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Potential of Zirconium-Based Metal Organic Frameworks Double Ligands with Amine-Carboxylic Acid (NH_2-H_2BDC) in Removing Humic Acid from Stabilized Landfill Leachate

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ABSTRACT

In this study, the characteristics of landfill leachate, the potential mechanism, and the performance of the nano-adsorbent Zirconium-Based Metal Organic Frameworks double ligands with amine and carboxylic acid (UiO-66-NH_2-D), were investigated for humic acid (HA) removal. The landfill leachate characteristic analysis revealed that the leachate is classified as stabilised landfill leachate, as the biodegradability ratio (BOD_5/COD) was recorded at 0.046. Most of the measured parameters exceeded the standard discharge limitations, including Chemical Oxygen Demand (COD), Ammoniacal Nitrogen (NH_3-N), and HA, which were recorded at 3681 mg/L, 2250 mg/L, and 186.4 mg/L, respectively. Characterisation analysis of UiO-66-NH_2-D confirmed that this adsorbent possesses a high degree of crystallinity and abundant active sites, which significantly contributes to its strong adsorption performance through electrostatic forces (between negatively charged HA and positively charged adsorbent, or vice versa), hydrogen bonding (involving N-H, O-H, or F-H bonds and lone pairs), and π-π interactions (non-covalent stacking of aromatic rings). The mesoporous structure and active sites of UiO-66-NH_2-D were optimised by varying the molar concentration of ligands from 2 mmol to 6 mmol during synthesis to enhance its adsorption capabilities. The sample with a 4 mmol ligand concentration exhibited the highest HA removal efficiency, achieving 44.4% at a dosage of 1 g and a reaction time of 30 minutes. This concentration was found optimal due to a balance of surface functionality and minimal pore blockage. These findings emphasise UiO-66's potential as an effective adsorbent for removing HA in landfill leachate, contributing to improvements in existing conventional treatment plants.

Keywords: UiO-66; humic acid; adsorption; landfill leachate treatment; wastewater treatment; nano adsorbent

INTRODUCTION

The significant increase in solid waste generation has highlighted the detrimental effects of landfill leachate on groundwater, raising serious concerns for public health and environmental safety. The decomposition of *municipal solid waste (MSW)* releases hazardous materials, including heavy metals, organic pollutants, and toxic chemicals, which lead to the formation of landfill leachate (Dagwar & Dutta 2024). If not properly managed, this leachate can seep into the environment, threatening groundwater sources that are crucial for the drinking water supply. According to Abdul Gani et al. (2022), landfill sites that lack adequate planning and treatment facilities for gas or leachate collection may cause wastewater to contaminate groundwater, leading to excessive emissions of carbon and methane into the atmosphere.

Typically, landfill leachate is characterised by its dark colour, unpleasant odour, extreme pH levels, high concentrations of inorganic salts, *chemical oxygen demand (COD)*, *biological oxygen demand (BOD_5)*, and *ammoniacal nitrogen (NH_3-N)* (Kamarrudin et al. 2017; Sossou et al. 2024). Besides having an intense colour and unpleasant odour, leachate from landfills has been found to contain approximately 200 organic compounds, including *humic substances (HS)* (Silva et al. 2019). Notably, 35 of these compounds may pose a hazard to both human and environmental health (Zakaria, 2020). According to Bernat et al. (2021), biological treatment methods are challenging to use for breaking down these elements in leachate. Due to the chemical complexity of leachate (less than 0.1), particularly from older landfills, conventional biological treatment techniques are often ineffective (Zakaria et al. 2023).

In the meantime, the quality of the leachate is correlated with the phase of the landfill's deterioration process. The anaerobic degradation process consists of three phases: acid fermentation, the intermediate anaerobic phase, and anaerobic degradation. According to Zakaria and Aziz (2018), aerobic activity and the acid fermentation phase predominate in young or newly established landfill sites, resulting in a significant production of *volatile fatty acids (VFAs)* within a short period. However, during the intermediate anaerobic phase, ammonia is released, *VFA* is reduced, and *methanogenic bacteria* begins to develop. The final phase, anaerobic degradation, also known as stabilised leachate, occurs in older landfills (those older than ten years). Biological treatment techniques can effectively treat young leachate, but they are ineffective for leachate from older landfills due to its complexity (Shadi et al. 2020).

Humic acid (HA), a major component of landfill leachate, hinders biological treatment methods, which are typically cost-effective, easy to operate, and environmentally friendly. According to Zhang et al. (2018), the presence of *humic acids* in untreated water inhibits the oxidation of target pollutants through competing reactions. It generates toxic disinfection by-products during the classical disinfection method of chlorination. Therefore, it is necessary to remove *HA* from water and wastewater. *HA* is a naturally occurring organic substance formed during the breakdown of organic matter. It belongs to the *HS* group, which also includes *humins (HU)* and *fulvic acids (FA)* (Lomińska, 2016). According to Rosli et al. (2017), *HS* are complex macromolecular compounds composed of any organic matter, including microfauna, biological waste, insecticides, and plant and animal waste (such as lignin, carbohydrates, and proteins). Niza et al. (2020) also state that humic materials are organic in nature, consisting of a complex system of acid-base molecules, such as carboxyl, polymerised organic, and carbohydrate.

Humic acid is identifiable by its brownish appearance at concentrations above 5 mg/L (Abdullah et al. 2018). In landfill leachate, *HS* concentrations range between 118 and 228 mg/g, with *HA* comprising 40-44% (Liu et al. 2019). In young landfills, organic carbon primarily exists as *VFA*. In contrast, older landfills contain humic materials (*HU, FA, and HA*), which dominate up to 60% of the organic fraction (Martínez-Cruz and Rojas-Valencia, 2023). According to earlier research, it was reported that 50-60% of the *COD* level in a leachate sample taken after landfill stabilisation was constituted by *HS* (Moravia et al. 2021), making it highly resistant to biological treatments (Costa et al. 2019). Therefore, an additional treatment is required to remove *HA* as well as to improve the current treatment facilities in landfill sites.

Currently, a variety of treatment studies have been done in removing *HA* from aqueous solution, such as by using microwave irradiation (Zhang et al. 2018), *UV/ZnO* nano-photocatalysis and adsorption (Oskoei et al. 2016), novel hydrogarnet/zeolite composite (Maeda et al. 2020), and Sono-Persulphate process (Alizadeh et al. 2022). However, few studies have been conducted on recalcitrant pollutant samples, such as landfill leachate. Adsorption methods are widely recognised as an effective approach for treating wastewater, particularly for addressing the challenge of incomplete pollutant removal. This process involves the transfer of pollutant molecules from the bulk phase of the solution into the active pores of adsorbent materials, where they are captured on the surface (Kumar et al. 2019; Siipola et al. 2020). Wang et al. (2018) highlight materials such as carbon nanotubes (*CNTs*), graphene-based substances, metal organic frameworks (*MOFs*), and carbon-based activated carbon as effective options for the

adsorption process. Table 1 provides a summary of various adsorbents used for removing *HA* in wastewater treatment.

Based on Table 1, it can be demonstrated that several adsorbents exhibit a variety of uses and efficiencies in removing *HA* from wastewater. Qin et al. (2017) reveal that adsorbents, such as nitrogen-containing activated carbon, are able to adsorb *HA* up to 48.47 mg/g in landfill leachate. *Zr-MOFs*, also known as *University of Oslo-66 (UiO-66)*, are among the good and stable MOF materials in the adsorption field. According to Ahmadijokani et al. (2022), *UiO-66* has become a promising adsorbent in wastewater treatment due to its intriguing properties, which include high thermal stability, superior chemical resistance to a variety of solvents, including acetone, benzene, different alcohols, dimethylformamide, acidic and basic solution, excellent chemical stability against a variety of conditions, including air, water, and chloroform, and exceptional resistance to high external pressure. These properties are primarily the result of the strong *Zr-O* bond and high coordination number between the Zr clusters and organic ligands.

TABLE 1. Summary of Studies on Humic Acid Removal in Wastewater

No	Types of Adsorbents	Adsorption Capacity (mg/g)	Source
1	Nitrogen-Containing Activated Carbon	48.47	Qin et al. (2017)
2	Aminopropyl Functionalized Silica Coated Fe_3O_4 Nanoparticles	181.82	Wang et al. (2015)
3	Combined Magnetic Maghemite with Nanosized Hydroxyapatite	601.92	Shi et al. (2016)
4	Magnetically Separable Polyaniline	36.36	Wang et al. (2014)

Researchers have recently conducted several studies to enhance the adsorption capacity of *UiO-66* and expand its range of applications for various undesirable contaminants. Furthermore, the linker can accelerate the removal mechanism of *MOFs* by adding potential organic ligands, such as *Fe*, -NH_2, and -NO_2 to the surface of *UiO-66* (Cheng et al. 2022). Each of these possible organic ligands will provide the composite a positive surface charge, enabling interaction between the pollutant's (negative charge) and the composite by electrostatic attraction (Cheng et al. 2022). A modification of the surface of *UiO-66* with -NO_2 has been studied to improve the adsorption capacity of *UiO-66*. According to Cheng et al. (2022), the adsorption of *UiO-66* improved up to 127.32 mg/g for Co^{2+} and *Methylene blue*.

Therefore, this study focused on characterising and evaluating the potential of *UiO-66* double ligands with *NH_2-H_2BDC* (positive charge) as an adsorbent for stabilised landfill leachate treatment, as well as monitoring the characteristics of landfill leachate over one year at a nearby landfill site to validate its phase. This study hypothesises that the synthesis of *UiO-66* with *NH_2-H_2BDC* (positive charge) organic ligand can maximise the adsorption capacity of *HA* through an electrostatic attraction mechanism between the sample (negative charge) and *UiO-66* double ligands with *NH_2-H_2BDC* (positive charge). The natural properties of *UiO-66*, which feature large mesoporosity and an active site, also positively initiate the adsorption mechanism of *HA* into the adsorbent, enhancing the removal of *HA* from the sample. In this study, the concentrations of *UiO-66* and the ligand *UiO-66-NH_2-D* will be varied (during synthesis) to examine their characteristics at different mmol levels and identify the optimal synthesis design based on their removal performance. Although *UiO-66* has been extensively researched as an adsorbent for water treatment, its application in stabilised landfill leachate treatment remains limited. To the best of our knowledge, no studies have specifically investigated the removal of *HA* using *UiO-66-NH_2-D* as an adsorbent. Therefore, this study examines the potential of *UiO-66-NH_2-D* in removing *HA* from stabilised landfill leachate.

METHODOLOGY

SAMPLING OF ANAEROBIC STABILISED LANDFILL LEACHATE

The monitoring and collection of raw leachate samples were conducted at the leachate detention pond (Figure 1) of a municipal landfill site near Kota Kinabalu, Sabah, using the grab-sampling method. The samples were collected in 5 L high-density polyethylene (HDPE) bottles and immediately transported to the Environmental

Laboratory at the Faculty of Engineering, Universiti Malaysia Sabah (UMS), for storage and preservation in a cold room at 4 °C (APHA, 2017). Samples were analysed within 24 hours of collection to ensure reliable results. Leachate sampling was conducted monthly over 12 consecutive months, from December 2023 to November 2024, yielding an average of 24 data sets.

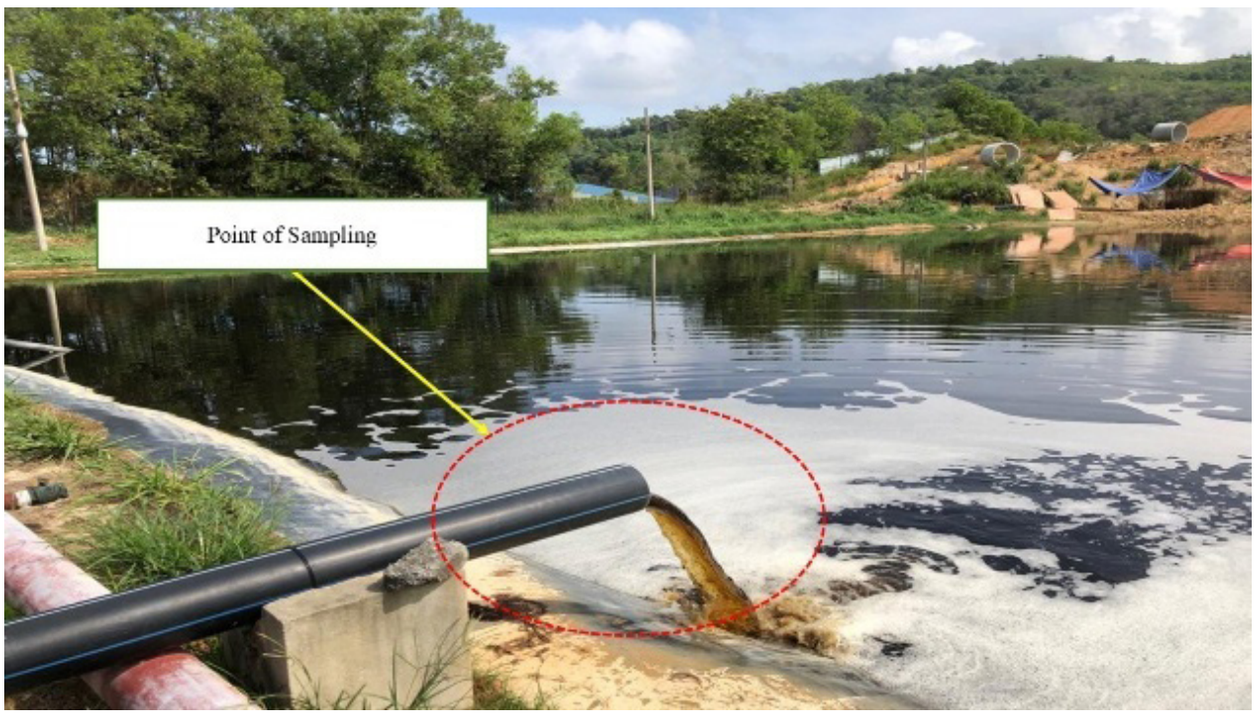

FIGURE 1. Detention Pond in Sampling Site

LEACHATE CHARACTERISATION

In this study, temperature, pH, conductivity, total dissolved solids (TDS), dissolved oxygen (DO) and BOD_5, were measured following the standard method procedure (APHA, 2017). Colour, chemical oxygen demand (COD), ammoniacal nitrogen (NH_3-N), and suspended solids (SS) concentrations were determined using a DR6000 HACH spectrophotometer. COD concentration was tested using a high-range (HR) method. In contrast, NH_3-N concentration in stabilised landfill leachate (*SAL*) was determined using the Salicylate Method (Method 10031, HACH, USA). Lastly, the concentration of *HA* was determined using a UV-VIS spectrophotometer. All values for the mentioned parameters were measured in triplicate. The obtained data were then compared to the Environmental Quality (Control of Pollution from Solid Waste Transfer Stations and Landfills) Regulations 2009, under the Laws of Malaysia, as per the Malaysia Environmental Quality Act (MEQA) standard (MDC, 2014).

PREPARATION AND SYNTHESIS OF *UIO-66-NH_2-D*

The chemicals and reagents used in this study were all of analytical grade including *zirconium tetrachloride ($ZrCl_4$, 99.9%, Sigma-Aldrich, Germany), terephthalic acid (H_2BDC, 98%, Sigma-Aldrich, Germany), 2-amino terephthalic acid (NH_2-H_2BDC, 95%, Sigma-Aldrich, Germany), N, N-dimethylformamide (DMF, ≥99%, Sigma-Aldrich, Germany), and ethanol (Ethanol, 95%)*.

For the preparation of *UiO-66* (*Zr-MOF*), *UiO-66* double ligands with NH_2-H_2BDC were synthesised using the solvothermal method, following the procedure described by Jiang et al. (2022), with minor modifications, at a temperature of 120 °C for 24 hours. Figure 2 depicts the steps involved in the synthesis process of *UiO-66* double ligands with NH_2-H_2BDC. As shown in Figure 2, Step 1, Solution A was prepared by adding varying masses of $ZrCl_4$ to 50 mL of DMF, then dissolving it using an ultrasonic machine for 10 minutes.

The following step was the production of Solution B. In a separate beaker, the desired ratios of H_2BDC and NH_2-H_2BDC were added to 50 mL of DMF, and the mixture was

then dissolved by ultrasonication for 10 minutes (Figure 2). In Step 3, Solution A was mixed with Solution B and dissolved using an ultrasonic machine for another 10 minutes. In Step 4, the result of the mixed solution was transferred into a Teflon-lined bottle and heated in an oven at 120 °C for 24 hours. After that, the obtained product was then divided into 10 mL centrifuge tubes and centrifuged for 10 minutes at 4000 rpm. Following centrifugation, the product was washed alternately with diluted ethanol three times for 10 minutes each to remove impurities. Finally, the washed product was dried in a drying oven at 120 °C for 24 hours prior to use.

The same procedure was repeated to synthesise *UiO-66-NH_2-D* at different mmol levels (2 mmol, 3 mmol, 4 mmol, 5 mmol and 6 mmol). The corresponding masses of *H_2BDC* and *NH_2-H_2BDC* were calculated based on the given mmol values at a 1:1 ratio (*H_2BDC* and *NH_2-H_2BDC*), as shown in Table 2. Based on a study conducted by Abdullah et al. (2018), the optimal mass ratio of *$ZrCl_4$* to organic ligands is 1:4, which means the mass of *$ZrCl_4$* was one-fourth of the total mass of the organic ligands used.

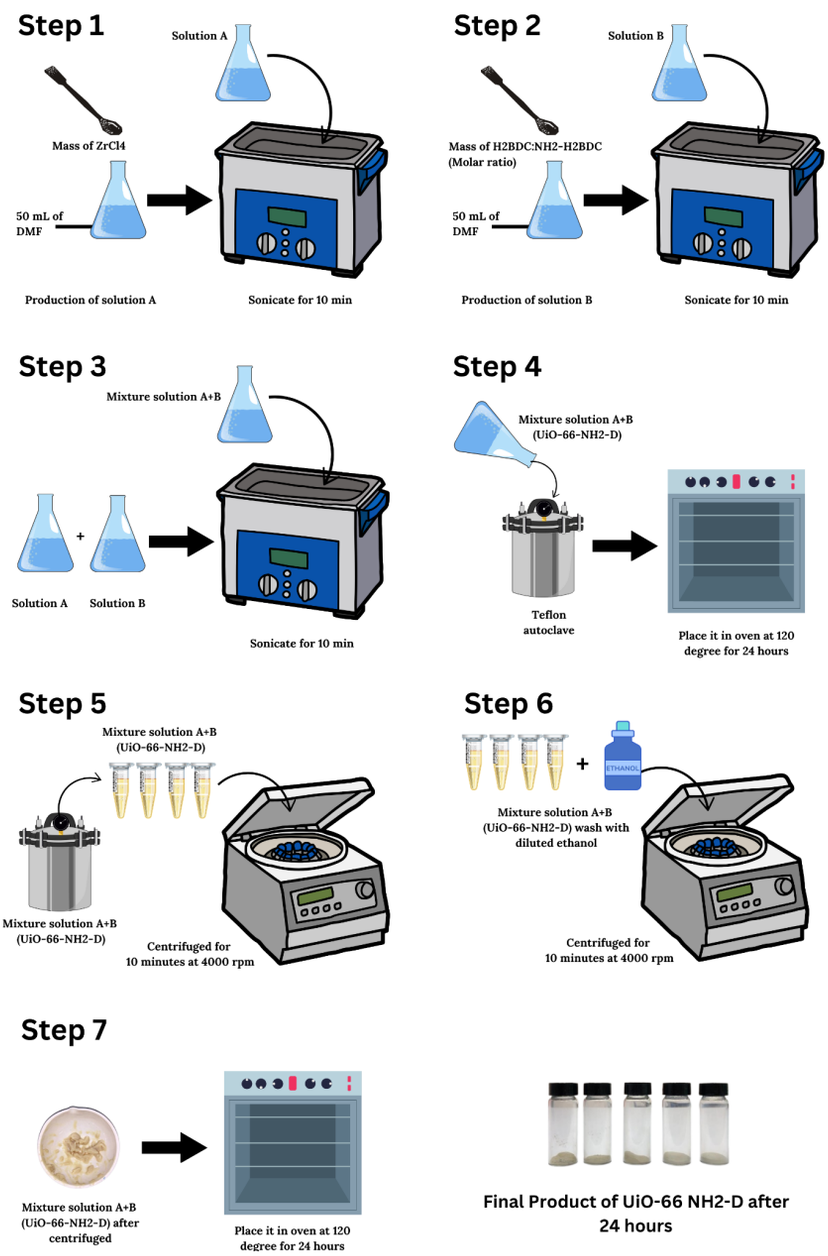

FIGURE 2. Schematic Diagram Illustrating the Synthesis Process of UiO-66-NH_2-D, Highlighting the Reagent Preparation, Ultrasonic Dissolution, Solvothermal Reaction, and Post-Treatment Steps

TABLE 2. Summary of Ligand and $ZrCl_4$ ratios for UiO-66-NH_2-D Synthesis at Different Molar Concentrations (2 mmol to 6 mmol), used to Assess Adsorption Performance

Sample Design	Ratio of H_2BDC:NH_2-H_2BDC	Mass of ligands (H_2BDC + NH_2-H_2BDC (g)	Mass of $ZrCl_4$ (g)
S1 (2 mmol)	1:1	0.6948	0.1737
S2 (3 mmol)	1:1	1.0420	0.2605
S3 (4 mmol)	1:1	1.3892	0.3473
S4 (5 mmol)	1:1	1.7364	0.4341
S5 (6 mmol)	1:1	2.0836	0.5209

CHARACTERISATIONS OF *UIO-66* DOUBLE LIGANDS WITH *NH_2-H_2BDC*

The synthesised *UiO-66* was sent to the Centre for Instrumentation and Science Services at Universiti Malaysia Sabah (UMS) for characterisation purposes. The functional groups and crystallinity of the synthesised *UiO-66 (Zr-MOF)* were analysed using a Fourier Transform Infrared 2D Spectroscopy, PerkinElmer Frontier model (FTIR) and X-ray Diffractometer, Rigaku SmartLab Model (XRD), respectively.

ADSORPTION PROCESS

The adsorption tests were conducted using an orbital shaker. The effectiveness of *UiO-66-NH_2-D* as an adsorbent was tested at raw leachate pH (pH 8) with varying ligand concentrations (2 mmol to 6 mmol). In this study, the dosage of adsorbent, sample volume and reaction time were set as constant parameters at 1 g, 50 mL and 30 minutes, respectively, with stirring at 150 rpm. After that, the samples were left undisturbed for 30 minutes to allow the floc to settle. The supernatant was analysed to determine the percentage removal of *HA* using Equation 1. The schematic diagram for the adsorption process is illustrated in Figure 3. All adsorption experiments were performed in triplicate. Results are expressed as mean ± standard deviation, and error bars represent the standard deviation of the measurements (Figure 6). While no formal statistical tests were conducted, the inclusion of error bars provides a visual representation of variability across replicates.

$$Removal\ efficiency\ of\ HA\ (\%) = \frac{c_o - c_t}{c_o} \times 100 \quad (1)$$

where C_o (mg/L) and C_t (mg/L) refer to the initial concentration and final concentration of HA in the sample, respectively.

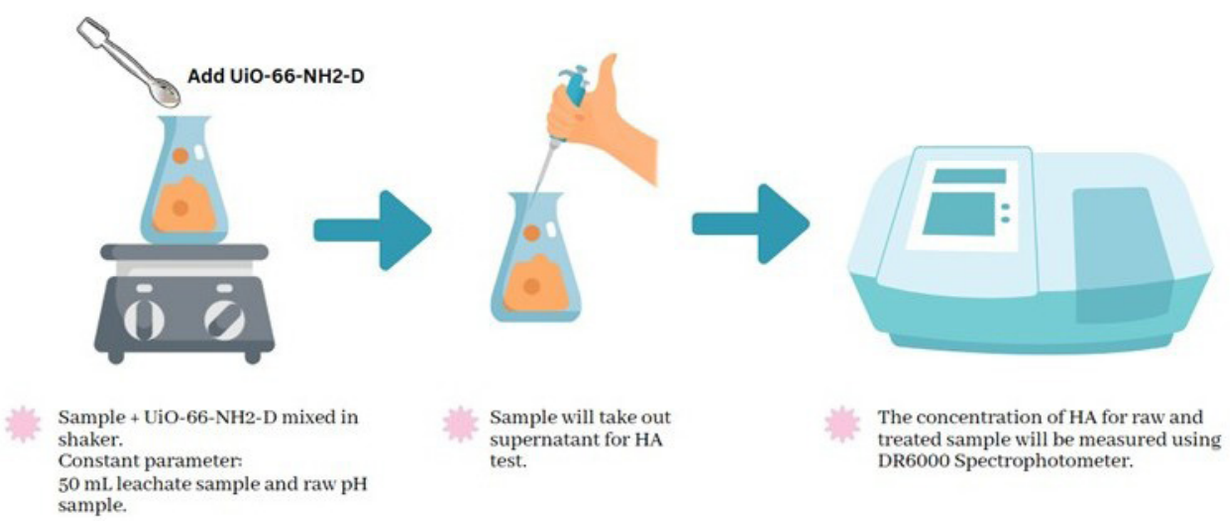

FIGURE 3. Schematic Diagram for Adsorption Test Process

RESULTS AND DISCUSSION

LANDFILL LEACHATE CHARACTERISTICS

The characterisation procedure was conducted to validate the phase and evaluate the quality of the leachate. Table 3 summarises the landfill leachate characteristics. Based on the data presented, most parameters exceed the standard limits by MEQA, such as colour, *COD*, NH_3-*N*, BOD_5 and *SS*. As shown in Table 3, the pH of the leachate samples ranged from 7.2 to 8.4, with an average of 8.1. These results are consistent with the pH range that is expected to be over 7.5 in old landfill leachate (landfill age > 10 years) (Zailani and Zin, 2018). Based on the pH values, the leachate can also be categorised as being in the methanogenic phase.

The monitoring data recorded an average concentration of *HA* at 186.4 mg/L, indicating the presence of decomposed organic material. According to Silva et al. (2019), high *HA* concentrations can lead to biological instability and promote the accumulation of heavy metals.

Next, the parameter tested was colour, with an average concentration of 3,643 PtCo units (Table 3). According to Zakaria and Aziz (2018), a higher colour concentration is typically associated with an increase in pH. Additionally, Aziz et al. (2023) noted that a considerable contribution to colour concentration stems from the presence of large amounts of organic compounds. Specifically, the abundance of non-degraded organic matter, such as humic and fulvic compounds, has been detected in older leachate samples (Zakaria and Aziz, 2018).

Generally, overall pollutant concentration can be represented by using the COD test. As shown in Table 3, the average COD value was 3,681 mg/L. According to Zakaria and Aziz (2018), the average COD value indicates that the landfill site is in the methanogenic phase, where COD levels typically range from 500 to 5,000 mg/L.

Another parameter that exceeds the standard limit set by the MEQA is NH_3-*N*. The average concentration of NH_3-*N* was recorded as 2,250 mg/L, with minimum and maximum values of 1,138 mg/L and 3,800 mg/L, respectively. Kamaruddin et al. (2013) noted that the hydrolysis and fermentation of nitrogenous fractions from biodegradable substrates frequently result in leachate that is high in ammonia nitrogen. Therefore, additional leachate treatment, such as physicochemical methods, is required to meet the MEQA discharge standards.

Additionally, the quantity of organic pollutants that can be biologically oxidised in a sample of water or wastewater is indicated by BOD_5. The average BOD_5 value for the landfill site under study was 163 mg/L, with minimum and maximum values of 62 and 262 mg/L, respectively. According to Zailani and Zin (2018), BOD_5 levels for older landfills (those more than ten years old) typically range from 100 to 200 mg/L. As the BOD_5 values from this site fall within this range, the landfill is classified as an old landfill. However, the MEQA standard for permissible BOD_5 levels is only 20 mg/L, meaning the observed BOD_5 levels significantly exceed the acceptable limit.

Leachate's phase is often determined by the biodegradability ratio, which provides a direct indication of the sample's state. The average biodegradability of the leachate at this landfill site is poor, with a BOD_5/COD ratio of 0.046 and minimum and maximum values of 0.020 and 0.101, respectively. With a BOD_5/COD ratio of less than 0.1, these values classify the leachate as old landfill leachate (Zailani and Zin, 2018). According to a study by Zakaria and Aziz (2018), a low BOD_5/COD ratio suggests that the leachate is persistent and will be challenging for biological degradation. According to the monitoring data presented above, it can be concluded that the landfill leachate at this site is categorised as old landfill leachate and is in the methanogenic phase. Therefore, this landfill leachate is suitable for use as a sample in this study.

TABLE 3. Characteristics of Leachate Landfill near Kota Kinabalu, Sabah from December 2023 until November 2024

No.	Parameter	Unit	Min	Max	Value (Average)	MEQA*
1	Temperature	**°C**	23.5	30.9	26.9	40
2	pH	-	7.2	8.4	8.1	6.0 – 9.0
3	Colour	PtCo	203	7300	3643	100 ADMI
4	COD	mg/L	1251	6000	3681	400
5	NH_3N	mg/L	1138	3800	2250	5
6	BOD_5	mg/L	62	262	263	20
7	BOD_5/COD	-	0.020	0.101	0.046	-
8	DO	mg/L	0.0	5.1	0.6	-
9	SS	mg/L	13	294	146	50
10	Conductivity	**µS/cm**	750	7233	4482	-
11	TDS	mg/L	347	4663	2779	-
12	HA	mg/L	15.8	210.6	186.4	-

Note: *MEQA (MDC, 2014)

FTIR ANALYSIS OF *UIO-66* DOUBLE LIGANDS WITH NH_2-H_2BDC

The FTIR spectra of the adsorbent (*UiO-66*) were analysed to identify the functional groups. The peaks in an FTIR spectrum correspond to specific vibrational modes of chemical bonds within the sample. Each type of bond absorbs infrared radiation at characteristic wavenumbers, and the positions of these peaks can be used to identify the functional groups present in the sample (Naser et al. 2021). The spectra of *UiO-66-NH_2-D* with different molar amounts of ligands are presented in Figure 4. At the same time, Table 4 summarises the wavenumbers obtained for all five samples.

As seen in Table 4, in terms of N-H stretching, S1 (2 mmol), S2 (3 mmol), S4 (5 mmol), and S5 (6 mmol) fall within the range of 3460-3280 cm^{-1}, corresponding to the functional group of primary amines. The intensity of this class is medium. However, for S3 (4 mmol), the N-H stretching is in the range of 3350-3050 cm^{-1} for the functional group of ammonium ions (NH^{4+}). The intensity of this class is very strong. This could indicate the presence of protonated amine groups. For example, the amine group may have accepted a proton to form NH^{4+}, potentially due to acidic conditions during synthesis. Thus, adsorption can occur through NH^{4+} groups, which carry a positive charge, enabling them to interact with negatively charged species in the leachate sample and trap pollutants such as *HA*. This mechanism aligns with the findings of Peng et al. (2022), who highlighted that NH^{4+} groups can establish electrostatic attractions with negatively charged molecules.

Moreover, only S3 (4 mmol) exhibits both O-H stretching and O-H bending vibrations characteristic of the carboxylic acid functional group. The O-H stretching shows strong intensity, while the O-H bending displays medium intensity. The O-H stretching indicates the presence of the carboxylic acid group and is typically associated with hydrogen bonding. According to Francis et al. (2017), the O-H bending further confirms the presence of carboxylic acid groups and can help distinguish whether the acid is free or involved in hydrogen bonding.

Hydrogen bonding plays a crucial role in enhancing adsorption by creating specific interactions between the adsorbent (*UiO-66*) and the adsorbate (*HA* in the leachate). In the case of S3 (4 mmol), the presence of O-H stretching and bending vibrations characteristic of carboxylic acid groups suggests the potential for hydrogen bonding. This can enhance adsorption through strong specific interactions. According to Tan et al. (2021), hydrogen bonds are directional and form specifically between hydrogen atoms bonded to electronegative atoms, such as oxygen in the carboxylic acid group, and electronegative atoms, such as oxygen or nitrogen in the adsorbate molecules. These linkages strengthen the interaction between the adsorbent and contaminants, enabling better entrapment and retention.

In terms of C-H bending, all the samples show peaks in the range of 2000-1650 cm^{-1}, corresponding to the functional group of aromatic compounds. The intensity in this range is weak. For C-N stretching, all the samples exhibit peaks in the range of 1020-1250 cm^{-1}, indicating the presence of amines, with a medium intensity. However, only S3 (4 mmol) shows a strong C-N stretching peak for the aromatic amines functional group (where the amine group is attached to an aromatic ring). This suggests that the interaction between the amine group and the aromatic ring causes a slight shift in the stretching frequency, resulting in a higher wavenumber compared to regular amines. Therefore, it can be concluded that these results, as reflected in the chemical structure of *UiO-66-NH_2-D*, indicate that all the five samples of *UiO-66-NH_2-D* possess an abundance of active sites.

The FTIR analysis revealed weak C-H bending peaks in all samples, indicating the presence of aromatic compounds. Although these vibrations do not directly contribute to adsorption, they indicate the presence of aromatic rings, which can facilitate π-π interactions with organic molecules like *HA*. Due to its significant N-H stretching (3063 cm^{-1}) and O-H vibrations (2665 cm^{-1} and 1424 cm^{-1}), S3 (4 mmol) showed the highest potential for adsorption among the samples. This suggests the presence of abundant active sites for electrostatic interactions and hydrogen bonding with *HA*.

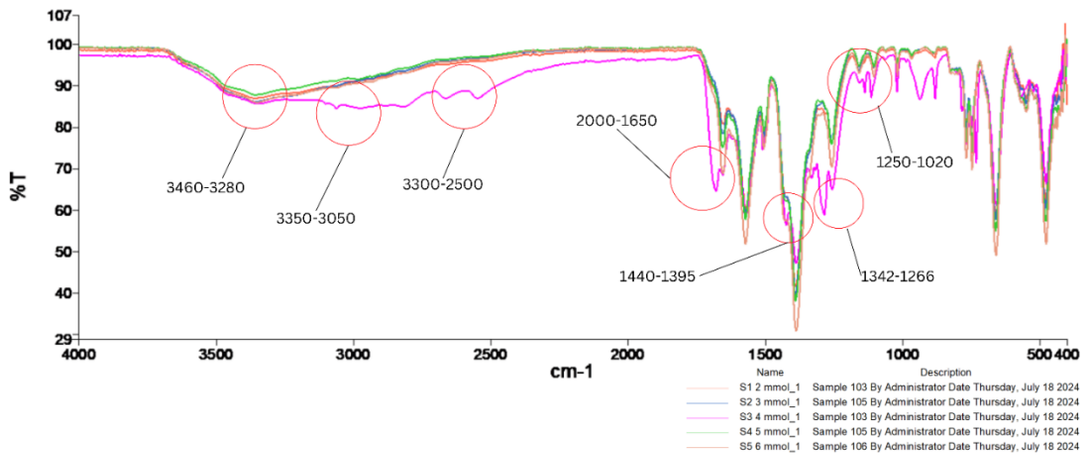

FIGURE 4. FTIR Spectra of UiO-66 Synthesized with Varying Molar Amounts of Ligands (2 mmol to 6 mmol)

TABLE 4. Summary of Wavenumbers Obtained for Five Samples of UiO-66-NH_2-D with Varying Molar Amounts of Ligands

Sample	Wavenumbers (cm^{-1})	Transmittance (%T)	Bond	Group Vibration	Functional Group
S1 (2 mmol)	3363	87.10	N-H	Stretching	Primary Amines
	1651	80.95	C-H	Bending	Aromatic Compound
	1158	93.58	C-N	Stretching	Amine
S2 (3 mmol)	3361	86.44	N-H	Stretching	Primary Amines
	1653	78.59	C-H	Bending	Aromatic Compound
	1158	93.98	C-N	Stretching	Amine
S3 (4 mmol)	3064	84.70	N-H	Stretching	Ammonium (NH^{4+})
	2665	87.16	O-H	Stretching	Carboxylic Acid
	1679	64.57	C-H	Bending	Aromatic Compound
	1424	56.34	O-H	Bending	Carboxylic Acid
	1285	58.84	C-N	Stretching	Aromatic Amine
	1137	88.58	C-N	Stretching	Amine
S4 (5 mmol)	3358	87.93	N-H	Stretching	Primary Amines
	1655	75.18	C-H	Bending	Aromatic Compound
	1158	94.95	C-N	Stretching	Amine
S5 (6 mmol)	3354	86.25	N-H	Stretching	Primary Amines
	1655	68.92	C-H	Bending	Aromatic Compound
	1157	93.30	C-N	Stretching	Amine

XRD ANALYSIS OF *UIO-66* DOUBLE LIGANDS WITH *NH_2-H_2BDC*

X-ray diffraction (XRD) is a non-destructive analytical method in solid-state chemistry, used to determine crystal structures and characterise crystals through unique diffraction patterns (Bunaciu et al. 2015). The analysis was conducted over a 2θ range of 5° to 80°, with a scanning rate of 4.00°/min and a step size of 0.01°. XRD analysis was employed to determine the phase identification, degree of crystallinity, and structural characteristics of *UiO-66-NH_2-D*.

As shown in Figure 5, the most prominent diffraction peaks for the synthesised *UiO-66-NH_2-D*, with varying molar amounts of ligands, were observed below a scattering angle (2θ) of 10°, confirming its identity as a MOF with high crystallinity. The three main peaks for all samples appeared at 7.3°, 8.5°, and 12.0°, aligning with the characteristic diffraction patterns of *UiO-66-NH_2-D* reported in previous studies. Rahmawati et al. (2014) revealed that the intensity of peaks in the XRD pattern provides information about the degree of crystallinity of *UiO-66*, particularly at 2θ values of 7.3°, 8.5°, and 25.6°. Similarly, Zhang et al. (2020) reported prominent peaks at 7.4°, 8.5°, and 25.8°. Table 6 summarises the three main

peaks obtained from the synthesis of *UiO-66-NH_2-D*, with varying molar amounts of ligands, as illustrated in Figure 5.

Based on Table 5, the signal peaks of the five different *UiO-66-NH_2-D* samples showed no significant differences, except for a slight drop in the second peak at S3 (4 mmol) to 8.4°. This result indicates that the phase of *UiO-66-NH_2-D* remained unchanged. According to Kebede Gurmessa et al. (2023), porous materials, characterised by numerous pores or cavities, exhibit intense peaks at small 2θ angles due to the inverse relationship between 2θ and the adsorbent's porosity. Similarly, Rahmawati et al. (2014) stated that peaks below 10° signify high crystallinity, often regarded as a standard for 100% crystallinity. Thus, it can be concluded that all five samples of *UiO-66* exhibit a well-defined structure and high crystallinity.

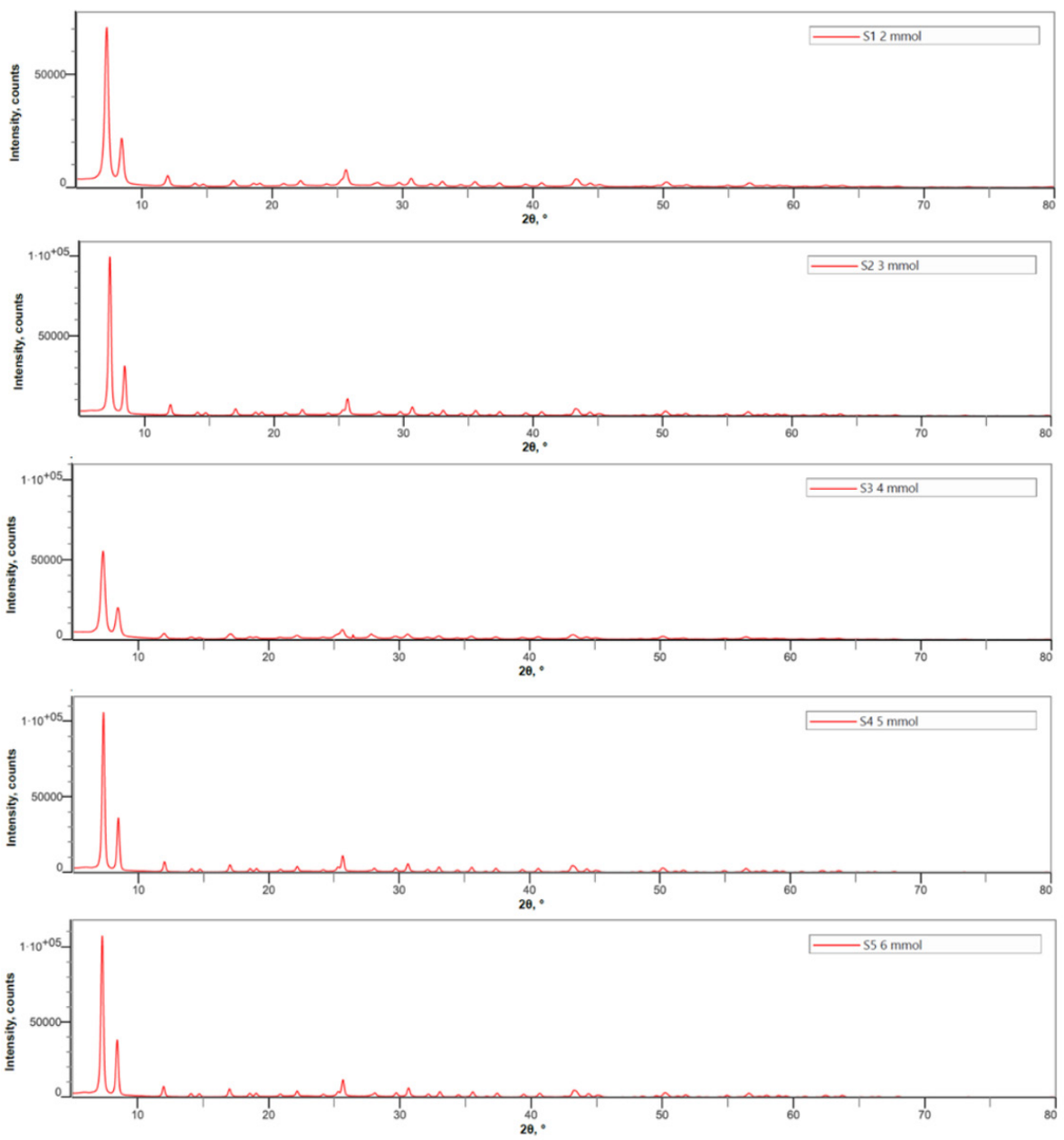

FIGURE 5. XRD Patterns of UiO-66-NH_2-D Synthesized with Varying Molar Amounts of Ligands (2 mmol to 6 mmol)

TABLE 5. The Three Main Peaks of UiO-66 Synthesized with Varying Molar Amounts of Ligands

Sample	Description
S1 (2 mmol)	The three main peaks obtained were 7.3°, 8.5°, and 12°.
S2 (3 mmol)	The three main peaks obtained were 7.3°, 8.5°, and 12°.
S3 (4 mmol)	The three main peaks obtained were 7.3°, 8.4°, and 12°.
S4 (5 mmol)	The three main peaks obtained were 7.3°, 8.5°, and 12°.
S5 (6 mmol)	The three main peaks obtained were 7.3°, 8.5°, and 12°.

PERFORMANCE OF *UIO-66-NH_2-D* AS ADSORBENT

The effectiveness of *UiO-66-NH_2-D* as an adsorbent was tested by varying molar amounts of ligands (2 mmol to 6 mmol) and under consistent experimental conditions. The results are presented in Figure 6.

As illustrated in Figure 6, the removal effectiveness of *HA* increases steadily as the molar number of ligands in *UiO-66-NH_2-D* rises from 2 mmol to 4 mmol. Specifically, the removal percentage starts at 38.8% at 2 mmol, increases to 43.1% at 3 mmol, and reaches a peak of 44.4% at 4 mmol. A study by Zaimee et al. (2021) on adsorption revealed that increasing the dosage of adsorbent enhances the availability of active adsorption sites, which trap *HA* and improve *HA* removal. Based on a study by Al-Saedi et al. (2021), the N-H stretching of ammonium ions (NH^{4+}) may influence the porosity and the number of available adsorption sites. This effect could be beneficial, as leachate carries a negative charge and can interact with NH^{4+} through electrostatic interactions. Moreover, at this molar amount, the balance between the number of active adsorption sites and the concentration of *HA* molecules in the leachate may be at its most effective point.

Prior FTIR results shown in Table 4 are also consistent with *UiO-66's* efficacy in removing *HA* (Figure 6). For instance, the protonated amine group (NH^{4+}) is responsible for the significant N-H stretching seen at 3063 cm^{-1} in S3 (4 mmol), which increases electrostatic interaction with negatively charged *HA* molecules. Additionally, the adsorption process is further aided by the presence of O-H stretching and bending vibrations in S3 (4 mmol), which demonstrate the function of carboxylic acid groups in hydrogen bonding. The 4 mmol sample had the maximum removal efficiency, which can be attributed to the active sites discovered using FTIR.

However, the *HA* removal decreases slightly beyond the optimal value of 4 mmol, with removal percentages of 40.1% and 40.8% observed at 5 mmol and 6 mmol, respectively. Although these values remain higher than the efficiency at 2 mmol, the reduction in performance highlights diminishing returns at higher ligand concentrations. This decline may be attributed to the oversaturation of active sites or particle aggregation. At high ligand concentrations, excess functional groups may lead to increased steric hindrance, blocking access to the internal pores and limiting interaction between *HA* molecules and active sites.

Additionally, the higher ligand concentrations may promote the formation of denser agglomerates during synthesis, reducing surface area and pore accessibility. Such aggregation can negatively affect diffusion and adsorption dynamics, ultimately lowering removal efficiency. These observations are supported by Obayomi et al. (2024), who reported that higher molar amounts can obstruct active adsorption sites by adsorbate (*HA*) molecules, thereby slightly lowering the removal efficiency. Thus, 4 mmol represents the optimal balance between sufficient active functionalisation and structural accessibility for effective *HA* adsorption.

To summarise, this study offers valuable insights into *SAL* treatment. It helps with optimising *HA* removal while minimising expenses by determining that 4 mmol is the ideal molar amount for synthesising *UiO-66-NH_2-D*. This balance is crucial for large-scale applications, where excessive use of ligands could lead to unnecessary expenses and reduced cost efficiency. Furthermore, the decrease in *HA* concentrations from 210.6 mg/L to 117.1 mg/L emphasises *UiO-66's* potential as a valuable and efficient adsorbent for the treatment of *SAL*.

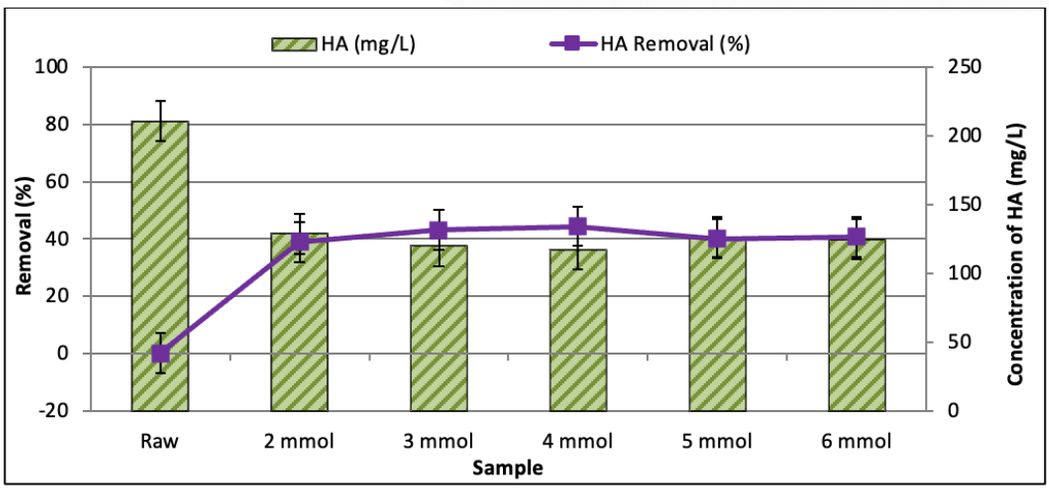

FIGURE 6. Performance of UiO-66 Double Ligands with NH_2-H_2BDC towards HA Removal

CONCLUSION

Monitoring the characteristics of landfill leachate at near Kota Kinabalu, Sabah, shows that the landfill leachate is categorised as old and stabilised, with low *BOD_5/COD* ratio (< 0.1), high *COD* levels (3681 mg/L on average), pH 8.1, high *NH_3-N* (2250 mg/L) and notable *HA* concentrations (186.4 mg/L). The performance of *UiO-66-NH_2-D* for the adsorptive removal of *HA* was evaluated in batch mode by varying the molar amounts of ligands (2 mmol to 6 mmol) while keeping dosage, pH, and reaction time constant. The results demonstrated that *UiO-66-NH_2-D* effectively removed *HA* from landfill leachate, with the 4 mmol sample achieving the highest removal efficiency of 44.4% at a dosage of 1 g and a reaction time of 30 minutes. Characterisation analyses (*FTIR* and *XRD*) confirmed that *UiO-66-NH_2-D* possesses a high degree of crystallinity and abundant active sites, which significantly contribute to *UiO-66's* strong adsorption performance. Thus, considering the *FTIR* and *XRD* results, the adsorption mechanisms to remove *HA* are likely to involve electrostatic interactions and hydrogen bonding.

Additionally, π-π interactions may also play a role, as the aromatic rings in *HA* can interact with the benzene rings of the *UiO-66-NH_2-D*, forming stable non-covalent interactions that enhance adsorption performance. This interaction is supported by the *FTIR* results, which show C-H bending within the aromatic region, indicating the presence of aromatic structures that can facilitate such stacking interactions. Based on the results, it can be concluded that *UiO-66-NH_2-D* is a promising adsorbent and could serve as an alternative method for removing *HA* from stabilised landfill leachate. The authors recommend that future studies should focus on analysing *UiO-66-NH_2-D's* long-term stability and regeneration potential, evaluating its performance under various operating conditions, such as pH, temperature, and reaction time, and investigating the feasibility of scaling up the synthesis process. Additionally, studies should investigate the integration of this adsorbent into existing treatment systems to enhance the overall efficiency of conventional leachate treatment technologies.

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DECLARATION OF COMPETING INTEREST

None.

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