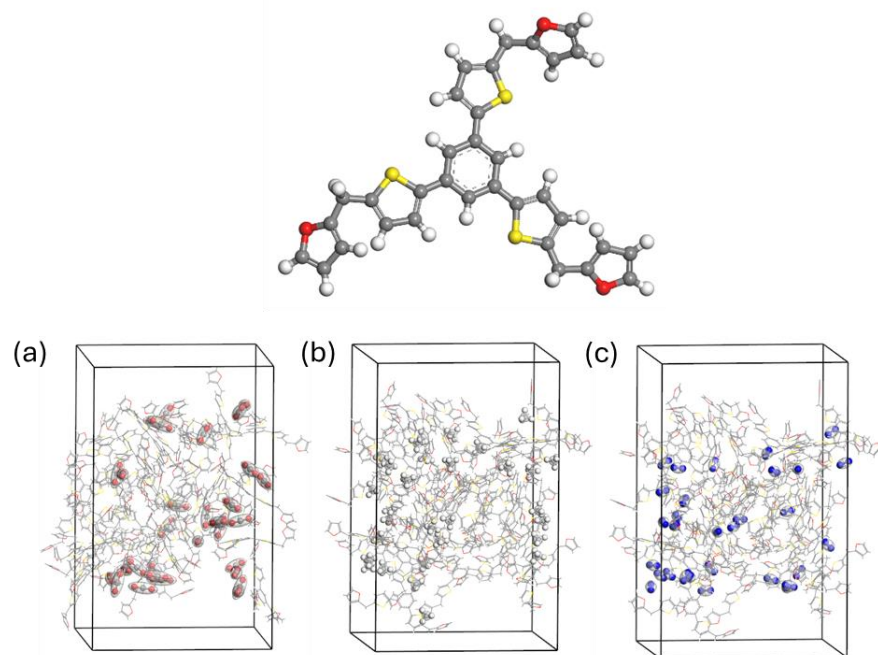


Figure 26: Optimized geometry of the polymer HAF, and the supercells comprising of (a) CO₂, (b) CH₄ and (c) N₂ gases.

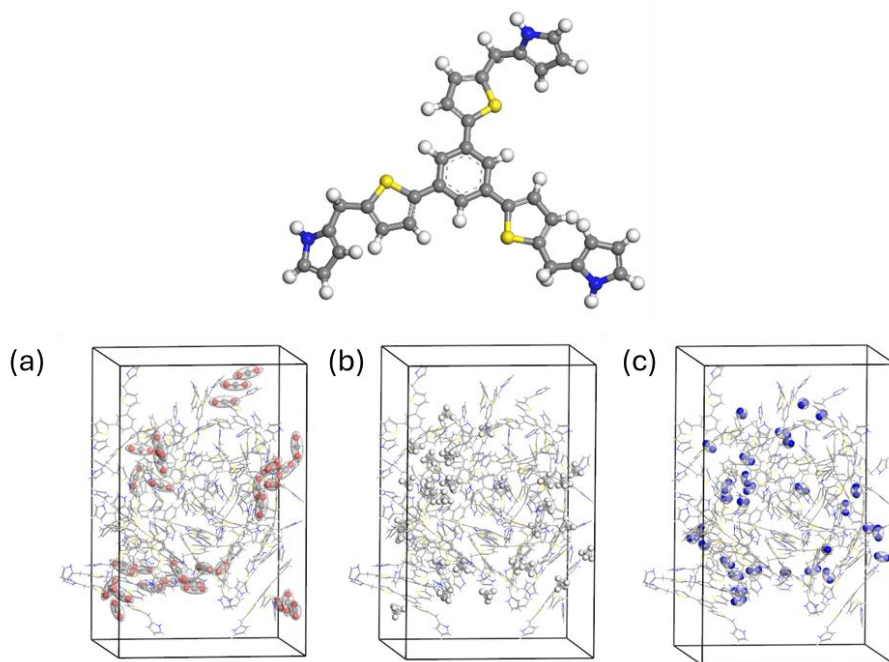


Figure 27: Optimized geometry of the polymer HAP, and the supercells comprising of (a) CO₂, (b) CH₄ and (c) N₂ gases.

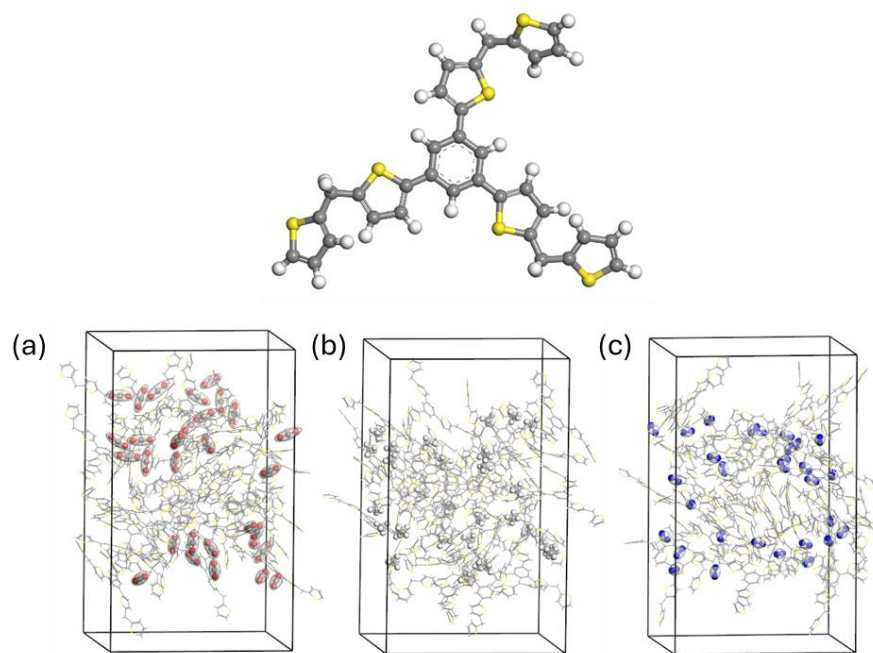


Figure 28: Optimized geometry of the polymer HAT, and the supercells comprising of (a) CO₂, (b) CH₄ and (c) N₂ gases.

Table 8: Theoretical Q_{st} values of the polymers in binary gas mixtures

Polymer	Theoretical Q _{st}			
	CO ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄	CO ₂ /CH ₄
	273 K	298K	273K	298 K
HAF	35.48	24.04	13.79	7.11
HAT	34.66	16.59	8.55	5.10
HAP	62.78	35.40	19.59	12.59

References

1. Rahman, F. A., Aziz, M. M. A., Saidur, R., Bakar, W. A. W. A., Hainin, M. R., Putrajaya, R., & Hassan, N. A. (2017). Pollution to solution: Capture and sequestration of carbon dioxide (CO₂) and its utilization as a renewable energy source for a sustainable future. In *Renewable and Sustainable Energy Reviews* (Vol. 71, pp. 112–126). Elsevier Ltd. <https://doi.org/10.1016/j.rser.2017.01.011>
2. Gür, T. M. (2022). Carbon Dioxide Emissions, Capture, Storage and Utilization: Review of Materials, Processes and Technologies. In *Progress in Energy and Combustion Science* (Vol. 89). Elsevier Ltd. <https://doi.org/10.1016/j.pecs.2021.100965>
3. United Nations Environment Programme. (n.d.). *The emissions gap report 2019*.
4. Dziejarski, B., Krzyżyńska, R., & Andersson, K. (2023). Current status of carbon capture, utilization, and storage technologies in the global economy: A survey of technical assessment. In *Fuel* (Vol. 342). Elsevier Ltd. <https://doi.org/10.1016/j.fuel.2023.127776>
5. John P. Smol. (2012). Climate Change: A planet in flux. *Nature*, 2012, 1–3.
6. Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B., Bland, A. E., & Wright, I. (2008). Progress in carbon dioxide separation and capture: A review. In *Journal of Environmental Sciences* (Vol. 20).
7. Crippa, M., Guizzardi, D., Schaaf, M., Ferrario, M., Banja, F., Olivier, G. J. G., Rossi, G., & Vignati, S. (n.d.). *GHG emissions of all world countries 2021 Report*. <https://doi.org/10.2760/173513>

8. Bruce G. Miller. (2010). *Clean Coal Engineering Technology*. Butterworth-Heinemann.
9. Wilberforce, T., Olabi, A. G., Sayed, E. T., Elsaid, K., & Abdelkareem, M. A. (2021). Progress in carbon capture technologies. *Science of the Total Environment*, 761. <https://doi.org/10.1016/j.scitotenv.2020.143203>
10. Snæbjörnsdóttir, S. Ó., & Sigfússon, B. , M. (2020). Carbon dioxide storage through mineral carbonation. *Nat Rev Earth Environ*, 2020.
11. Thonemann, N., Zacharopoulos, L., Fromme, F., & Nühlen, J. (2022). Environmental impacts of carbon capture and utilization by mineral carbonation: A systematic literature review and meta life cycle assessment. In *Journal of Cleaner Production* (Vol. 332). Elsevier Ltd. <https://doi.org/10.1016/j.jclepro.2021.130067>
12. Osman, A. I., Hefny, M., Abdel Maksoud, M. I. A., Elgarahy, A. M., & Rooney, D. W. (2021). Recent advances in carbon capture storage and utilisation technologies: a review. In *Environmental Chemistry Letters* (Vol. 19, Issue 2, pp. 797–849). Springer Science and Business Media Deutschland GmbH. <https://doi.org/10.1007/s10311-020-01133-3>
13. IEA. (2021). *Direct Air Capture*. IEA. Paris.
14. Yusuf, M., & Ibrahim, H. (2023). A comprehensive review on recent trends in carbon capture, utilization, and storage techniques. In *Journal of Environmental Chemical Engineering* (Vol. 11, Issue 6). Elsevier Ltd. <https://doi.org/10.1016/j.jece.2023.111393>
15. Leroutier, M., & Quirion, P. (2022). Air pollution and CO2 from daily mobility: Who emits and Why? Evidence from Paris. *Energy Economics*, 109. <https://doi.org/10.1016/j.eneco.2022.105941>

16. Koytsoumpa, E. I., Bergins, C., & Kakaras, E. (2018). The CO₂ economy: Review of CO₂ capture and reuse technologies. In *Journal of Supercritical Fluids* (Vol. 132, pp. 3–16). Elsevier B.V. <https://doi.org/10.1016/j.supflu.2017.07.029>
17. Aminu, M. D., Nabavi, S. A., Rochelle, C. A., & Manovic, V. (2017). A review of developments in carbon dioxide storage. In *Applied Energy* (Vol. 208, pp. 1389–1419). Elsevier Ltd. <https://doi.org/10.1016/j.apenergy.2017.09.015>
18. Araújo, O. de Q. F., & de Medeiros, J. L. (2017). Carbon capture and storage technologies: present scenario and drivers of innovation. In *Current Opinion in Chemical Engineering* (Vol. 17, pp. 22–34). Elsevier Ltd. <https://doi.org/10.1016/j.coche.2017.05.004>
19. Rubin, E. S., Davison, J. E., & Herzog, H. J. (2015). The cost of CO₂ capture and storage. *International Journal of Greenhouse Gas Control*, 40, 378–400. <https://doi.org/10.1016/j.ijggc.2015.05.018>
20. D'Alessandro, D. M., Smit, B., & Long, J. R. (2010). Carbon dioxide capture: Prospects for new materials. In *Angewandte Chemie - International Edition* (Vol. 49, Issue 35, pp. 6058–6082). <https://doi.org/10.1002/anie.201000431>
21. Yu, C. H., Huang, C. H., & Tan, C. S. (2012). A review of CO₂ capture by absorption and adsorption. In *Aerosol and Air Quality Research* (Vol. 12, Issue 5, pp. 745–769). <https://doi.org/10.4209/aaqr.2012.05.0132>
22. Bachu, S., Bonijoly, D., Bradshaw, J., Burruss, R., Holloway, S., Christensen, N. P., & Mathiassen, O. M. (2007). CO₂ storage capacity estimation: Methodology and gaps.

International Journal of Greenhouse Gas Control, 1(4), 430–443.

[https://doi.org/10.1016/S1750-5836\(07\)00086-2](https://doi.org/10.1016/S1750-5836(07)00086-2)

23. Song, C. (2006). Global challenges and strategies for control, conversion and utilization of CO₂ for sustainable development involving energy, catalysis, adsorption and chemical processing. *Catalysis Today*, 115(1–4), 2–32. <https://doi.org/10.1016/j.cattod.2006.02.029>
24. Crippa, M., Guizzardi, D., Banja, M., Solazzo, E., Muntean, M., Schaaf, E., Pagani F., Monforti-Ferrario, F., Olivier, J. G. J., Quadrelli, R., Risquez Martin, A., Taghavi-Moharamli, P., Grassi, G., Rossi, S., Oom, D., Branco, A., San-Miguel, J., Vignati, E., & European Commission. Joint Research Centre. (n.d.). *CO₂ emissions of all world countries: JRC/IEA/PBL 2022 report*.
25. Davis, S. J., Peters, G. P., & Caldeira, K. (2011). The supply chain of CO₂ emissions. *Proceedings of the National Academy of Sciences of the United States of America*, 108(45), 18554–18559. <https://doi.org/10.1073/pnas.1107409108>
26. Becattini, V., Gabrielli, P., & Mazzotti, M. (2021). Role of carbon capture, storage, and utilization to enable a Net-Zero-CO₂-emissions aviation sector. *Industrial and Engineering Chemistry Research*, 60(18), 6848–6862. <https://doi.org/10.1021/acs.iecr.0c05392>
27. Liu, L. C., Li, Q., Zhang, J. T., & Cao, D. (2016). Toward a framework of environmental risk management for CO₂ geological storage in china: gaps and suggestions for future regulations. *Mitigation and Adaptation Strategies for Global Change*, 21(2), 191–207. <https://doi.org/10.1007/s11027-014-9589-9>

28. Ajayi, T., Gomes, J. S., & Bera, A. (2019). A review of CO₂ storage in geological formations emphasizing modeling, monitoring and capacity estimation approaches. In *Petroleum Science* (Vol. 16, Issue 5, pp. 1028–1063). China University of Petroleum Beijing.
<https://doi.org/10.1007/s12182-019-0340-8>
29. *STATE OF THE ART: CCS TECHNOLOGIES 2023*. (n.d.).
30. Leeson, D., Mac Dowell, N., Shah, N., Petit, C., & Fennell, P. S. (2017). A Techno-economic analysis and systematic review of carbon capture and storage (CCS) applied to the iron and steel, cement, oil refining and pulp and paper industries, as well as other high purity sources. *International Journal of Greenhouse Gas Control*, 61, 71–84.
<https://doi.org/10.1016/j.ijggc.2017.03.020>
31. Blomen, E., Hendriks, C., & Neele, F. (2009). Capture technologies: Improvements and promising developments. *Energy Procedia*, 1(1), 1505–1512.
<https://doi.org/10.1016/j.egypro.2009.01.197>
32. Dziejarski, B., Serafin, J., Andersson, K., & Krzyżyńska, R. (2023). CO₂ capture materials: a review of current trends and future challenges. In *Materials Today Sustainability* (Vol. 24). Elsevier Ltd. <https://doi.org/10.1016/j.mtsust.2023.100483>
33. Energy Agency, I. (2050). *Net Zero by 2050 - A Roadmap for the Global Energy Sector*.
www.iea.org/t&c/
34. Hon Chung Lau, Seeram Ramakrishna, Kai Zhang, & Adiyodi Veettil Radhamani. (2021). The Role of Carbon Capture and Storage in the Energy Transition. *Energy & Fuels*, 2021.

35. Panwar, N. L., Kaushik, S. C., & Kothari, S. (2011). Role of renewable energy sources in environmental protection: A review. In *Renewable and Sustainable Energy Reviews* (Vol. 15, Issue 3, pp. 1513–1524). <https://doi.org/10.1016/j.rser.2010.11.037>
36. Rehm, T. E. (2023). Advanced nuclear energy: the safest and most renewable clean energy. In *Current Opinion in Chemical Engineering* (Vol. 39). Elsevier Ltd. <https://doi.org/10.1016/j.coche.2022.100878>
37. Herzog, A. V, Lipman, T. E., & Kammen, D. M. (n.d.). *RENEWABLE ENERGY SOURCES*.
38. Dincer, I. (n.d.). *Renewable energy and sustainable development: a crucial review*. www.elsevier.com/locate/rser
39. Brook, B. W., Alonso, A., Meneley, D. A., Misak, J., Blees, T., & van Erp, J. B. (2014). Why nuclear energy is sustainable and has to be part of the energy mix. *Sustainable Materials and Technologies*, 1, 8–16. <https://doi.org/10.1016/j.susmat.2014.11.001>
40. Pepper, S. E., Baker, A., Maher, C. J., Carrott, M. J., Turner, J., & Hanson, B. C. (2024). Iodine behaviour in spent nuclear fuel dissolution. *Progress in Nuclear Energy*, 169. <https://doi.org/10.1016/j.pnucene.2024.105062>
41. Brunnengräber, A., Rosaria, M., Nucci, D., María, A., Losada, I., Lutz Mez, ., & Schreurs Editors, M. A. (n.d.). *Challenges of Nuclear Waste Governance Energiepolitik und Klimaschutz Energy Policy and Climate Protection*. <http://www.springer.com/series/12516>
42. Ekin, A. A., Antonov, K. L., Vasyanovich, M. E., Kapustin, I. A., & Filatov, I. Y. (2019). Radioiodine Release into the Atmosphere during Normal Operation of Nuclear Power Plants. *Radiochemistry*, 61(3), 352–364. <https://doi.org/10.1134/S1066362219030111>

43. Lee, U. J., Kim, M. J., & Kim, H. R. (2018). Radioactive iodine analysis in environmental samples around nuclear facilities and sewage treatment plants. *Nuclear Engineering and Technology*, 50(8), 1355–1363. <https://doi.org/10.1016/j.net.2018.07.017>
44. Hao, Y., Tian, Z., Liu, C., & Xiao, C. (2023). Recent advances in the removal of radioactive iodine by bismuth-based materials. In *Frontiers in Chemistry* (Vol. 11). Frontiers Media S.A. <https://doi.org/10.3389/fchem.2023.1122484>
45. Wang, X., Meng, R., Zhao, S., Jing, Z., Jin, Y., Zhang, J., Pi, X., Du, Q., Chen, L., & Li, Y. (2024). Efficient adsorption of radioactive iodine by covalent organic framework/chitosan aerogel. *International Journal of Biological Macromolecules*, 260. <https://doi.org/10.1016/j.ijbiomac.2024.129690>
46. Arora, N., Debnath, T., Senarathna, M. C., Johnson, R. M., Roske, I. G., Cisneros, G. A., & Smaldone, R. A. (2024). Rapid, high-capacity adsorption of iodine from aqueous environments with amide functionalized covalent organic frameworks. *Chemical Science*, 15(10), 3571–3577. <https://doi.org/10.1039/d3sc06004g>
47. Xu, S., Wang, J., Feng, Y., Liu, Y., & Liu, J. (2023). Study on the adsorption mechanism and properties of silver-loaded zeolite for radioactive iodine. *Nuclear Materials and Energy*, 37. <https://doi.org/10.1016/j.nme.2023.101517>
48. Zheng, Z., Lin, Q., Gao, Y., Ji, X., Sessler, J. L., & Wang, H. (2024). Recent advances in iodine adsorption from water. In *Coordination Chemistry Reviews* (Vol. 511). Elsevier B.V. <https://doi.org/10.1016/j.ccr.2024.215860>

49. Umadevi, K., & Mandal, D. (2021). Performance of radio-iodine discharge control methods of nuclear reprocessing plants. In *Journal of Environmental Radioactivity* (Vol. 234). Elsevier Ltd. <https://doi.org/10.1016/j.jenvrad.2021.106623>
50. Song, W., Zhang, Y., Tran, C. H., Choi, H. K., Yu, D. G., & Kim, I. (2023). Porous organic polymers with defined morphologies: Synthesis, assembly, and emerging applications. In *Progress in Polymer Science* (Vol. 142). Elsevier Ltd. <https://doi.org/10.1016/j.progpolymsci.2023.101691>
51. Tian, Y., & Zhu, G. (2020). Porous Aromatic Frameworks (PAFs). In *Chemical Reviews* (Vol. 120, Issue 16, pp. 8934–8986). American Chemical Society. <https://doi.org/10.1021/acs.chemrev.9b00687>
52. Taheri, N., Dinari, M., & Asgari, M. (2022). Recent Applications of Porous Organic Polymers Prepared via Friedel-Crafts Reaction under the Catalysis of AlCl₃: A Review. In *ACS Applied Polymer Materials* (Vol. 4, Issue 9, pp. 6288–6302). American Chemical Society. <https://doi.org/10.1021/acsapm.2c00927>
53. Ahmadi, Y., & Kim, K. H. (2023). Recent Progress in the Development of Hyper-Cross-Linked Polymers for Adsorption of Gaseous Volatile Organic Compounds. In *Polymer Reviews* (Vol. 63, Issue 2, pp. 365–393). Taylor and Francis Ltd. <https://doi.org/10.1080/15583724.2022.2082470>
54. Begni, F., Gullo, F., Paul, G., Rea, R., Ferrari, M. C., Mangano, E., Cossi, M., Gatti, G., & Marchese, L. (2022). Optimization of the Friedel-Crafts Alkylation for the Synthesis of Hyper-Cross-Linked Polymers. *ACS Applied Polymer Materials*, 4(8), 5281–5286. <https://doi.org/10.1021/acsapm.2c00973>

55. Jiao, S., Deng, L., Zhang, X., Zhang, Y., Liu, K., Li, S., Wang, L., & Ma, D. (2021). Evaluation of an Ionic Porous Organic Polymer for Water Remediation. *ACS Applied Materials and Interfaces*, 13(33), 39404–39413. <https://doi.org/10.1021/acsami.1c10464>
56. Wang, J., & Zhuang, S. (2019). Covalent organic frameworks (COFs) for environmental applications. In *Coordination Chemistry Reviews* (Vol. 400). Elsevier B.V. <https://doi.org/10.1016/j.ccr.2019.213046>
57. Li, B., Gong, R., Wang, W., Huang, X., Zhang, W., Li, H., Hu, C., & Tan, B. (2011). A new strategy to microporous polymers: Knitting rigid aromatic building blocks by external cross-linker. *Macromolecules*, 44(8), 2410–2414. <https://doi.org/10.1021/ma200630s>
58. Luo, Y., Li, B., Wang, W., Wu, K., & Tan, B. (2012). Hypercrosslinked aromatic heterocyclic microporous polymers: A new class of highly selective CO₂ capturing materials. *Advanced Materials*, 24(42), 5703–5707. <https://doi.org/10.1002/adma.201202447>
59. Liu, G., Wang, Y., Shen, C., Ju, Z., & Yuan, D. (2015). A facile synthesis of microporous organic polymers for efficient gas storage and separation. *Journal of Materials Chemistry A*, 3(6), 3051–3058. <https://doi.org/10.1039/c4ta05349d>
60. Kundu, S. K., & Bhaumik, A. (2016). Novel nitrogen and sulfur rich hyper-cross-linked microporous poly-triazine-thiophene copolymer for superior CO₂ capture. *ACS Sustainable Chemistry and Engineering*, 4(7), 3697–3703. <https://doi.org/10.1021/acssuschemeng.6b00262>

61. Shao, L., Li, Y., Huang, J., & Liu, Y. N. (2018). Synthesis of Triazine-Based Porous Organic Polymers Derived N-Enriched Porous Carbons for CO₂ Capture. *Industrial and Engineering Chemistry Research*, 57(8), 2856–2865.
<https://doi.org/10.1021/acs.iecr.7b04533>
62. Jiangfei, G., Lizhi, W., Zhang, D., & Huang, J. (2020). Amino-Functionalized Porphyrin-Based Porous Organic Polymers for CO₂ Capture and Hg²⁺ Removal. *Energy and Fuels*, 34(8), 9771–9778. <https://doi.org/10.1021/acs.energyfuels.9b04206>
63. Alloush, A. M., Abdelnaby, M. M., Cordova, K. E., Qasem, N. A. A., Al-Maythalony, B. A., Jalilov, A., Mankour, Y., & Al Hamouz, O. C. S. (2020). Selectively capturing carbon dioxide from mixed gas streams using a new microporous organic copolymer. *Microporous and Mesoporous Materials*, 305. <https://doi.org/10.1016/j.micromeso.2020.110391>
64. Abdelnaby, M. M., Cordova, K. E., Abdulazeez, I., Alloush, A. M., Al-Maythalony, B. A., Mankour, Y., Alhooshani, K., Saleh, T. A., & Al Hamouz, O. C. S. (2020). Novel porous organic polymer for the concurrent and selective removal of hydrogen sulfide and carbon dioxide from natural gas streams. *ACS Applied Materials and Interfaces*, 12(42), 47984–47992. <https://doi.org/10.1021/acsami.0c14259>
65. Zhou, H., Rayer, C., Antonangelo, A. R., Hawkins, N., & Carta, M. (2022). Adjustable Functionalization of Hyper-Cross-Linked Polymers of Intrinsic Microporosity for Enhanced CO₂ Adsorption and Selectivity over N₂ and CH₄. *ACS Applied Materials and Interfaces*, 14(18), 20997–21006. <https://doi.org/10.1021/acsami.2c02604>

66. Wang, J., Wang, L., Wang, Y., Zhang, D., Xiao, Q., Huang, J., & Liu, Y. N. (2022). Recent progress in porous organic polymers and their application for CO₂ capture. *Chinese Journal of Chemical Engineering*, 42, 91–103. <https://doi.org/10.1016/j.cjche.2021.08.028>
67. Kumar, S., Hassan, A., Das, N., & Koh, J. (2022). Triazine based nanoarchitectonics of porous organic polymers for CO₂ storage. *Materials Letters*, 313. <https://doi.org/10.1016/j.matlet.2022.131757>
68. Song, K. S., Fritz, P. W., & Coskun, A. (2022). Porous organic polymers for CO₂ capture, separation and conversion. In *Chemical Society Reviews* (Vol. 51, Issue 23, pp. 9831–9852). Royal Society of Chemistry. <https://doi.org/10.1039/d2cs00727d>
69. Abdelnaby, M. M., Ahmed, H. M., Alloush, A. M., Zeama, M., Habib, M. A., Asmaly, H., & Saleh, T. A. (2023). New carbazole-based conjugated frameworks for carbon dioxide capture and water purification: Insights on the adsorptive sites' chemistry. *Microporous and Mesoporous Materials*, 349. <https://doi.org/10.1016/j.micromeso.2022.112427>
70. Abdelnaby, M. M., Aliyu, M., Nemitallah, M. A., Alloush, A. M., Mahmoud, E. H. M., Ossoss, K. M., Zeama, M., & Dowaidar, M. (2023). Design and Synthesis of N-Doped Porous Carbons for the Selective Carbon Dioxide Capture under Humid Flue Gas Conditions. *Polymers*, 15(11). <https://doi.org/10.3390/polym15112475>
71. Zhu, Y., Ji, Y. J., Wang, D. G., Zhang, Y., Tang, H., Jia, X. R., Song, M., Yu, G., & Kuang, G. C. (2017). BODIPY-based conjugated porous polymers for highly efficient volatile iodine capture. *Journal of Materials Chemistry A*, 5(14), 6622–6629. <https://doi.org/10.1039/c7ta00026j>

72. Li, X., Chen, G., & Jia, Q. (2019). One-pot synthesis of viologen-based hypercrosslinked polymers for efficient volatile iodine capture. *Microporous and Mesoporous Materials*, 279, 186–192. <https://doi.org/10.1016/j.micromeso.2018.12.029>
73. Pan, X., Ding, C., Zhang, Z., Ke, H., & Cheng, G. (2020). Functional porous organic polymer with high S and N for reversible iodine capture. *Microporous and Mesoporous Materials*, 300. <https://doi.org/10.1016/j.micromeso.2020.110161>
74. Albakri, M. A., Saleh, T. A., Mankour, Y., Garrison, T. F., & Al Hamouz, O. C. S. (2021). Synthesis of a new thiophenol-thiophene polymer for the removal of mercury from wastewater and liquid hydrocarbons. *Journal of Colloid and Interface Science*, 582, 428–438. <https://doi.org/10.1016/j.jcis.2020.07.103>
75. Wang, Y., Cao, Y., Zeng, X., Huang, J., & Liu, Y. N. (2021). Furan- And Thiophene-Modified Hyper-Crosslinked Polymers and Their Adsorption of Phenol from Aqueous Solution. *Industrial and Engineering Chemistry Research*, 60(2), 931–938. <https://doi.org/10.1021/acs.iecr.0c04784>
76. Xu, X. H., Li, Y. X., Zhou, L., Liu, N., & Wu, Z. Q. (2022). Precise fabrication of porous polymer frameworks using rigid polyisocyanides as building blocks: From structural regulation to efficient iodine capture. *Chemical Science*, 13(4), 1111–1118. <https://doi.org/10.1039/d1sc05361b>
77. Wang, H., Qiu, N., Kong, X., Hu, Z., Zhong, F., Li, Y., & Tan, H. (2023). Novel Carbazole-Based Porous Organic Polymer for Efficient Iodine Capture and Rhodamine B Adsorption. *ACS Applied Materials and Interfaces*. <https://doi.org/10.1021/acsami.3c00918>

78. Liu, N., Ma, H., Sun, R., Zhang, Q. P., Tan, B., & Zhang, C. (2023). Porous Triptycene Network Based on Tröger's Base for CO₂ Capture and Iodine Enrichment. *ACS Applied Materials and Interfaces*, 15(25), 30402–30408. <https://doi.org/10.1021/acsami.3c06700>
79. Qiu, N., Wang, H., Tang, R., Yang, Y., Kong, X., Hu, Z., Zhong, F., & Tan, H. (2024). Synthesis of phenothiazine-based porous organic polymer and its application to iodine adsorption. *Microporous and Mesoporous Materials*, 363. <https://doi.org/10.1016/j.micromeso.2023.112833>
80. Mondal, B., & Das, G. (2024). Dual functional porous organic polymer: Reversible iodine capture and selective sensing of picric acid. *Reactive and Functional Polymers*, 194. <https://doi.org/10.1016/j.reactfunctpolym.2023.105800>
81. Roja, A., Srividhya, S., & Arunachalam, M. (2024). Tripodal receptor cross-linked polymer as a promising adsorbent for iodine vapor capture and adsorption from water. *Polymer*, 294, 126688. <https://doi.org/10.1016/j.polymer.2024.126688>
82. Zhao, Y., Lu, W., Zhang, Y., Liu, X., & Sun, B. (2024). Room temperature synthesis of piperazine-based nitrogen-rich porous organic polymers for efficient iodine adsorption. *Microporous and Mesoporous Materials*, 366. <https://doi.org/10.1016/j.micromeso.2023.112954>
83. Bera, S., Garg, K., & Samanta, S. K. (2023). Amide-Linked cis, cis-1,3,5-Cyclohexanetricarbonyl-Based Porous Organic Polymers for the Uptake of Iodine in Solution and Vapor Phase. *ACS Applied Nano Materials*. <https://doi.org/10.1021/acsanm.3c04973>

84. Hassan, A., & Das, N. (2023). Chemically Stable and Heteroatom Containing Porous Organic Polymers for Efficient Iodine Vapor Capture and its Storage. *ACS Applied Polymer Materials*, 5(7), 5349–5359. <https://doi.org/10.1021/acsapm.3c00746>
85. Paramati, S. R., Shahzad, U., & Doğan, B. (2022). The role of environmental technology for energy demand and energy efficiency: Evidence from OECD countries. *Renewable and Sustainable Energy Reviews*, 153, 111735. <https://doi.org/10.1016/J.RSER.2021.111735>
86. Alloush, A. M., Abdulghani, H., Amasha, H. A., Saleh, T. A., & Al Hamouz, O. C. S. (2022). Microwave-assisted synthesis of novel porous organic polymers for effective selective capture of CO₂. *Journal of Industrial and Engineering Chemistry*, 113, 215–225. <https://doi.org/10.1016/j.jiec.2022.05.049>
87. Oschatz, M., & Antonietti, M. (2018). A search for selectivity to enable CO₂ capture with porous adsorbents. *Energy & Environmental Science*, 11(1), 57–70. <https://doi.org/10.1039/C7EE02110K>
88. Ahmed, A., Babarao, R., Huang, R., Medhekar, N., Todd, B. D., Hill, M. R., & Thornton, A. W. (2015). Porous aromatic frameworks impregnated with lithiated fullerenes for natural gas purification. *Journal of Physical Chemistry C*, 119(17), 9347–9354. <https://doi.org/10.1021/ACS.JPCC.5B01144>
89. Li, H., Dilipkumar, A., Abubakar, S., & Zhao, D. (2023). Covalent organic frameworks for CO₂ capture: from laboratory curiosity to industry implementation. *Chemical Society Reviews*, 52(18), 6294–6329. <https://doi.org/10.1039/D2CS00465H>

90. Kari, N. E. F., Ismail, M., Ahmad, A., Kamal, K., Chew, T. L., & Bustam, M. A. (2023). Screening and Experimental Validation for Selection of Open Metal Sites Metal-Organic Framework (M-CPO-27, M = Co, Mg, Ni and Zn) to Capture CO₂. *Separations 2023*, Vol. 10, Page 434, 10(8), 434. <https://doi.org/10.3390/SEPARATIONS10080434>

91. Ahmad, A., Pango, B., Ismail, M., & Bustam, M. A. (2023). Performance Evaluation of the Developed MOF-177 for CO₂ Capture. *Journal of Advanced Research in Applied Mechanics*, 111(1), 74–81. <https://doi.org/10.37934/ARAM.111.1.7481>

92. Belmabkhout, Y., Heymans, N., De Weireld, G., & Sayari, A. (2011). Simultaneous Adsorption of H₂S and CO₂ on Triamine-Grafted Pore-Expanded Mesoporous MCM-41 Silica. *Energy and Fuels*, 25(3), 1310–1315. <https://doi.org/10.1021/EF1015704>

93. Zhou, Y., Zhang, J., Wang, L., Cui, X., Liu, X., Wong, S. S., An, H., Yan, N., Xie, J., Yu, C., Zhang, P., Du, Y., Xi, S., Zheng, L., Cao, X., Wu, Y., Wang, Y., Wang, C., Wen, H., ... Wang, J. (2021). Self-assembled iron-containing mordenite monolith for carbon dioxide sieving. *Science*, 373(6552), 315–320. https://doi.org/10.1126/SCIENCE.AAX5776/SUPPL_FILE/AAX5776-ZHOU-SM.PDF

94. Abdelnaby, M. M., Cordova, K. E., Abdulazeez, I., Alloush, A. M., Al-Maythalony, B. A., Mankour, Y., Alhooshani, K., Saleh, T. A., & Al Hamouz, O. C. S. (2020). Novel porous organic polymer for the concurrent and selective removal of hydrogen sulfide and carbon dioxide from natural gas streams. *ACS Applied Materials and Interfaces*, 12(42), 47984–47992. https://doi.org/10.1021/ACSAMI.0C14259/SUPPL_FILE/AM0C14259_SI_001.PDF

95. Abdelnaby, M. M., Qasem, N. A. A., Al-Maythalony, B. A., Cordova, K. E., & Al Hamouz, O. C. S. (2019). A Microporous Organic Copolymer for Selective CO₂ Capture under Humid Conditions. *ACS Sustainable Chemistry and Engineering*, 7(16), 13941–13948. https://doi.org/10.1021/ACSSUSCHEMENG.9B02334/SUPPL_FILE/SC9B02334_SI_001.PDF
96. Kong, X., Li, S., Stromme, M., & Xu, C. (2019). Synthesis of Porous Organic Polymers with Tunable Amine Loadings for CO₂ Capture: Balanced Physisorption and Chemisorption. *Nanomaterials* 2019, Vol. 9, Page 1020, 9(7), 1020. <https://doi.org/10.3390/NANO9071020>
97. Song, K. S., Kim, D., Polychronopoulou, K., & Coskun, A. (2016). Synthesis of Highly Porous Coordination Polymers with Open Metal Sites for Enhanced Gas Uptake and Separation. *ACS Applied Materials and Interfaces*, 8(40), 26860–26867. https://doi.org/10.1021/ACSAMI.6B09156/SUPPL_FILE/AM6B09156_SI_001.PDF
98. Al-Bukhari, M. S., Abdulazeez, I., Abdelnaby, M. M., Aljundi, I. H., & Al Hamouz, O. C. S. (2023). 3D porous polymers for selective removal of CO₂ and H₂ storage: experimental and computational studies. *Frontiers in Chemistry*, 11. <https://doi.org/10.3389/FCHEM.2023.1265324/FULL>
99. Chen, L., Honsho, Y., Seki, S., & Jiang, D. (2010). Light-harvesting conjugated microporous polymers: Rapid and highly efficient flow of light energy with a porous polyphenylene framework as antenna. *Journal of the American Chemical Society*, 132(19), 6742–6748. https://doi.org/10.1021/JA100327H/SUPPL_FILE/JA100327H_SI_001.PDF
100. Jiang, J.-X., Su, F., Trewin, A., Wood, C. D., Campbell, N. L., Niu, H., Dickinson, C., Ganin, A. Y., Rosseinsky, M. J., Khimyak, Y. Z., & Cooper, A. I. (n.d.). *Angewandte*

101. Chen, Q., Luo, M., Hammershøj, Zhou, D., Han, Y., Laursen, B. W., Yan, C. G., & Han, B. H. (2012). Microporous polycarbazole with high specific surface area for gas storage and separation. *Journal of the American Chemical Society*, 134(14), 6084–6087.
https://doi.org/10.1021/JA300438W/SUPPL_FILE/JA300438W_SI_001.PDF
102. Schwab, M. G., Fassbender, B., Spiess, H. W., Thomas, A., Feng, X., & Müllen, K. (2009). Catalyst-free preparation of melamine-based microporous polymer networks through Schiff base chemistry. *Journal of the American Chemical Society*, 131(21), 7216–7217.
https://doi.org/10.1021/JA902116F/SUPPL_FILE/JA902116F_SI_001.PDF
103. Hashemi, L., & Morsali, A. (2012). Microwave assisted synthesis of a new lead (II) porous three-dimensional coordination polymer: study of nanostructured size effect on high iodide adsorption affinity. *CrystEngComm*, 14(3), 779–781. <https://doi.org/10.1039/C2CE06133C>
104. Díaz de Greñu, B., Torres, J., García-González, J., Muñoz-Pina, S., de los Reyes, R., Costero, A. M., Amorós, P., & Ros-Lis, J. V. (2021). Microwave-Assisted Synthesis of Covalent Organic Frameworks: A Review. *ChemSusChem*, 14(1), 208–233.
<https://doi.org/10.1002/CSSC.202001865>
105. Merukan Chola, N., Gajera, P., Kulkarni, H., Kumar, G., Parmar, R., Nagarale, R. K., & Sethia, G. (2023). Sorption of Carbon Dioxide and Nitrogen on Porous Hyper-Cross-Linked Aromatic Polymers: Effect of Textural Properties, Composition, and Electrostatic Interactions. *ACS Omega*, 8(28), 24761–24772.

https://doi.org/10.1021/ACSOMEGA.2C07553/ASSET/IMAGES/LARGE/AO2C07553_0016.JPEG

106. Meunier, M., & Robertson, S. (2021). Materials Studio 20th anniversary. *Molecular Simulation*, 47(7), 537–539. <https://doi.org/10.1080/08927022.2021.1892093>
107. Sun, H., Jin, Z., Yang, C., Akkermans, R. L. C., Robertson, S. H., Spenley, N. A., Miller, S., & Todd, S. M. (2016). COMPASS II: extended coverage for polymer and drug-like molecule databases. *Journal of Molecular Modeling*, 22(2), 1–10. <https://doi.org/10.1007/S00894-016-2909-0/TABLES/6>
108. Schlegel, H. B. (2011). Geometry optimization. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 1(5), 790–809. <https://doi.org/10.1002/WCMS.34>
109. Song, W., Yao, J., Ma, J., Li, A., Li, Y., Sun, H., & Zhang, L. (2018). Grand canonical Monte Carlo simulations of pore structure influence on methane adsorption in micro-porous carbons with applications to coal and shale systems. *Fuel*, 215, 196–203. <https://doi.org/10.1016/J.FUEL.2017.11.016>
110. Gao, D., Hong, L., Wang, J., & Zheng, D. (2020). Molecular simulation of gas adsorption characteristics and diffusion in micropores of lignite. *Fuel*, 269, 117443. <https://doi.org/10.1016/J.FUEL.2020.117443>
111. Aljamaan, H., Al Ismail, M., & Kovscek, A. R. (2017). Experimental investigation and Grand Canonical Monte Carlo simulation of gas shale adsorption from the macro to the nano scale. *Journal of Natural Gas Science and Engineering*, 48, 119–137. <https://doi.org/10.1016/J.JNGSE.2016.12.024>

112. Pan, L., Chen, Q., Zhu, J. H., Yu, J. G., He, Y. J., & Han, B. H. (2015). Hypercrosslinked porous polycarbazoles via one-step oxidative coupling reaction and Friedel–Crafts alkylation. *Polymer Chemistry*, 6(13), 2478–2487. <https://doi.org/10.1039/C4PY01797H>
113. Abdelnaby, M. M., Alloush, A. M., Qasem, N. A. A., Al-Maythalony, B. A., Mansour, R. B., Cordova, K. E., & Al Hamouz, O. C. S. (2018). Carbon dioxide capture in the presence of water by an amine-based crosslinked porous polymer. *Journal of Materials Chemistry A*, 6(15), 6455–6462. <https://doi.org/10.1039/C8TA00012C>
114. Mohamed, M. G., Zhang, X., Mansoure, T. H., EL-Mahdy, A. F. M., Huang, C. F., Danko, M., Xin, Z., & Kuo, S. W. (2020). Hypercrosslinked porous organic polymers based on tetraphenylanthraquinone for CO₂ uptake and high-performance supercapacitor. *Polymer*, 205. <https://doi.org/10.1016/j.polymer.2020.122857>
115. Das, S., Heasman, P., Ben, T., & Qiu, S. (2017). Porous Organic Materials: Strategic Design and Structure-Function Correlation. *Chemical Reviews*, 117(3), 1515–1563. https://doi.org/10.1021/ACS.CHEMREV.6B00439/ASSET/IMAGES/MEDIUM/CR-2016-004399_0056.GIF
116. Dey, S., Bhunia, A., Boldog, I., & Janiak, C. (2017). A mixed-linker approach towards improving covalent triazine-based frameworks for CO₂ capture and separation. *Microporous and Mesoporous Materials*, 241, 303–315. <https://doi.org/10.1016/J.MICROMESO.2016.11.033>
117. Lohse, M. S., & Bein, T. (2018). Covalent Organic Frameworks: Structures, Synthesis, and Applications. *Advanced Functional Materials*, 28(33), 1705553. <https://doi.org/10.1002/ADFM.201705553>

118. Alam, A., Mishra, S., Hassan, A., Bera, R., Dutta, S., Das Saha, K., & Das, N. (2020). Triptycene-Based and Schiff-Base-Linked Porous Networks: Efficient Gas Uptake, High CO₂/N₂ Selectivity, and Excellent Antiproliferative Activity. *ACS Omega*, 5(8), 4250–4260.
https://doi.org/10.1021/ACSOMEGA.9B04160/ASSET/IMAGES/LARGE/AO9B04160_0001.JPEG
119. Khosrowshahi, M. S., Abdol, M. A., Mashhadimoslem, H., Khakpour, E., Emrooz, H. B. M., Sadeghzadeh, S., & Ghaemi, A. (2022). The role of surface chemistry on CO₂ adsorption in biomass-derived porous carbons by experimental results and molecular dynamics simulations. *Scientific Reports* 2022 12:1, 12(1), 1–19.
<https://doi.org/10.1038/s41598-022-12596-5>
120. Abdulsalam, J., Mulopo, J., Bada, S. O., & Oboirien, B. (2020). Equilibria and Isosteric Heat of Adsorption of Methane on Activated Carbons Derived from South African Coal Discards. *ACS Omega*, 5(50), 32530–32539.
https://doi.org/10.1021/ACSOMEGA.0C04744/ASSET/IMAGES/MEDIUM/AO0C04744_M019.GIF
121. Tan, L. L., Zhu, Y., Long, H., Jin, Y., Zhang, W., & Yang, Y. W. (2017). Pillar[n]arene-based supramolecular organic frameworks with high hydrocarbon storage and selectivity. *Chemical Communications*, 53(48), 6409–6412. <https://doi.org/10.1039/C7CC03638H>
122. Garibay, S. J., Weston, M. H., Mondloch, J. E., Colón, Y. J., Farha, O. K., Hupp, J. T., & Nguyen, S. T. (2013). Accessing functionalized porous aromatic frameworks (PAFs)

- through a de novo approach. *CrystEngComm*, 15(8), 1515–1519.
<https://doi.org/10.1039/C2CE26595H>
123. Saleh, M., Lee, H. M., Kemp, K. C., & Kim, K. S. (2014). Highly stable CO₂/N₂ and CO₂/CH₄ selectivity in hyper-cross-linked heterocyclic porous polymers. *ACS Applied Materials and Interfaces*, 6(10), 7325–7333.
https://doi.org/10.1021/AM500728Q/SUPPL_FILE/AM500728Q_SI_001.PDF
124. Tan, L., & Tan, B. (2017). Hypercrosslinked porous polymer materials: design, synthesis, and applications. *Chemical Society Reviews*, 46(11), 3322–3356.
<https://doi.org/10.1039/C6CS00851H>
125. Hyun Je, S., Buyukcakil, O., Kim, D., & Coskun, A. (2016). *Direct Utilization of Elemental Sulfur in the Synthesis of Microporous Polymers for Natural Gas Sweetening*
HIGHLIGHTS Sulfur in porous polymer synthesis Solvent-and catalyst-free approach
 Exceptional CO₂ separation High-value application for sulfur Direct Utilization of
 Elemental Sulfur in the Synthesis of Microporous Polymers for Natural Gas Sweetening.
<https://doi.org/10.1016/j.chempr.2016.08.003>
126. Bera, R., Ansari, M., Alam, A., & Das, N. (2019). Triptycene, Phenolic-OH, and Azo-Functionalized Porous Organic Polymers: Efficient and Selective CO₂ Capture. *ACS Applied Polymer Materials*, 1(5), 959–968.
https://doi.org/10.1021/ACSAPM.8B00264/SUPPL_FILE/AP8B00264_SI_001.PDF
127. Yao, C., Cui, D., Zhu, Y., Xie, W., Zhang, S., Xu, G., & Xu, Y. (2019). Synthetic control of the polar units in poly(thiophene carbazole) porous networks for effective CO₂ capture. *New Journal of Chemistry*, 43(18), 6838–6842. <https://doi.org/10.1039/C9NJ00688E>

128. Mane, S., Gao, Z. Y., Li, Y. X., Liu, X. Q., & Sun, L. B. (2018). Rational Fabrication of Polyethylenimine-Linked Microbeads for Selective CO₂ Capture. *Industrial and Engineering Chemistry Research*, 57(1), 250–258.
https://doi.org/10.1021/ACS.IECR.7B04212/SUPPL_FILE/IE7B04212_SI_001.PDF
129. Wang, K., Huang, H., Liu, D., Wang, C., Li, J., & Zhong, C. (2016). Covalent Triazine-Based Frameworks with Ultramicropores and High Nitrogen Contents for Highly Selective CO₂ Capture. *Environmental Science and Technology*, 50(9), 4869–4876.
https://doi.org/10.1021/ACS.EST.6B00425/SUPPL_FILE/ES6B00425_SI_001.PDF
130. Yan, Z., Ren, H., Ma, H., Yuan, R., Yuan, Y., Zou, X., Sun, F., & Zhu, G. (2013). Construction and sorption properties of pyrene-based porous aromatic frameworks. *Microporous and Mesoporous Materials*, 173, 92–98.
<https://doi.org/10.1016/J.MICROMESO.2013.02.006>
131. Arab, P., Rabbani, M. G., Sekizkardes, A. K., Islamoğlu, T., & El-Kaderi, H. M. (2014). Copper(I)-catalyzed synthesis of nanoporous azo-linked polymers: Impact of textural properties on gas storage and selective carbon dioxide capture. *Chemistry of Materials*, 26(3), 1385–1392.
https://doi.org/10.1021/CM403161E/SUPPL_FILE/CM403161E_SI_001.PDF
132. Chattaraj, P. K., Lee, H., & Parr, R. G. (1991). HSAB Principle. *Journal of the American Chemical Society*, 113(5), 1855–1856.
https://doi.org/10.1021/JA00005A073/ASSET/JA00005A073.FP.PNG_V03
133. Erdogdu, E. (2007). Nuclear power in open energy markets: A case study of Turkey. *Energy Policy*, 35(5), 3061–3073. <https://doi.org/10.1016/J.ENPOL.2006.11.008>

134. Calcaterra, V., Mameli, C., Rossi, V., Massini, G., Gambino, M., Baldassarre, P., & Zuccotti, G. (2022). The Iodine Rush: Over- or Under-Iodination Risk in the Prophylactic Use of Iodine for Thyroid Blocking in the Event of a Nuclear Disaster. *Frontiers in Endocrinology*, 13, 901620. <https://doi.org/10.3389/FENDO.2022.901620/BIBTEX>
135. Steinhauser, G. (2014). Fukushimas forgotten radionuclides: A review of the understudied radioactive emissions. *Environmental Science and Technology*, 48(9), 4649–4663. https://doi.org/10.1021/ES405654C/SUPPL_FILE/ES405654C_SI_001.PDF
136. Council, N. R. (2003). Distribution and Administration of Potassium Iodide in the Event of a Nuclear Incident. *Distribution and Administration of Potassium Iodide in the Event of a Nuclear Incident*. <https://doi.org/10.17226/10868>
137. Remy, H., Borget, I., Leboulleux, S., Guilabert, N., Lavielle, F., Garsi, J., Bournaud, C., Gupta, S., Schlumberger, M., & Ricard, M. (2008). ¹³¹I Effective Half-Life and Dosimetry in Thyroid Cancer Patients. *Journal of Nuclear Medicine*, 49(9), 1445–1450. <https://doi.org/10.2967/JNUMED.108.052464>
138. Payolla, F. B., Massabni, A. C., & Orvig, C. (2019). Radiopharmaceuticals for diagnosis in nuclear medicine: a short review. *Eclética Química*, 44(3), 11–19. <https://doi.org/10.26850/1678-4618EQJ.V44.3.2019.P11-19>
139. Karunakara, N., Kumara, S., Prabhu, U., Ravi, P., Swain, K., Yashodhara, I., Ajith, N., Geetha, P., & Karpe, R. (2014). Grass to cow milk transfer coefficient (F_m) of Iodine for equilibrium and emergency situations. *Radiation Protection and Environment*, 37(1), 14. <https://doi.org/10.4103/0972-0464.146456>

140. Liu, S., Wang, N., Zhang, Y., Li, Y., Han, Z., & Na, P. (2015). Efficient removal of radioactive iodide ions from water by three-dimensional Ag₂O–Ag/TiO₂ composites under visible light irradiation. *Journal of Hazardous Materials*, 284, 171–181.
<https://doi.org/10.1016/J.JHAZMAT.2014.10.054>
141. Holladay, D. W. (1979). *Literature survey: methods for the removal of iodine species from off-gases and liquid waste streams of nuclear power and nuclear fuel reprocessing plants, with emphasis on solid sorbents*.
http://inis.iaea.org/Search/search.aspx?orig_q=RN:10454605
142. Zhang, X., Da Silva, I., Fazzi, R., Sheveleva, A. M., Han, X., Spencer, B. F., Sapchenko, S. A., Tuna, F., McInnes, E. J. L., Li, M., Yang, S., & Schröder, M. (2019). Iodine Adsorption in a Redox-Active Metal-Organic Framework: Electrical Conductivity Induced by Host-Guest Charge-Transfer. *Inorganic Chemistry*, 58(20), 14145–14150.
https://doi.org/10.1021/ACS.INORGCHEM.9B02176/ASSET/IMAGES/LARGE/IC9B02176_0004.JPEG
143. Sava, D. F., Garino, T. J., & Nenoff, T. M. (2011). Iodine Confinement into Metal–Organic Frameworks (MOFs): Low-Temperature Sintering Glasses To Form Novel Glass Composite Material (GCM) Alternative Waste Forms. *Industrial and Engineering Chemistry Research*, 51(2), 614–620. <https://doi.org/10.1021/IE200248G>
144. Pham, T. C. T., Docao, S., Hwang, I. C., Song, M. K., Choi, D. Y., Moon, D., Oleynikov, P., & Yoon, K. B. (2016). Capture of iodine and organic iodides using silica zeolites and the semiconductor behaviour of iodine in a silica zeolite. *Energy & Environmental Science*, 9(3), 1050–1062. <https://doi.org/10.1039/C5EE02843D>

145. Wang, P., Xu, Q., Li, Z., Jiang, W., Jiang, Q., Jiang, D., Wang, P., Xu, Q., Li, Z., Jiang, W., Jiang, Q., & Jiang, D. (2018). Exceptional Iodine Capture in 2D Covalent Organic Frameworks. *Advanced Materials*, 30(29), 1801991.
<https://doi.org/10.1002/ADMA.201801991>
146. Yang, Y., Xiong, X., Fan, Y., Lai, Z., Xu, Z., & Luo, F. (2019). Insight into volatile iodine uptake properties of covalent organic frameworks with different conjugated structures. *Journal of Solid State Chemistry*, 279, 120979. <https://doi.org/10.1016/J.JSSC.2019.120979>
147. Chapman, K. W., Chupas, P. J., & Nenoff, T. M. (2010). Radioactive iodine capture in silver-containing mordenites through nanoscale silver iodide formation. *Journal of the American Chemical Society*, 132(26), 8897–8899.
https://doi.org/10.1021/JA103110Y/SUPPL_FILE/JA103110Y_SI_001.PDF
148. Nenoff, T. M., Rodriguez, M. A., Soelberg, N. R., & Chapman, K. W. (2014). Silver-mordenite for radiologic gas capture from complex streams: Dual catalytic CH₃I decomposition and I confinement. *Microporous and Mesoporous Materials*, 200, 297–303.
<https://doi.org/10.1016/J.MICROMESO.2014.04.041>
149. Abney, C. W., Nan, Y., & Tavlarides, L. L. (2017). X-ray Absorption Spectroscopy Investigation of Iodine Capture by Silver-Exchanged Mordenite. *Industrial and Engineering Chemistry Research*, 56(16), 4837–4846.
https://doi.org/10.1021/ACS.IECR.7B00233/SUPPL_FILE/IE7B00233_SI_001.PDF
150. Nan, Y., Liu, J., Tang, S., Lin, R., & Tavlarides, L. L. (2018). Silver-Exchanged Mordenite for Capture of Water Vapor in Off-Gas Streams: A Study of Adsorption Kinetics. *Industrial and Engineering Chemistry Research*, 57(3), 1048–1058.

https://doi.org/10.1021/ACS.IECR.7B04420/ASSET/IMAGES/MEDIUM/IE-2017-04420M_0010.GIF

151. Subrahmanyam, K. S., Sarma, D., Malliakas, C. D., Polychronopoulou, K., Riley, B. J., Pierce, D. A., Chun, J., & Kanatzidis, M. G. (2015). Chalcogenide aerogels as sorbents for radioactive iodine. *Chemistry of Materials*, 27(7), 2619–2626.
https://doi.org/10.1021/ACS.CHEMMATER.5B00413/SUPPL_FILE/CM5B00413_SI_001.PDF
152. Yang, D., Liu, H., Liu, L., Sarina, S., Zheng, Z., & Zhu, H. (2013). Silver oxide nanocrystals anchored on titanate nanotubes and nanofibers: promising candidates for entrapment of radioactive iodine anions. *Nanoscale*, 5(22), 11011–11018.
<https://doi.org/10.1039/C3NR02412A>
153. Kurisingal, J. F., Yun, H., & Hong, C. S. (2023). Porous organic materials for iodine adsorption. *Journal of Hazardous Materials*, 458, 131835.
<https://doi.org/10.1016/J.JHAZMAT.2023.131835>
154. Francis Kurisingal, J., Kim, H., Hyeak Choe, J., & Seop Hong, C. (2022). Covalent organic framework-based catalysts for efficient CO₂ utilization reactions. *Coordination Chemistry Reviews*, 473, 214835. <https://doi.org/10.1016/J.CCR.2022.214835>
155. Xie, Y., Pan, T., Lei, Q., Chen, C., Dong, X., Yuan, Y., Maksoud, W. Al, Zhao, L., Cavallo, L., Pinnau, I., & Han, Y. (2022). Efficient and simultaneous capture of iodine and methyl iodide achieved by a covalent organic framework. *Nature Communications* 2022 13:1, 13(1), 1–10. <https://doi.org/10.1038/s41467-022-30663-3>

156. Chen, D., Fu, Y., Yu, W., Yu, G., & Pan, C. (2018). Versatile Adamantane-based porous polymers with enhanced microporosity for efficient CO₂ capture and iodine removal. *Chemical Engineering Journal*, 334, 900–906. <https://doi.org/10.1016/J.CEJ.2017.10.133>
157. Abdelmoaty, Y. H., Tessema, T. D., Choudhury, F. A., El-Kadri, O. M., & El-Kaderi, H. M. (2018). Nitrogen-Rich Porous Polymers for Carbon Dioxide and Iodine Sequestration for Environmental Remediation. *ACS Applied Materials and Interfaces*, 10(18), 16049–16058. https://doi.org/10.1021/ACSAMI.8B03772/SUPPL_FILE/AM8B03772_SI_001.PDF
158. AlRashidi, R. B., & Al Hamouz, O. C. S. (2022). Synthesis of Cross-Linked Pyrazine-Based Polymers for Selective Removal of Mercury (II) Ions from Wastewater Solutions. *Arabian Journal for Science and Engineering*, 47(6), 7207–7218. <https://doi.org/10.1007/S13369-022-06833-2/METRICS>
159. Ishii, K., Sato, K., Oaki, Y., & Imai, H. (2018). Highly porous polymer dendrites of pyrrole derivatives synthesized through rapid oxidative polymerization. *Polymer Journal* 2018 51:1, 51(1), 11–18. <https://doi.org/10.1038/s41428-018-0115-x>
160. Katsoulidis, A. P., Dyar, S. M., Carmieli, R., Malliakas, C. D., Wasielewski, M. R., & Kanatzidis, M. G. (2013). Copolymerization of terephthalaldehyde with pyrrole, indole and carbazole gives microporous POFs functionalized with unpaired electrons. *Journal of Materials Chemistry A*, 1(35), 10465–10473. <https://doi.org/10.1039/C3TA11934C>
161. Kurig, H., Russina, M., Tallo, I., Siebenbürger, M., Romann, T., & Lust, E. (2016). The suitability of infinite slit-shaped pore model to describe the pores in highly porous carbon materials. *Carbon*, 100, 617–624. <https://doi.org/10.1016/J.CARBON.2016.01.061>

162. Wang, Y., Tao, J., Xiong, S., Lu, P., Tang, J., He, J., Javaid, M. U., Pan, C., & Yu, G. (2020). Ferrocene-based porous organic polymers for high-affinity iodine capture. *Chemical Engineering Journal*, 380, 122420. <https://doi.org/10.1016/J.CEJ.2019.122420>
163. Al Hamouz, O. C. S. (2018). New Phenol–Glycol Cross-Linked Polymers for Efficient Removal of Mercury from Aqueous Solutions. *Arabian Journal for Science and Engineering*, 43(1), 211–219. <https://doi.org/10.1007/S13369-017-2847-X/METRICS>
164. Yan, C., Wu, Y., Lu, H., Liu, H., Yi, G., Li, M., Cai, X., Gao, S., & Yang, Z. (2022). Novel phenothiazine-based hyper-cross-linked porous polymers containing N, S double electrically rich atoms for efficient iodine capture. *Microporous and Mesoporous Materials*, 343, 112157. <https://doi.org/10.1016/J.MICROMESO.2022.112157>
165. Wang, X., Xie, L., Lin, K., Ma, W., Zhao, T., Ji, X., Alyami, M., Khashab, N. M., Wang, H., & Sessler, J. L. (2021). Calix [4]pyrrole-Crosslinked Porous Polymeric Networks for the Removal of Micropollutants from Water. *Angewandte Chemie International Edition*, 60(13), 7188–7196. <https://doi.org/10.1002/ANIE.202016364>
166. Avais, M., Kumari, S., & Chattopadhyay, S. (2021). Degradable and processable polymer monoliths with open-pore porosity for selective CO₂ and iodine adsorption. *Soft Matter*, 17(26), 6383–6393. <https://doi.org/10.1039/D1SM00441G>
167. Li, X., Peng, Y., & Jia, Q. (2020). Construction of hypercrosslinked polymers with dual nitrogen-enriched building blocks for efficient iodine capture. *Separation and Purification Technology*, 236, 116260. <https://doi.org/10.1016/J.SEPPUR.2019.116260>

168. Ryu, J., Lee, M. Y., Song, M. G., Baeck, S. H., Shim, S. E., & Qian, Y. (2020). Highly selective removal of Hg (II) ions from aqueous solution using thiol-modified porous polyaminal-networked polymer. *Separation and Purification Technology*, 250, 117120. <https://doi.org/10.1016/J.SEPPUR.2020.117120>
169. Nuhnen, A., & Janiak, C. (2020). A practical guide to calculate the isosteric heat/enthalpy of adsorption via adsorption isotherms in metal–organic frameworks, MOFs. *Dalton Transactions*, 49(30), 10295–10307. <https://doi.org/10.1039/D0DT01784A>

Vitae

Name: Hassan A. Amasha

Nationality: Saudi

Date of Birth: 2/8/1991

Email: amashahassan@gmail.com

Address: 7757 Al Najah, Al Aqrabiyah Dist. 34445 AL KHOBAR, SA

Academic Background: BSc in Chemistry, Taif University, Saudi Arabia

Professional work: Assistant Scientific Researcher (2018 – 2022) KFUPM, SA.
Scientist, (2022 – 2024), Halliburton, SA.

Publications:

- Microwave-assisted synthesis of novel porous organic polymers for effective selective capture of CO₂. Ahmed M. Alloush ^a, Hamza Abdulghani ^a, Hassan A. Amasha ^a, Tawfik A. Saleh ^a, Othman Charles S. Al Hamouz ^{a b}. Journal of Industrial and Engineering Chemistry, vol. 113, pp. 215–225, Sep. 2022