EVALUATION OF MOF-BASED ADSORBENTS FOR SAMPLING AND MEASUREMENTS OF SEMI-VOLATILE ORGANIC COMPOUNDS (SVOCS) FROM CONTAMINATED AIR

by

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Abstract

Understanding the challenges of effectively capturing and analyzing semi-volatile organic compounds (SVOCs) from contaminated air is crucial for environmental monitoring. In this study, selected Zr-containing metal-organic frameworks (MOFs), UiO-67 and UiO-67-Ni, have been investigated for their potential on adsorption of a group of nonpolar SVOCs so called as poly-aromatic hydrocarbons (PAHs). Acenaphthene (Acp) was used as a model SVOC, and adsorption tests were investigated using the static headspace sampling technique, and desorption technique using methanol under ultrasonic conditions. Parameters including desorption time and adsorbent dosage have been investigated as independent variables for extraction performance, where the General Full Factorial design method has been applied for an experimental design. Comparing two different MOFs with same crystal structure and different pore size has demonstrated the exact effect of pore accessibility and interaction of host-guest molecules in adsorption of SVOC.

The results showed superior sampling performance for UiO-67-Ni, with an adsorption capacity of 0.226 μ g mg⁻¹, representing a 47.8% improvement compared to UiO-67. The gas removal efficiency reached 17.45% for UiO-67-Ni, compared to 11.81% for UiO-67. A collective interpretation of the data from characterization techniques demonstrated that the presence of Ni in the framework substantially increased pore size and specific surface area, which positively impacted the adsorption performance of the MOF. The pronounced pore diameter difference between UiO-67 and UiO-67-Ni (22.4 Å to 25.3 Å), and the total surface area of 1450.5 m² g⁻¹ in the Ni-containing MOF, are the driving forces behind higher adsorption performance.

Keywords: MOF-based adsorbents; UiO-67; SVOCs; acenaphthene; contaminated air sampling; static headspace sampling

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1. Introduction

Considering the evolution of society, people in North America and Europe now spend approximately 90% of their time indoors [1]. Indoor air quality is crucial in creating healthy and comfortable environments, whether at work, home, or vehicles. Unfortunately, furniture and interior construction materials can release volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs).

As people start to pay more attention to the indoor environment, researchers have identified various porous materials as adsorbents. Various adsorbents developed by researchers, such as activated carbon, silica gel, zeolite, and other polymers, can effectively reduce the pollution level of indoor VOC and SVOC pollutants. Various mechanisms, including adsorption, absorption, and membrane separation, are employed to capture volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs) within the porous structure of materials. These mechanisms enhance the efficiency of retrieving and eliminating air pollutants by facilitating the interaction of these contaminants with the porous matrix, thereby improving their removal from the air [2]. Table 1 provides a comprehensive summary of the materials utilized in industrial and research contexts for removing VOC from the environment, categorized according to the desorption mechanisms employed and their respective applications.

Materials	Target pollutants	Desorption Mechanisms	Applications	Refs
Activated carbon	Acetone and Methyl ethyl Ketone	Thermal regeneration	Adsorbent	[3]
Coconut shell	CHCl ₃ , CCl ₄ , and CH ₂ Cl ₂	Water bath heating	High efficiency in removing halomethanes from gases	[2]
Silica gel	Xylene and Toluene	Thermal desorption	Adsorbent for adsorption of VOCs	[4]
MCM-41	CCl4 and n- hexane	Thermal desorption	Adsorbent for the removal of VOCs in high concentrations and humidity streams	[5]
Monolithic carbon aerogels	Toluene	Microwave heating	Toluene adsorbents	[6]
MIL-101	n-hexane	Vacuum desorption	VOC adsorbent	[7]

 Table 1 Target polluted VOC, desorption mechanisms and applications of different classes of porous material.

Nevertheless, several materials exhibit limitations, including restricted structure and humidity stability [8]. Carbon-based materials are limited in adsorbing polar gas molecules despite their non-polar nature. Furthermore, sampling temperature and humidity substantially affect the gas adsorption process. Elevated temperature and humidity reduce their adsorption capacity, indicating that carbon-based materials are less effective for adsorbing high-boiling point VOCs [2], [9], [10]. Moreover, zeolites have emerged as highly effective adsorbents for capturing VOC from gas streams, even under elevated concentrations and humidity [5]. However, the hydrophilicity of zeolite can reduce its adsorption capacity for VOCs due to competition from water molecules for available adsorption sites. When sampling under high humidity, the water molecules preferentially occupy the adsorption sites [11].

SVOCs, molecules with higher molecular weight and higher boiling point subgroups of VOCs, can be found in indoor air, including residential apartments and industrial settings where products containing these substances are utilized. SVOCs are challenging to detect and quantify accurately due to their low concentrations and semi-volatile nature, which causes them to partition between air and indoor surfaces. This results in continuous desorption and fluctuating air concentrations. Variations in temperature and humidity further affect the adsorption capacity and selectivity. This research addresses these challenges by focusing on metal-organic frameworks (MOFs), a promising material for effectively managing the complexities associated with SVOC adsorption under dynamic conditions.

1.1 Metal Organic Frameworks (MOFs).

Metal-organic frameworks (MOFs) are a new family of coordination polymers with crystalline structures formed by connecting metal ions or metal clusters as nodes to organic ligands, so-called linkers, as illustrated in Figure 1. After zeolites and carbon nanotubes, MOF have emerged as the most notable porous materials. They are identified as materials with high surface area, well-defined channels, and customizable density [12].

Carbon-based adsorbents are widely utilized in commercial VOC air purification systems and for effectively sampling atmospheric VOC, demonstrating their critical role in enhancing air quality. However, their non-deterministic structure limits the potential for structural optimization potential, which restricts improvements in pollutant adsorption efficiency [13].



Figure 1 Structure of Metal-Organic Frameworks (MOFs).

In contrast, due to the structural variability and large metal pore dimensions, MOF offers the potential for gas entrapment [14]. Furthermore, MOF benefits various applications, including gas storage, separation, catalysis, and sensing [15]. The broad application of MOF has brought considerable attention to their chemical, thermal, and mechanical stability. This primarily concerns the resistance of MOF materials to high humidity, pH, pressure, or temperature [16].

To fully leverage the potential of metal-organic frameworks (MOFs) in practical applications, enhancing their physical stability is a critical priority, particularly in industrial environments where sampling occurs at elevated temperatures. Strengthening MOF to withstand such conditions can help prevent structural degradation or collapse, enabling their successful use in demanding settings.

1.1.1 MOF structure modifications

At the molecular level, scientists can precisely control the porosity and functionality of MOF. This approach can substantially improve their structural stability and gas separation efficiency, leading to notable and optimized performance outcomes [17]. Therefore,

researchers actively investigate synthetic methods to obtain new compounds with different properties and applications. Methods including choice of linker and metal nodes, mixedmetal MOFs, specific synthesis conditions, post-synthetic modification, guest molecule inclusion, functionalization of linkers, and topochemical synthesis can be employed to optimize the pore environment [16]. Post-synthetic modification (PSM) is one of the most common methods used to tune the structural characteristics of MOF. Modification of linkers and nodes can affect both pore structure and adsorptive characteristics. For example, bimetallic MOFs developed by post-synthetic modification have greatly improved porosity, active site, adsorption, selectivity, and stability compared to monometallic MOFs [18]. Although modification through metal substitution at the metal sites is less common than incorporating side-chain functional groups into the MOF crystal structure, it has demonstrated considerable advantages [19]. For example, Pal et al. reported that Cu(II) substituted Zn(II)-MOF has higher water stability and selective adsorption of CO_2 from H_2 and CH₄ [20]. Canossa et al. [21] investigated the effects of different guest metals during the modification of IRMOF-9. Their findings revealed that substituting Zn(II) in IRMOF-9 with Co(II) resulted in higher porosity and increased availability of open metal sites [21].

In terms of the adsorption and removal of SVOC from contaminated air, post-synthetic modified MOF with increased porosity and more active sites can markedly enhance Van Der Waals forces and π - π interaction between the metal nodes and the target pollutants [22]. This is particularly relevant for polycyclic aromatic hydrocarbons (PAHs) in this study. Therefore, optimizing these interactions aims to achieve superior adsorption capacities for the target pollutants, which is the primary objective of this study.

1.1.2 UiO-67

Zirconium (Zr) -based MOFs are highly regarded for their exceptional structural robustness and durability, attributed to their high coordination numbers and the formation of bonds with eight or more ligands [23]. Enhancing MOF stability is achieved through designing rigid structures with high connectivity, which strengthens their overall framework integrity. Zr serves as a central metal ion, enabling the formation of hexacoordinate solid bonds with oxygen atoms in organic linkers [24]. These frameworks typically feature Zr(IV) nodes, stabilized by oxygen-donating ligands, including water (H₂O), hydroxyl groups (-OH), and as many as 12 carboxylate-functionalized organic ligands [25]. The resulting threedimensional network contributes to the mechanical strength and stability of the MOF.

In the context of UiO (University of Oslo) MOFs, the Zr-terephthalate MOF UiO-66 is one of the most studied structures with notable structure stability. By altering the length or functional groups of the organic linker, typically terephthalic acid in UiO-66, the researchers were able to develop iso-reticular variants [26]. UiO-67, also known as Zr (IV) biphenyl dicarboxylate metal-organic framework, is an iso-reticular analog of UiO-66. Its longer biphenyl-4,4'-dicarboxylate (BPDC) organic linker increases the spacing between the zirconium-based nodes in the framework. This extended linker produces larger pore diameters than UiO-66 [27]. The increased pore size enhances the potential of UiO-67 for applications in gas adsorption. Figure 2 illustrates the exact chemical structure of UiO-66 and UiO-67.

Furthermore, biphenyl-4,4'-dicarboxylic acid (BPDC) provides a substantial number of phenyl groups, which facilitate strong π - π interactions with SVOC, such as polycyclic aromatic hydrocarbons. Therefore, UiO-67 exhibits better adsorption capacity in the gas phase than UiO-66 [28].



Figure 2 Chemical structure of (a) UiO-66 [29], and (b) UiO-67 [30].

1.2 Volatile Organic Compounds and Semi-Volatile Organic Compounds

A family of organic compounds known as volatile organic compounds (VOCs) have a high vapor pressure at room temperature, which makes them tend to evaporate and diffuse into the atmosphere [31]. These chemical species, which include a wide range of compounds such as benzene, toluene, formaldehyde, and xylene, present serious health risks [32]. Upon inhalation, they can penetrate the pulmonary system, disseminating throughout the respiratory tract before entering the bloodstream [9]. Prolonged exposure to some VOCs can cause adverse health effects, such as neurological impairment, respiratory issues, and an elevated risk of cancer. Many VOCs contribute substantially to air pollution in addition to their direct impact on human health. When exposed to sunlight, they can go through

photochemical processes that generate secondary pollutants, including ozone and particulate matter [33]. These processes can result in the formation of photochemical fog, which can further harm ecosystems, human health, and air quality. The relevance of VOC as environmental contaminants and public health threats is highlighted by their abundance in indoor and outdoor contexts [34].

The U.S. Environmental Protection Agency (EPA) categorizes certain volatile organic compounds (VOCs) as semi-volatile organic compounds (SVOCs). This classification applies to VOCs that have a higher molecular weight. Additionally, these compounds demonstrate reduced volatility within a temperature range of 240/260 to 380/400 °C [35]. These SVOC have properties that allow them to suspend in the air as tiny droplets or adhere to dust and other surfaces. Consequently, they can penetrate human lungs, potentially leading to immune system suppression and even cancer, as emphasized by Sonne, C. et al. [36]. These compounds primarily originate from flame retardants, plasticizers present in indoor building materials, and PAHs produced through combustion or incomplete combustion, as noted by Melymuk, L. et al. [37]. Table 2 shows the health effects and sources of seven classes of SVOCs in an indoor environment.

Pollutants	Health Effect [38]	Sources of SVOCs	Refs
*PCBs	Melanomas, cancer, endocrine disruption, and osteoporosis.	Electronics; building materials	[36]
*PAHs	Cataracts, kidney and liver damage, and skin disease.	Coal, crude oil, and gasoline	[39]

 Table 2 Health effect of SVOCs and their indoor sources.

*PFASs	Cancer, endocrine disruption, immune suppression, and neonatal mortality.	Clothing; electronics; furniture; building materials; cleaning products; cosmetics	[40]
*PBDEs	Diabetes, cancer, reproductive health effects, and thyroid disruption.	Clothing; electronics; furniture; building materials	[40]
*BFRs and *EBFRs	Immune system suppression, liver toxicity, endocrine disruption, and cancer.	Clothing; electronics; building materials	[36]
*OPFRs	Cancer, endocrine disruption, neurotoxicity, and liver & kidney damage	Clothing; electronics; furniture; building materials; cosmetics	[36]
*Phthalate and *Esters	Asthma, hypersensitivity, obesity, diabetes, and infertility.	Canadian indoor dust	[41]

*Seven classes of pollutants, including Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), Polyfluorinated Alkyl Substances (PFASs), Polybrominated Diphenyl Ethers (PBDEs), Brominated Flame Retardants (BFRs), Emerging Brominated Flame Retardants (EBFRs), Organophosphate Flame Retardants (OPFRs), and Phthalate Esters.

1.2.1 Polycyclic aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are compounds containing two or more benzene rings, composed only of carbon and hydrogen atoms, interconnected in various ring structural configurations [42], [43], [44]. PAHs originate from a variety of sources, including both natural and anthropogenic activities [39]. They are released into the atmosphere through various pathways, including the incomplete combustion of organic matter in wildfires, emissions from volcanic eruptions, biological activities, and geological processes [45], [46]. However, due to increased human activities, polycyclic aromatic hydrocarbons (PAHs) have become a primary contributor to indoor pollution, stemming from routine human activities and everyday necessities [47]. Additionally, workers in the mining and metal processing industries face a considerable risk of exposure to respiratory exhaust fumes containing high concentration levels of PAHs [48], [49]. According to the National Pollutant Release Inventory (NPRI) Substance Overview [47], a total of 32 polycyclic aromatic hydrocarbons (PAHs) were reported, with acenaphthene consistently exhibiting high levels of reported emissions between 2011 and 2021. Annual emissions of naphthalene peaked at 66 tons during this period [48]. Exposure to PAHs pollutants can result in symptoms like eye irritation, skin disease, vomiting, and diarrhea [52], [53]. Considering these challenges, there is a growing need to develop and implement advanced technologies and innovative materials capable of efficiently capturing, removing, and reducing PAH concentrations in the atmosphere.

1.2.2 Acenaphthene (Acp)

Among low molecular weight polycyclic aromatic compounds, acenaphthene is widely used in industrial manufacturing and has attracted public attention due to its unique reactivity and hazards to human health [54]. It is crucial for scientists to develop a method to assess the health risks associated with exposure to individual PAH species. Instead of relying on total PAH concentrations to evaluate their potential health risk to humans and the environment [55], they have developed and assessed toxic equivalency factors (TEF) for common PAHs through the toxic equivalency factor method [56], [57]. Given that benzo[a]pyrene (BaP) is one of the most common toxic compounds, Nisbet and Lagoy established the BaP equivalent concentration as 1, reflecting the carcinogenic potency of other PAHs in comparison to BaP [58], [59]. Among them, acenaphthene (Acp) is listed alongside 16 other compounds on the National Priorities List (NPL) as the compound with the highest concentration at hazardous waste disposal sites, as well as the PAH most commonly encountered by the public [60], from which the toxic equivalent factors of acenaphthene is 0.001.

Acenaphthene, a versatile compound utilized in manufacturing dyes, plastics, and medicines, is employed as an insecticide and fungicide in coal tar and presents unique challenges in measurement. The physical and chemical characteristics of acenaphthene are listed in Table 3. Occupational exposure limits for acenaphthene have yet to be established, highlighting an area for future research and regulatory development [61]. According to the United States Environmental Protection Agency (EPA) and the American Conference of Governmental Industrial Hygienists (ACGIH), acenaphthene has been identified as a hazardous substance due to its toxicological properties and potential adverse effects on human health and the environment [62]. Acenaphthene targets the skin, blood, stomach, intestines, and lymphatic system once it penetrates the body. Breathing in high quantities over brief periods may damage these systems [63]. Therefore, acenaphthene was studied as a model SVOC to explore the adsorption capacity of the synthesized MOF.

Table 3	Physica	and cl	hemical c	haracte	eristics	01	acenaphthene.

Chemical	*b.p. (°C)	*V.P. (hPa)	M.W. (g mol ⁻¹)	Radius (Å)	Ref
	279	13.3 (131°C)	154.21	3.353-3.561	[64]
Acenaphthene					

* b.p. is boiling point; V.P. is vapor pressure; M.W. is molecular weight.

1.3 Air sampling techniques and analysis methods

Air sampling and extraction techniques, as well as their associated analytical methods, are critical for assessing the performance of MOFs in gas-phase applications. These methods provide essential insights into the efficiency and effectiveness of MOF in various industrial and research contexts.

1.3.1 Sampling techniques

In environmental research, air sampling techniques are essential, especially for assessing air quality and identifying contaminants. These methods are critical for determining pollutant concentrations and understanding the dispersion of pollutants in different contexts [65]. The two primary air sampling methods are static sampling and active sampling. Active sampling typically provides a more accurate estimate of the air volume sampled than passive sampling. In passive sampling, the collection of contaminants relies on the natural diffusion or movement of particles onto the collector.

In contrast, active sampling uses a pump to create a vacuum, drawing air into the sampler and ensuring a more controlled and precise measurement of the sampled air volume [66]. However, because of the pump needed and the associated volumetric requirements for setup, it is typically more expensive than passive sampling. In passive sampling, contaminants diffuse through the air and are collected onto a substrate. Systems such as diffusion and permeation collectors, which do not utilize pumps or other active air-moving components, rely on the natural movement of contaminants [67]. In our study, minimizing changes in sample composition is critical for the quantitative analysis of air pollutant removal using adsorbents. Static headspace sampling is a widely recognized technique for its effectiveness in capturing volatile components, in which specific volumes of the test sample and extractant gas are contacted in a closed system for a given time, offering several notable advantages [68], [69]. This method is particularly valued as being environmentally friendly, as it reduces the reliance on hazardous solvents and reduces waste generation.

Static headspace sampling allows volatile compounds to equilibrate between the gas phase above a sample and the sample matrix. In this process, the sample is sealed in a container, and the VOCs that evaporate from the sample into the headspace above are allowed to reach a state of equilibrium [70]. After putting the adsorbent into the system, the synthesized MOFs were used as adsorbent materials in this study, and a new equilibrium was established between adsorbents and adsorbate from the gas phase. This dynamic equilibrium enables efficient capture of the pollutants, making the method highly suitable for quantitative analysis in air purification applications [71], [72].

Additionally, the ease of operation associated with static headspace sampling makes it userfriendly for laboratory applications, facilitating straightforward implementation by researchers [70]. Given these advantages, static headspace sampling emerges as the preferred method for a range of analytical applications in this study, ensuring reliable and accurate results while preserving sample integrity.

1.3.2 Extraction techniques

Various extraction methods are employed to isolate or extract PAHs. The combination of thermal desorption (TD) and gas chromatography (GC) is recognized as a highly effective technology. It is a widely employed technology for removing contaminants from materials and quantitatively analyzing VOC [73]. However, this technology requires the material to withstand high temperatures and pressures applied during desorption. Furthermore, the effectiveness of thermal desorption can vary depending on the type of contamination.

Additionally, solid-phase extraction (SPE) and liquid-liquid extraction (LLE) are widely utilized [74], as outlined in Table 4. These methods are essential for preparing samples before analytical quantification, ensuring that PAHs are effectively separated from the complex PM matrix. The National Institute for Occupational Safety and Health (NIOSH) method 5515 [75] specifies using ultrasound-assisted and Soxhlet extraction methods for PAHs extraction from filters. The ultrasonic bath method employs high-frequency sound waves to interact with the adsorbent. This process facilitates the release of polycyclic aromatic hydrocarbons (PAHs) from the material, which is valued for its simplicity and relatively short extraction time.

 Table 4 Sampling technique and desorption techniques and analysis method used in gasphase applications of MOF.

Materials	Target molecules	Sampling and desorption techniques	Analysis	Refs
MOF-5	Formaldehyde	Thermal desorption (TD)	GC- MS	[76]
TiO ₂ / MIL-101	Degrading VOCs	Thermal desorption (TD)	GC-FID	[7]

Quartz glass filter disk	PAHs	SPME	GC-MS	[58]
Coated SPME	VOCs	Headspace- SPME	GC-MS	[77]
DHA-80 filters	Nitro-phenolic compounds	Ultrasonication- HF- SPME	CE-ITR- MS	[78]
XAD-2 adsorbent	PAHs	Ultrasonication- SPME	GC-MS	[79]
Ui O-6 6	SVOCs	DI-SPME	GC-MS	[80]

From the literature review conducted in this section, UiO-67 has yet to be used for SVOC removal in the air through the passive air sampling method, no similar studies could be used for direct comparison. Therefore, in this research, the evaluation focuses on comparing the removal efficiency of the material before and after modification of synthesized MOFs.

1.3.3 Analytical methods

Furthermore, analytical methods such as gas chromatography (GC), fluorescence spectroscopy, and liquid chromatography (LC) are commonly used to provide detailed information on targeted analytes. Additionally, GC can detect PAHs at deficient concentrations when coupled with a sensitive detector, such as a flame ionization detector (FID) or a mass spectrometer (MS). This is particularly important in environmental analysis, where PAHs are often present in trace amounts.

A comprehensive method is necessary to rigorously investigate the adsorption and analytical behavior of PAHs on MOF structures. The static headspace sampling technique was used to accurately quantify PAHs in the gas phase. Ultrasonic extraction efficiently desorbed PAHs from the MOF, ensuring high recovery without damaging the structure. Moreover, GC-FID provided sensitive and accurate quantification of the desorbed analytes, enabling a thorough assessment of the adsorption efficiency of synthesized MOF. These methods allow for the quantification and identification of specific compounds, offering valuable insights into the efficiency and selectivity of the adsorption process. Therefore, in this project, the static headspace sampling technique was employed as the adsorption method, ultrasonic was used to extract analytes from the MOF structure, and gas chromatography coupled with a flame-ionized detector was employed as an analytical method to quantify the desorbed analytes accurately.

2. Research Objectives

The objectives of this research were twofold:

(i) To compare the efficiency and selectivity of different MOF-based adsorbents for sampling and measuring SVOC from contaminated air.

(ii) To identify the key factors influencing the adsorption capacity and stability of MOFbased adsorbents in the presence of SVOC in contaminated air and to optimize these factors for environmental sampling applications.

3. Materials and methods

3.1 Materials

This section outlines the reagents utilized in this investigation, including their respective purities and sources. Notably, all chemicals were used as received without further purification to maintain their efficacy and ensure the integrity of the synthesized materials. Zirconium (IV) chloride (ZrCl4, \geq 98%, anhydrous, for synthesis, Millipore sigma), 4,4'-Biphenyl dicarboxylic acid (BPDC, > 97.0%, TCI), Nickel (II) nitrate hexahydrate (Ni (NO₃)₂· 6H₂O, > 98%, Thermo Scientific), Acenaphthene (C₁₂H₁₀, 99%, Millipore sigma). N, N-Dimethylformamide (DMF, \geq 99.9%, Millipore sigma), Hydrochloric Acid (HCl, VWR chemicals), Methanol (CH₄O, Fisher chemical), and Reagent Alcohol 95% (VWR chemicals).

3.2 Synthesis of UiO-67 and UiO-67-Ni

MOFs have garnered significant research interest, particularly regarding developing alternative synthesis methods beyond conventional thermal heating. Diverse synthetic approaches enable the production of novel MOF compounds with distinct properties and tailored applications. Furthermore, the pursuit of convenient, cost-effective, and rapid synthesis methodologies aligns closely with the demands of contemporary industrial advancements. From our preliminary experiments in different synthesis methods, solvothermal synthesis allows precise control over reaction parameters such as temperature, solvent type, and time, optimizing material properties, including pore size, surface area, and adsorption capacity [81].

3.2.1 Synthesis of UiO-67

Following the synthesis method reported by Audu, C. O., et al. [82], UiO-67 was synthesized using the solvothermal method, following the detailed procedure described below. The reaction scheme for the synthesis of UiO-67 is shown in Figure 3.

In a 50 mL beaker, zirconium solution ZrCl₄ (335.58 mg, 1.44 mmol) was dissolved in 25 mL of N, N-Dimethylformamide (DMF), and 2.5 mL of HCl. At the same time, biphenyl-4,4'-dicarboxylic acid (BPDC, 450.55 mg, 1.86 mmol) was partially dissolved by sonicating in 25 mL of DMF. The metal and organic linker solution mixture was poured into Teflon reactors, sealed, and left in a programmable oven set to 80 °C for 24 hours. After that, it cooled to room temperature.





UiO-67- Octahedral Cage

Figure 3 Reaction scheme for the synthesis of UiO-67 [83].

The solid was collected followed by centrifuge at 7500 rpm for 10 minutes and washed twice with 20 mL DMF and 20 mL ethanol. Finally, the collected UiO-67 was dried using

a vacuum oven at room temperature for 24 hours. The resulting white solid was then stored at room temperature for subsequent analysis and application use.

3.2.2 Synthesis of UiO-67-Ni

The post-synthetic modification (PSM) method introduced the nickel metal ions to the UiO-67 structure following the synthesis method reported by Fatemeh et al. [19]. The reaction scheme for the synthesis of UiO-67-Ni is shown in Figure 4, and the green dot represents the possible sites of nickel metal ions within the UiO-67 crystal structure.



Figure 4 Reaction scheme for the synthesis of UiO-67-Ni [84].

Freshly synthesized UiO-67 was suspended in a nickel nitrate hexahydrate Ni(NO₃)₂·6H₂O (209.37 mg, 0.72 mmol) in 25 mL DMF. This resulting mixture was subjected to solvothermal aging at 100 °C for 36 hours. The procedure was then continued as described in Section 3.2.1. The resulting light-green solid was collected, followed by centrifuge at 7500 rpm for 5 minutes, and washed twice with 20 mL of DMF, followed by two washing with 20 mL of ethanol. Finally, the collected UiO-67 was dried using a vacuum oven at room temperature for 24 hours.

3.3 Characterization

Fourier transform infrared (FTIR) spectra, Platinum ATR Alpha II FTIR spectrophotometer, Bruker, in a 400-4000 cm⁻¹ range was employed to characterize the functional groups of UiO-67 and UiO-67-Ni. The X-ray diffraction (XRD) pattern of the synthesized MOFs was recorded with a Rigaku Mini-flex 600 6G X-ray using CuK α 1 radiation ($\lambda = 1.5418$ Å, 40 kV, 15 mA), in the 2θ range from 3° to 60°. Brunauer–Emmett–Teller (BET) analysis and adsorption/desorption isotherm was performed using Micromeritics 3Flex, using Nitrogen gas, 12 mm flat bottom sample tube with check seal, samples adsorption-desorption isotherms were measured at 77.300 K using ultra-pure grade N_2 gas. The morphologies and structures were investigated by the Hitachi SU5000 Scanning Electron Microscope (SEM) with a decelerated landing voltage of 2 kV, using a BSE detector, and energy dispersive spectroscopy (EDS) using an Oxford Ultima 65, the approximate detection limit of EDS is around 0.1 wt% to 1 wt%. All the samples were prepared on a 15 mm aluminum screw-style stub with double-sided carbon tape as an adhesive before measurement. The thermal gravimetric analysis (TGA) was performed to investigate the thermal stability of MOFs using (TA Instruments 954000.901) on an aluminum pan from 35 °C to 600 °C at a rate of $10 \,^{\circ}\mathrm{C} \,\mathrm{min}^{-1}$.

3.4 PAH sampling

3.4.1 Prepare Acenaphthene standards

A standard solution of 1000 ppm acenaphthene was prepared. An analytical balance was employed to accurately weigh 10 mg of acenaphthene into a 10 mL volumetric flask. The acenaphthene was diluted to the calibration mark on the volumetric flask using methanol, a solvent well-known for its high purity and compatibility with the analyte.

Subsequently, a series of standard solutions with concentrations of 10, 5, 2, 1, 0.5, 0.2, and 0.1 ppm were prepared to establish a calibration curve necessary for quantitative analysis. These concentrations were selected based on the anticipated detection limits of the gas chromatography-flame ionization detector (GC-FID) system. Each standard was carefully prepared by serial dilution from the 1000 ppm stock solution.

For method validation, a standard solution of 50 ppm was utilized to determine the retention time of the target analyte under the specified given GC-FID conditions, ensuring consistency and reliability in the chromatographic separation. A standard solution of 100 ppm was also prepared for further quantitative analysis. After the standard solutions were prepared, each solution was analyzed using the GC-FID. The peak area corresponding to each concentration was recorded, providing the necessary data for plotting the calibration curve. This curve is critical for determining the concentration of acenaphthene in unknown samples based on their GC-FID responses.

3.4.2 Static headspace sampling

As discussed in Section 1.3, the static headspace sampling method was chosen as the gas adsorption technique for this study. In this method, the synthesized MOFs were used to do the static sampling of gas samples from the equilibrated headspace atmosphere within a sealed environment maintained at room temperature. As shown in Figure 5, a sealed bottle containing 4 mL of 100 ppm acenaphthene standard solution was prepared for the

experiment. The sampling plastic tube was packed following the NIOSH-5515 standard [75] to guarantee an appropriate surface of adsorbent interaction with the gas-phase acenaphthene. A minimum of 50 mg of MOF was used and packed with quartz wool to prevent direct contact between the MOF and any liquid phase.



Figure 5 Gas adsorption- static headspace sampling set-up.

Following the standard practices in environmental sampling, indoor and outdoor samples are typically collected over 24 hours. In this study, the sealed vial was carefully opened at room temperature after the 24-hour sampling period to avoid contamination or loss of the adsorbed samples. The adsorbents, after sampling, were divided into 10 mg portions to meet the designed extraction condition, then transferred into an Eppendorf tube and sealed for subsequent analysis. The specific mass value was written down for each sample for calculation.

3.5 Desorption

This study employed an ultrasonic bath was employed to assess gas desorption efficiency over different time intervals. Based on preliminary experiments, different adsorbent dosages subjected to ultrasonic treatment for 5, 10, 15, and 20 minutes were explored and followed by ultrasonication at 7500 rpm for 5 minutes. The resulting solution was injected into the gas chromatograph (GC) for further analysis.

3.5.1 GC-FID parameters used for analytes quantification

Analysis was conducted using an Agilent 6890 GC gas chromatograph connected to a Flame-ionized detector (FID) equipped with a split/splitless inlet and autosampler. The detailed programming information is listed in Table 5.

Oven Prog	ram				
#	Rate	Final temperature	Final time		
Initial	-	120 °C	1		
1	25 °C min ⁻¹	240 °C	0.00		
2	10 °C min ⁻¹	300 °C	8.20		
Front Inlet	(Split/splitless)				
Mode		Split			
Initial temp	erature	300 °C			
Pressure 22.7 psi					
Split ratio		20:1			
Total Flow ((He)	38.1 mL min ⁻¹			
Purge Flow	to Split Vent	34.0 mL min ⁻¹			
Column					
Flow Set Po	oint	1.7 mL min ⁻¹	1.7 mL min ⁻¹		
Post Run		1.7 mL min ⁻¹	1.7 mL min ⁻¹		
Column Information ValcoBond VB-5MS					
Temperature Range -60 °C- 325 °C (350 °C)					
Dimensions	ons 30 m x 250 μm x 0.25 μm				
Heater	Ieater Oven				

Table 5 Detailed information on GC-FID conditions.

In	Front inlet
Out (Initial)	Front Detector FID, 40 °C
Pressure	22.7 psi
Average Velocity	41 cm sec^{-1}
Control Mode	Constant Flow
Column Outlet Pressure	Ambient
Front Detector FID	
Makeup	N ₂
Makeup Heater	N ₂ 300 °C
Makeup Heater H ₂ Flow	N ₂ 300 °C 35 mL min ⁻¹
Makeup Heater H ₂ Flow Air Flow	N ₂ 300 °C 35 mL min ⁻¹ 300 mL min ⁻¹
Makeup Heater H ₂ Flow Air Flow Makeup Flow	N ₂ 300 °C 35 mL min ⁻¹ 300 mL min ⁻¹ 13.3 mL min ⁻¹
Makeup Heater H ₂ Flow Air Flow Makeup Flow Carrier Gas Flow Correction	N ₂ 300 °C 35 mL min ⁻¹ 300 mL min ⁻¹ 13.3 mL min ⁻¹ Constant Col + Makeup

3.6 Experimental design

The experimental design of this study was created using the General Full Factorial design method, which enables the creation of factors with varying levels. It will create an experiment that includes all possible combinations of all factor levels.

The impact of varying adsorbent dosages on extraction efficiency was systematically evaluated based on the method reported by Liu and colleagues [85] and subsequent optimizations. To identify the key factors affecting the adsorption capacity of Acp from the gas phase using different MOFs (UiO-67 and UiO-67-Ni), two independent variables have been investigated, including the desorption time and adsorbent dosage.

a. Adsorbent dosage

Low Level (-1): 2.5 g L⁻¹

■ High Level (+1): 10 g L⁻¹

Different adsorbent dosages, specifically 2.5 g L^{-1} and 10 g L^{-1} , were related to the extraction solvent (methanol) volume of acenaphthene from MOFs, which is 4 mL and 1 mL, respectively, were evaluated to assess their impact on extraction efficiency. The performance was quantified by analyzing the resulting gas chromatography (GC) signals, providing a detailed assessment of the extraction efficiency for each adsorbent dosage.

b. Desorption time

5 mins, 10 mins, 15 mins, and 20 mins

A series of desorption times ranging from 5 to 20 minutes were systematically evaluated to optimize and ensure maximum extraction efficiency. This approach was involved in determining the optimal duration for achieving the highest level of analyte recovery during the desorption process.

In this study, each condition was tested in triplicate to ensure the reliability and repeatability of the results. These values are reported to explain variations and provide a more accurate representation of the results. Therefore, 24 experimental runs for each synthesized MOF were investigated for the desorption conditions process in Table 6 for this purpose.

Table 6	General	Full	Factorial	design	of experiments	for	24	trial	runs	including	two
independ	lent varia	bles.									

Run Order	Dosage (g L ⁻¹)	Minutes (mins)
1	2.5	15
2	10	20
3	10	5
4	10	15

5	2.5	20
6	2.5	5
7	10	15
8	2.5	20
9	2.5	20
10	10	20
11	2.5	5
12	10	10
13	2.5	15
14	2.5	10
15	2.5	10
16	10	15
17	10	10
18	10	20
19	10	5
20	2.5	5
21	10	10
22	10	5
23	2.5	15
24	2.5	10

3.7 Calculation method

The relationship between the liquid phase and the gas phase within the headspace system is governed by Henry's Law, which describes how the concentration in the liquid phase affects the equilibrium concentration in the gas phase, as well as the distribution constant. The evaporation process is dynamic, and the adsorbent adsorbs analyte, as well as the system compensates by transferring more analyte from the liquid to the gas phase [72], [86]. In systems with analytes distributed between the three phases, the equation of material balance has the following form expressed in Equation 1.

$$C_L^0 V_L^0 = C_L V_L + C_G V_G + C_S V_S$$
 (Equation 1)

where C_L , C_G , and C_S are the equilibrium concentration of the analyte in liquid phase, gaseous phase, and sorbing phase, respectively. V_L , V_G , and V_S are the volumes of these phases.

Given the system volume of 20 mL with the headspace volume of 16 mL and the concentration of the acenaphthene stock solution of 100 μ g mL⁻¹ employed in this study, the analytes that adsorbed in the sorbing phase will establish a second equilibrium. In addition, C_s is a relatively small amount compared to the whole system, therefore, ignoring its presence in the equilibrium can be an assumption. To investigate the amount of error by this assumption, MOFs accessible surface area can be calculated by Equation 2.

$$V_S = V_{total} \times m_{Adsorbent}$$
 (Equation 2)

where V_{total} is the total pore volume of synthesized MOFs (cm³ g⁻¹), $m_{Adsorbent}$ is the mass of the dosed MOF into the system, which is 50 mg in this study.

The calculated surface volumes based on BET analysis and assuming 50 mg of the solid used in each setup, which occupies 0.31 cm³ in the column, are 0.0285 and 0.0345 cm³ for UiO-67 and UiO-67-Ni, respectively. Consequently, this assures that the assumption is within the context of the static headspace extraction concept.

According to Henry's Law and distribution coefficient formula, the distribution coefficient of acenaphthene from methanol to air (K_{MA}) can be evaluated. Based on the Octanol-Water partition coefficient of Methanol (K_{MW}), Octanol-Air partition coefficient of acenaphthene (K_{OA}), Octanol-Water partition coefficient of acenaphthene (K_{OA}), Henry's Law constant of acenaphthene (H_A), the value of each constant and calculated constant was listed in Table 7 [87], [88].

The constant should be converted to dimensionless form to use H_A for partitioning calculations. Assuming 1 atm pressure and 1 mol of gas occupies 22.4 L (0.0224 m³) at standard conditions, which can be described as Equation 3, the dimensionless form is

$$H_A' = \frac{H_A}{0.0224 m^3 mol^{-1}}$$
 (Equation 3)

Given the distribution coefficient formula and Henry's law constant, calculated K_{OA} values from dimensionless Henry's law constant (H_A ') and Octanol–Water partition coefficient (K_{OW}) can be expressed by the following Equation 4 [89],

$$K_{OA} = \frac{K_{OW}}{H'_A}$$
 (Equation 4)

From the relationship between partition coefficients,

$$K_{MA} = \frac{K_{OA}}{K_{OM}}$$
 (Equation 5) and $K_{OM} = \frac{K_{OW}}{K_{MW}}$ (Equation 6)

Thus,

$$K_{MA} = \frac{K_{OA} \times K_{MW}}{K_{OW}}$$
 (Equation 7)

The initial amount of acenaphthene in methanol

$$M(g) = C_A \times V_A \quad \text{(Equation 8)}$$

where C_A is the concentration of acenaphthene; V_A is the volume of the methanol solution.

Use the partition coefficient and mass balance Equation 9,

$$M = V_{methanol} \times C_{methanol} + V_{air} \times C_{air}$$
$$= V_{methanol} \times K_{OA} \times C_{air} + V_{air} \times C_{air}$$
(Equation 9)

where $C_{methanol}$ and C_{air} are the equilibrium concentrations of acenaphthene in methanol and air, respectively.

Thus, the equilibrium concentration of acenaphthene in air can be calculated using Equation 10,

$$C_{air}(g L^{-1}) = \frac{M}{V_{(W_{methanol} \times K_{OA} + V_{air})}$$
(Equation 10)

Thus, the equilibrium amount of acenaphthene in the air phase can be obtained according to Equation 11,

$$M_{air}(\mu g) = V_{air} \times C_{air}$$
 (Equation 11)

 Table 7 The value of each constant and calculated constant.

Constant [88]	Value
Log Kow	3.92 (at 25 °C)
$H_A(atm m^3 mol^{-1})$	1.84 x 10 ⁻⁴ (at 25 °C)
Log K _{MW}	-0.77 (at 25 °C)
H_A '	8.21 x 10 ⁻³
Koa	967513.08
Log K _{OA}	5.99
K _{MA}	20.17
$C_{air} (g L^{-1})$	4.05 x 10 ⁻³
$M_{air} (\mu g)$	64.75

4. Results and discussion

A comprehensive characterization was performed to evaluate the stability of all adsorbents in terms of crystal structure and molecular composition before and after gas adsorption. The structural integrity and functional properties of the synthesized MOF have been carefully analyzed and compared with the published data from peer-reviewed journals, which have been discussed in sections 4.1 and 4.2. Subsequently, results from sampling and extraction are discussed in section 4.3, following the complete analysis of data collected from the experimental work.

4.1 Characterizations of UiO-67, UiO-67-Ni

The synthesized UiO-67 and UiO-67-Ni were extensively characterized using various analytical techniques, including Fourier Transform Infrared Spectroscopy (FT-IR), X-ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) analysis, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), and Thermogravimetric Analysis (TGA). XRD was employed to assess the crystallinity and confirm the successful synthesis of MOF. At the same time, BET analysis provided detailed information regarding the surface area and porosity, which are critical factors for enhancing gas uptake. The thermal stability of the frameworks was evaluated using TGA, ensuring that the materials can withstand the operational conditions of industrial gas separations. SEM and EDX were used to analyze surface morphology and elemental composition.

4.1.1 Fourier transform infrared (FT-IR)

FT-IR characterization analysis was conducted on the synthesized UiO-67 and UiO-67-Ni, as illustrated in Figure 6. The FTIR spectrum of UiO-67 is dominated by a strong and broad band centered at 3412 cm^{-1} , highlighted in a blue band, which is due to the O–H stretching peak of inter-crystalline water and physically adsorbed water in the pores [90]. The stretching vibration peaks of aromatic C–H of benzene rings can be seen in the range of $3100-3000 \text{ cm}^{-1}$, and there is an apparent aliphatic C–H stretching vibration peak of methyl (–CH₃) at 2975 cm⁻¹. Both were highlighted in orange bands. The absorption peak at 1660 cm⁻¹ belongs to the C=O stretching vibration peak of BPDC, while the absorption peaks at 1597, 1545, and 1406 cm⁻¹ are related to the C=C stretching vibration of benzene rings, and the symmetrical and asymmetrical stretching of COO⁻ vibration pattern [91]. In the green bar highlighted area, which represents the Zr-O₂ mode, there is a triplet peak of longitudinal and transverse modes at 768, 660, and 458 cm⁻¹, respectively [92].

On the other hand, UiO-67-Ni exhibits an infrared spectrum closely resembling that of the parent structure. Notably, UiO-67-Ni displays a distinctive absorption peak near 1041 cm⁻¹ [93], attributable to the Ni-O-Ni stretching vibration mode.



Figure 6 FT-IR spectra of UiO-67 and UiO-67-Ni.

4.1.2 X-Ray diffraction (XRD)

The XRD characterization of UiO-67 and UiO-67-Ni composites is shown in Figure 7. The information illustrates that the XRD patterns of MOF crystal structures before and after modification are similar. They both have firm diffraction patterns at 20 at 5.65°, 6.53°, 9.26°, 10.86°, and 11.35°, which corresponds to the (111), (200), (220), (311) and (222) crystal planes, respectively [94] and are consistent with the standard crystal structure information of UiO-67 [27], which indicated that they were highly crystalline.

After modification with nickel, as shown in the enlarged graph on the diffraction pattern observed in the 2θ range from 4° to 12° , the enlarged section of the XRD pattern within this range provides detailed insight into the structural modifications induced by the incorporation of nickel into the UiO-67 framework. Despite these modifications, the XRD

pattern of UiO-67-Ni closely resembles that of the unmodified UiO-67, indicating successful retention of the framework structure after post-treatment. Notably, distinct diffraction patterns are observed at 20 values of 13.17°, 37.28°, and 48.56°, corresponding to the (001), (101), and (102) crystal planes of Ni-O-Ni, as reported by Pramana Y. B. [95], However, in our findings, the nickel-related diffraction patterns are less pronounced, which suggests a lower amount of nickel incorporated into the structure in comparison with other species or possible differences in the crystallinity of the nickel species within the framework.



Figure 7 XRD patterns for UiO-67 and UiO-67-Ni, with a particular emphasis on the diffraction patterns observed in the 2θ range from 4° to 12° .

4.1.3 Brunauer–Emmett–Teller (BET)

Based on the data presented in Table 8, the BET surface area of UiO-67-Ni is considerably higher than that of the original UiO-67. The post-synthetic process, wherein nickel was incorporated into the UiO-67 framework, resulted in an increase in the specific surface area of UiO-67-Ni, reaching 1450.5 m² g⁻¹.

Table 8 Specific surface area, total pore volume, micropore volume, micropore surface area, and external surface area for both UiO-67 and UiO-67-Ni.

MOF	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Micropore surface area (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	Pore size (Å)
Ui O-67	1137	0.57	0.23	563	573	22.4
UiO-67-Ni	1450	0.69	0.30	752	698	25.3

Additionally, a substantial increase in pore size and other vital parameters, such as total pore volume, micropore volume, micropore surface area, and external surface area, which also refers to the t-plot outer surface area, were also observed to be more prominent in UiO-67-Ni. These findings align with results from complementary analyses, indicating a substantial enhancement in the porosity and surface characteristics of the material due to the nickel modification.

Furthermore, the N₂ adsorption-desorption isotherm of UiO-67 and UiO-67-Ni are shown in Figure 8. The information represents the qualitative and descriptive performance of the adsorption and desorption processes, along with the material surface area and pore structure. Referring to the IUPAC classification of isotherms resembles the type IV isotherm. The presence of a continuous hysteresis loop belonging to the H4 type at P/Po of 0.1–0.3 for both UiO-67 and UiO-67-Ni represents the microporosity of these structures.

Nonetheless, as shown in the enlarged graph of relative pressure from 0.1 to 0.3, the gap between the adsorption/desorption curve, depicted for UiO-67-Ni, is much narrower than that of the original MOF, as shown in Figure 8. The narrow hysteresis curve corresponds to the mild development of micropores [78]. This behavior can be attributed to the variation in pore width between UiO-67 and UiO-67-Ni, and the discrepancy in pore dimensions between these two frameworks results in the narrow hysteresis loop observed in the adsorption-desorption isotherms.



Figure 8 Nitrogen adsorption/desorption isotherms for UiO-67 and UiO-67-Ni, as well as the enlarged graph of relative pressure from 0.1 to 0.3.

4.1.4 Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS)

The SEM images of (a) UiO-67 and (b) UiO-67-Ni, together with EDS analysis, are shown in Figure 9. As the results show, no pronounced changes in morphology have been observed under the post-synthetic modification conditions. Additionally, the presence of 2.252% of Nickel in EDS analysis (Figure 9 (c) and 9 (d)) means that during the post-modification, nickel ions have been incorporated into the structure of UiO-67. As the collective interpretation of the characterization technique data shows, this study suggests that Nickel ions are in contact with the zirconium metal nodes. The atomic ratio of the introduced Ni and Zr was 1:6.3, which is consistent with the analysis data from triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ).



Figure 9 SEM analysis of (a) UiO-67 and (b) UiO-67-Ni together with EDS spectrum of (c) UiO-67 and (d) UiO-67-Ni.

4.1.5 Thermogravimetric analysis (TGA)

The TGA test results, illustrated in Figure 10, reveal distinctive features. The TGA of UiO-67 exhibits two distinct stages of mass loss, which is consistent with the findings reported by Peng et al. [90]. In the first stage, from 43 to 162 °C, the UiO-67 lost 30.5 % of its initial mass, which was attributed to the volatilization of residual DMF solvent within UiO-67. During the plateau period of 162~526 °C, due to the stable crystal structure, UiO-67 material experiences minimal loss until 526 °C. Subsequently, weight loss in the third stage was marked by a sharp drop in the range of 526~534 °C, with a total weight loss of 38.3 %, which signifies the destruction of the crystal structure attributed to the cleavage of the benzene ring and carboxylic acid group in the UiO-67 organic chain [96]. A second plateau appears at 524~600 °C, where only a trace of ZrO_2 with very low crystallinity is present, accounting for 31.2 % of the initial mass. Therefore, UiO-67 exhibits commendable thermal stability and maintains a stable crystal structure below 526 °C. The detailed information is listed in Table 9.



Figure 10 Thermogravimetric analysis (TGA/DTG) of UiO-67, UiO-67-Ni.

	Temperature	Weight loss	Mechanism
Stage 1	43-162 °C	30.5 %	Volatilization of DMF solvent
Stage 2	162-526 °C	-	MOF structure stable
Stage 3	526-534 °C	38.3 %	Cleavage of the benzene ring and carboxylic acid group
Stage 4	534-600 °C	-	ZrO ₂ , low crystallinity

Table 9 Weight loss and mechanisms at different stages of UiO-67 during TGA.

UiO-67 incorporated with nickel exhibits a decrease in thermal stability, as evidenced by the TGA/ DTG curve of UiO-67-Ni (drawn in red solid and dotted line in Figure 10, portraying two different stages of mass loss. In the first stage, from 47 to 162 °C, the material experiences a loss of 31.3 % of its initial mass, possibly due to the volatilization of the residual DMF solvent in synthesized MOF. With temperatures between 162 and 422 °C, UiO-67-Ni has a stable structure, slightly decreasing compared to UiO-67. Subsequently, in the third stage, a sharp drop in weight loss occurs within the range of 422-428 °C, with a total of 38.0 %, indicating the destruction of the UiO-67 crystal structure in the material. Finally, a plateau appears at 428~600 °C, where only 29.8% of ZrO₂ and NiO with very low crystallinity is present. The detailed information is listed in Table 10.

 Table 10 Weight loss and mechanisms at different stages of UiO-67-Ni during TGA.

	Temperature	Weight loss	Mechanism
Stage 1	47-162 °C	31.3 %	Volatilization of DMF solvent
Stage 2	162-422 °C	-	MOF structure stable
Stage 3	422-428 °C	38.0 %	Destruction of UiO-67 crystal structure

4.2 Characterization of UiO-67 and UiO-67-Ni after adsorption

4.2.1 Fourier transform infrared (FT-IR) after adsorption

The FT-IR spectra of UiO-67 and UiO-67-Ni, as presented in Figure 11 (a), exhibit absorption peaks at 1597, 1545, and 1406 cm⁻¹ are related to the C=C stretching vibration of benzene rings, and the symmetrical and asymmetrical stretching vibration of the COO⁻ groups. The similarity of the spectra before and after adsorption indicates that the MOF structure remains unchanged upon interaction with analytes. Figure 11 (b) provides an enlarged view of the FT-IR region from 1800 to 350 cm⁻¹. The FT-IR spectrum of acenaphthene, represented by the blue line, overlaps with the original MOF peaks because of the small quantity of analyte captured onto the structures. Furthermore, after the adsorption of acenaphthene, distinct variations in the spectral peaks, highlighted in gray, were observed. These changes are likely attributable to the interaction of the analyte with the MOF structure, suggesting its successful adsorption.



Figure 11 FT-IR of (a) UiO-67, UiO-67-Acp, UiO-67-Ni, UiO-67-Ni-Acp, and acenaphthene, and (b) enlarged FT-IR peak at the range of wavelength between 1800 and 350 cm⁻¹.

4.2.2 X-Ray diffraction (XRD) after adsorption

The XRD patterns of (a) UiO-67 and UiO-67-Ni, as well as the patterns after desorption illustrated in Figure 12 (a), and the enlarged XRD pattern of the grey color heightened region in (a) is shown in Figure 12 (b). The data in the figure indicates that after desorption, the crystal structures of UiO-67 and UiO-67-Ni substantially hold constant to their original forms. Notably, after the modification of UiO-67, the crystal structure is preserved effectively. This suggests that the nickel atoms play a crucial role in enhancing the stability of the MOF.



Figure 12 XRD pattern of (a) UiO-67, UiO-67-after, UiO-67-Ni, UiO-67-Ni-after, and (b) enlarged XRD pattern with a particular emphasis on the diffraction patterns observed in the 2θ range from 3° to 15°.

4.2.3 Thermogravimetric analysis (TGA) after adsorption

The TGA curves for the various adsorbents post-sampling are presented in Figure 13. As outlined in Section 4.1.5, the observed weight loss corresponds well with the temperature variations, indicating that the UiO-67 framework retains its structural integrity following

acenaphthene adsorption. The two distinct weight loss stages in the initial stage are attributed to the desorption of methanol, which was used as solvent, and acenaphthene, respectively.



Figure 13 Thermogravimetric analysis (TGA and DTGA) of UiO-67, UiO-67-Ni, as well as the curve after adsorbing the acenaphthene.

4.3 GC-FID analysis

The effects of different dosages of adsorbents and extraction intervals on gas desorption efficiency were systematically investigated. The adsorption and desorption efficiency of acenaphthene on different materials was assessed using the partition coefficient of acenaphthene in methanol in conjunction with gas chromatography data. This approach provided critical evidence regarding the potential applicability of modified MOF in industrial gas capture systems. By analyzing these parameters, we obtained critical insights into the performance and feasibility of the MOF for efficient gas separation and capture applications.

4.3.1 Quantity adsorbed of acenaphthene

Following the calculation introduced in section 3.7, the partition coefficient between methanol and air K_{MA} is 20.71. To calculate the amount of acenaphthene transferred from a 4 mL 100 ppm acenaphthene solution in methanol to 16 mL of air in a sealed container, the methanol- air partition coefficient K_{MA} and Equation 12 was used.

To establish a calibration curve necessary for quantitative analysis, a series of standard solutions were used with concentrations of 10, 5, 2, 1, 0.5, 0.2, and 0.1 ppm. The peak areas of the standard solutions were obtained through GC-FID analysis. The linear regression equation and correlation coefficient R^2 of the acenaphthene standard solution are shown in Figure 14. The linear regression equation is Y= 1.6893×X- 0.1983, and the correlation coefficient R^2 = 0.9996, where X is the concentration of standard solutions, while Y represents the corresponding peak area.



Figure 14 Calibration curve of acenaphthene standard.

After obtaining the chromatogram of each sample, the EIC technique is used for data analysis. The peak area of the extraction solution was recorded, and the quantity adsorbed of acenaphthene of different conditions was calculated by Equation 12. After calculation, a linear regression equation was needed to calculate the concentration of components (ppm).

$$M_{adsorbed} (\mu g \ mg^{-1}) = \frac{(A + 0.1983/1.6893) \times V_m}{M_{MOF}}$$
 (Equation 12)

where, A is the peak area of the analyte, V_m is the desorption solvent volume (mL), and M_{MOF} is the dosage of ultrasonic desorption (mg).

According to the experimental design, the quantity adsorbed of acenaphthene was measured for UiO-67 and UiO-67-Ni under eight distinct conditions, including three replicates expressed in μ g mg⁻¹. The processed data from GC are listed in Table 11.

Run Order	Dosage (g L ⁻¹)	Minutes (mins)	*Response1 (µg mg ⁻¹)	*Response2 (µg mg ⁻¹)
1	2.5	15	0.08	0.08
2	10	20	0.16	0.23
3	10	5	0.11	0.11
4	10	15	0.12	0.20
5	2.5	20	0.10	0.12
6	2.5	5	0.03	0.04
7	10	15	0.10	0.20
8	2.5	20	0.11	0.11
9	2.5	20	0.10	0.11
10	10	20	0.16	0.22
11	2.5	5	0.03	0.04
12	10	10	0.13	0.11
13	2.5	15	0.08	0.06
14	2.5	10	0.05	0.08
15	2.5	10	0.05	0.06
16	10	15	0.10	0.20
17	10	10	0.14	0.11
18	10	20	0.14	0.23
19	10	5	0.11	0.14
20	2.5	5	0.03	0.05
21	10	10	0.11	0.11
22	10	5	0.12	0.10
23	2.5	15	0.08	0.08
24	2.5	10	0.05	0.06

Table 11 Quantity of acenaphthene adsorbed by UiO-67 and UiO-67-Ni.

**Response1* represents the quantity adsorbed of acenaphthene by UiO-67, while *Response2* represents the quantity adsorbed of acenaphthene by UiO-67-Ni.

To identify the relationship between two independent variables, a general linear model ANOVA analysis was conducted, and the adsorption capacities for all replicates were plotted in a contour map to explore the relationship between two independent variables, which is drawn in Figure 15.



Figure 15 Contour plot of quantity adsorbed of acenaphthene of different adsorbent dosage and desorption time of (a) UiO-67, and (b) UiO-67-Ni.

As the information displayed in Figure 15, the extraction efficiency of analytes increased progressively as the desorption time was increased from 5 to 20 minutes. For UiO-67, the extraction efficiency exhibited minimal variation when the time was increased from 5 to 15 minutes. However, a considerable increase was observed at 20 minutes, reaching the highest extraction efficiency of 0.153 μ g mg⁻¹. Moreover, the extraction efficiency exhibited minimal variation when the desorption time was 10–15 minutes, the group of independent variables did not exhibit a statistically significant association with the dependent variable (p>0.05), which is also in line with the data displayed in the contour plot.

Meanwhile, for UiO-67-Ni, the higher adsorbent dosage was associated with higher extraction efficiency. The extraction efficiency exhibited minimal variation as the desorption time was extended from 15 to 20 minutes, 0.200 and 0.227 μ g mg⁻¹, respectively. However, desorption time shows a non-linear pattern, when experimental conditions are 5 and 10 minutes, the quantity of adsorbed acenaphthene decreases significantly, while when time increased from 15 to 20 minutes, there would be an increase in adsorption efficiency. Considering the high efficiency and expedited sample extraction requirements, 15 minutes was the optimal ultrasonic duration.

In this study, the adsorption and desorption behavior of the acenaphthene were investigated using different methods. The adsorption of gaseous acenaphthene molecules on the MOF surface was facilitated by π - π interaction, which belongs to the physisorption mechanisms [97]. Given the reversible nature of physisorption, ultrasonic was employed as the energy source. However, although the π - π interactions have relatively weak strength, the ultrasonic energy may not be sufficient to destroy these interactions. Therefore, this could result in incomplete desorption of the adsorbed gas molecules, potentially limiting the efficiency of the desorption process. This also explains why the gas desorption efficiency is not linear when the desorption time is around 10 to 15 minutes.

4.3.2 Removal efficiency

50 mg MOF dozed into the plastic tube for the static headspace sampling set-up. Therefore, the total gas-phase acenaphthene adsorbed amount can be expressed as M_{total} (µg), using Equation 13,

$M_{total}(\mu g) = 50 \times M_{adsorbed}$ (Equation 13)

Thus, the removal efficiency (%) of the optimal condition can be calculated through Equation 14,

Removal efficiency, R (%) =
$$\frac{M_{total}}{64.75}$$
 (Equation 14)

Where the amount of acenaphthene in the headspace was calculated according to Equation 3 to Equation 11, which is $64.75 \ \mu g$.

The improvement of removal efficiency between two different adsorbents was calculated using Equation 15.

Improvement (%) =
$$\frac{R_2 - R_1}{R_1}$$
 (Equation 15)

where, R_1 is the removal efficiency of UiO-67, and R_2 is the removal efficiency of UiO-67-Ni.

Therefore, the calculated removal efficiency of UiO-67 is 11.81%, while the removal efficiency of UiO-67-Ni is 17.45% by using the equation illustrated above. The results showed that UiO-67-Ni has a 47.8% improvement in removal efficiency compared to UiO-67.

Incorporating nickel (Ni²⁺) ions into the structure of UiO-67 considerably alters the coordination environment of the metal nodes, leading to a denser metal node population. Due to this, densification weakens coordination bonds between the zirconium-based metal nodes and the biphenyl-4,4'-dicarboxylate (BPDC) linkers. Therefore, this weakened

interaction enhances the π - π stacking interactions between the BPDC linkers and guest molecules such as acenaphthene.

Brunauer-Emmett-Teller (BET) analysis reveals that the Ni-modified UiO-67 (UiO-67-Ni) exhibits a larger pore size than the parent UiO-67 framework. This observation is consistent with the hypothesis that incorporating Ni²⁺ ions weaken the connectivity between the ligands and metal nodes, resulting in a more open pore structure. The increase in pore size facilitates more substantial guest molecule adsorption, further corroborating the strengthened π - π interactions observed with acenaphthene.

5. Conclusion and Further Studies

This study has explored two Zr-containing MOFs, UiO-67 and UiO-67-Ni, for their potential for adsorption of acenaphthene as a model compound for PAHs. Both MOFs demonstrated considerable adsorption capacities at an adsorbent dosage of 10 g L⁻¹. Specifically, UiO-67 achieved the highest extraction efficiency of 0.153 μ g mg⁻¹ within 20 minutes, while UiO-67-Ni reached an extraction efficiency of 0.200 μ g mg⁻¹ within 15 minutes. In addition, the adsorption efficiency of acenaphthene on different MOF was further quantified, where the removal efficiency of acenaphthene reached 11.81% and 17.45% for UiO-67 and UiO-67-Ni, respectively. Notably, UiO-67-Ni exhibited a 47.8% improvement in removal efficiency compared to UiO-67, highlighting its superior performance in acenaphthene adsorption.

The results of the study indicate that larger pores and post-synthetic modification improved acenaphthene adsorption. With increased porosity, the modified UiO-67 framework demonstrated enhanced gas desorption efficiency while maintaining crystallographic integrity. These characteristics align with operation conditions on demand for sampling and analysis in environmental and industrial applications.

While this study showed improved gas capture efficiency, future research could explore the scalability of MOF for industrial use, such as the membrane material for portable autosamplers in the workplace. Besides, for future studies, systematically analyze PAHs of varying molecular weights to understand their π - π interactions.

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