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Environmental assessment of metal-organic framework DUT-4 synthesis and its application for siloxane removal

Sandra Pioquinto-García^{†§}, Juana María Rosas[§], Margarita Loredo-Cancino[†], Sylvain Giraudet^{†,‡}, Eduardo Soto-Regalado[†], Pasiano Rivas-García^{†}, Nancy E. Dávila-Guzmán^{†*}.*

[†] Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, UANL, Av. Universidad S/N, Cd. Universitaria, San Nicolás de los Garza, Nuevo León, 66455, México.

[‡] Centro de Investigación en Biotecnología y Nanotecnología, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León. Parque de Investigación e Innovación Tecnológica, km 10 Highway to the International Airport Mariano Escobedo, Apodaca, Nuevo León, 66629, México.

[§] Departamento de Ingeniería Química, Facultad de Ciencias, Universidad de Málaga, Andalucía TECH, Campus de Teatinos s/n, Málaga, 29010, Spain.

^{†,‡} Ecole Nationale Supérieure de Chimie de Rennes, 11 Allée de Beaulieu, 35708 Rennes, France.

Corresponding Authors

* Nancy Elizabeth Dávila-Guzmán, **E-mail:** nancy.davilagz@uanl.edu.mx, **Phone number:** 52-8183294000, ext. 3475

* Pasiano Rivas García, **E-mail:** pasiano.rivasgr@uanl.edu.mx

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ABSTRACT

In this study, the effect of different solvents in metal-organic framework (MOF) synthesis was evaluated in a technical study and an environmental study. The technical study considered the octamethylcyclotetrasiloxane (D4) adsorption on MOF DUT-4 for biogas purification, while the environmental study was implemented using the Life Cycle Assessment (LCA) methodology. In addition, the obtained DUT-4 adsorbents were characterized by X-ray diffraction, N₂ adsorption-desorption isotherms, solid-state ²⁷Al magic-angle spinning nuclear magnetic resonance, scanning electron microscopy, and Fourier transform infrared spectroscopy techniques. The results indicated that technically similar materials are obtained through solvothermal synthesis with similar D4 siloxane adsorption capacities (9.8 mg/g). Conversely, hydrothermal synthesis led to a low D4 siloxane adsorption capacity (1.8 mg/g). The environmental study demonstrated that the solvothermal synthesis had the highest contribution to the environmental damage due to the use of toxic solvents in the synthesis, cleaning, and solvent exchange stages (environmental score factor up to 244 mPt). In addition, a techno-environmental impact factor was introduced to identify the most suitable synthesis route of DUT-4. The overall results pointed out that

solvothermal synthesis is the best scenario for DUT-4 production due to its low environmental impact/adsorption capacity ratio (11.44). This study is a step toward a more holistic approach integrating technical and environmental criteria in MOF synthesis for adsorption applications.

INTRODUCTION

Renewable energies have been the focus of attention among countries due to the continuous increases in the price of fossil fuels and the need for environmental care. Biogas is a green energy source that is used as a cleaner transportation fuel [1]. Basically, the biogas is a mixture of methane (35–70 %), carbon dioxide (15–50 %), and small amounts of undesirable compounds (<2 %) such as H₂S (~1560 ppmv), NH₃ (~91 ppmv), CO (~416 ppmv), H₂ (~367 ppmv), moisture, and volatile compounds [2-5].

Among the volatile compounds found in biogas, siloxanes are of great interest given their adverse effects on combustion systems. After combustion, the siloxanes decompose into two new products: formaldehyde and orthosilicic acid [6]; these products form a soft paste that contributes to abrasion, metal friction, and failure of mechanical elements of the combustion system.

Siloxane removal from biogas is a priority for advancing the energy recovery potential of biogas. Current technologies for siloxane removal from biogas include adsorption, absorption, cryogenics, separation by membranes, and biological processes [7-10]. Nevertheless, the adsorption process with activated carbon (AC) is the most used siloxane removal technique due to its relatively low acquisition cost [10-12] and efficiency (90–99 %), achieving siloxanes concentration up to 0.1 mg/m³ in the biogas [9]. However, the main drawback of using AC is the high regeneration temperature (>400 °C), causing high operation costs. Accordingly, new

adsorbent materials as metal-organic frameworks (MOF) have been recently developed to overcome the shortcomings of several conventional adsorption processes.

MOF are porous materials formed by metal centers linked with organic ligands (coordination compounds). Their type of permanent pore and cavity depends on the geometric characteristics of the metallic units and the organic ligands of the MOF. Due to high porosity and surface area, easy modification, thermal stability, and regeneration [13], MOF have been widely used in catalysis, gas adsorption [14,15], optics, magnetism [13], and chemical sensors [16]. Recently, Mito-oka et al. [17] employed the MOF developed by Dresden University Technology 4 (DUT-4) and conventional AC for siloxane adsorption. The results showed that the DUT-4 has high selectivity and uptake even in wet conditions compared to AC performance. The DUT-4 removal efficiency at 30 °C was higher than 90 %, and the AC removal efficiency was 70 % at 500 min of operation. The DUT-4 removal efficiency was attributed to its strong hydrophobicity and optimal chemical interactions with siloxane octamethylcyclotetrasiloxane (D4). Secondly, Gargiulo et al. [18] demonstrated the high affinity of the MOF MIL-101(Cr) for the removal of siloxane D4 as well as the complete regeneration of this adsorbent at moderated temperature (150 °C). The authors indicated that contrary to AC and silica gel (SG), D4 removal by MIL-101(Cr) does not cause polymerization of D4 on the adsorbent surface, which allowed its reusability.

Although MOF have been pointed out as "green materials" for sustainable processes, the environmental impact of their synthesis has been barely evaluated. The Life Cycle Assessment (LCA) is a methodology that can determine how green a material is [19]. For example, LCA has been used by Loya-González et al. [20] and Sepúlveda-Cervantes et al. [21] to determine the impacts of some adsorbent materials such as AC synthesized from biomass waste. In these works, the impregnation stage of the AC production was found to be the largest contributor to

environmental damage, owed to the high energy consumption and the use of chemicals such as ZnCl_2 and KOH . Grande et al. [22] evaluated the environmental impact of the MOF CPO-27-Ni synthesized by four different routes. They found that the main contributors to the environmental impact of CPO-27-Ni were the synthesis and cleaning stages, mainly associated with the toxicity of tetrahydrofuran and dimethylformamide. When water was used in the synthesis or cleaning stages, the environmental impact was reduced from 1136.2 to 12.3 kg CO_2 eq per kg of MOF.

To the authors' knowledge, there is no literature available that addresses the environmental impact assessment of the synthesis of DUT-4, and this is of particular interest because DUT-4 is a promising material for cleaner biogas production. Therefore, this work aims to evaluate the environmental impact of the MOF DUT-4 through the LCA methodology, proposing alternatives to reduce its environmental impact. In addition, a new techno-environmental impact factor is introduced to choose the most suitable synthesis route of MOF for adsorption applications.

MATERIALS AND METHODS

DUT-4 synthesis routes

Synthesis of DUT-4(DMF). The synthesis of DUT-4(DMF) is based on the procedure described by Senkovska et al. [23]. A solution of 0.26 g 2,6-naphthalene dicarboxylic acid in 30 mL of N,N-dimethylformamide (DMF), and 0.52 g nonahydrate aluminum nitrate was mixed in a Teflon liner. The liner was placed into a 250 mL autoclave and heated at 120 °C for 24 h. Afterwards, the autoclave was allowed to cool to room temperature before it was opened. The product was washed three times with 20 mL portions of DMF and centrifuged for 2.5 min at 10,000 rpm between each washing step. The final product was dried in an oven at 120 °C for 4 h.

Synthesis of DUT-4(DCM). The synthesis of DUT-4(DCM) was carried out by including a solvent exchange step in the synthesis of DUT-4(DMF). After the washes with DMF, the product was washed three times with 20 mL of dichloromethane (DCM) for 20 min and centrifuged for 2.5 min at 10,000 rpm between each wash. The final product was dried in an oven at 120 °C for 4 h.

Synthesis of DUT-4(H). In the synthesis of DUT-4(H), a second solvent exchange stage was included in the DUT-4(DMF) procedure synthesis. After the solvent exchange of DCM, the powder was washed three times with portions of 20 mL of hexane for 20 min. Then, the product was centrifuged and dried in the same manner as in the synthesis of DUT-4(DMF).

Synthesis of DUT-4(W). This synthesis was carried out using deionized water instead of DMF to contribute to a greener production. A solution of 0.26 g 2,6-naphthalene dicarboxylic acid in 30 mL of water and 0.52 g nonahydrate aluminum nitrate were mixed in a Teflon liner. The liner was placed into a 250 mL autoclave at 120 °C for 24 h. The autoclave was cooled to room temperature before it was opened. The content was centrifuged for 2.5 min at 10,000 rpm, then washed three times with portions of 20 mL of water. Finally, the product was dried in an oven at 120 °C for 4 h.

Characterization techniques of the adsorbents

Physicochemical characterization. X-ray diffraction patterns (XRD) were recorded on a X'Pert PRO MPD diffractometer (PANalytical, Germany) using Cu-K α radiation (40 mA and 45 kV). The relative crystallinity was determined by the area under the curve of the crystalline peaks (after baseline correction). The specific surface area (A_s) of DUT-4 was obtained by N₂ physisorption at 77 K using automatic equipment ASAP 2020 (Micromeritics, USA), after out-

gassing the DUT-4 at 150 °C for 8 h. Solid-state ^{27}Al MAS NMR spectra were recorded at room temperature in an AVANCE III HD 600 MHz (Bruker, Germany) NMR spectrometer using triple resonance DVT probe of 2.5 mm at a spinning rate of 20kHz, with a length pulse of 0.27 μs and a 1 s delay with ^1H decoupling and summing up 2000 scans. Scanning electron microscopy (SEM) images were obtained using a JSM-6490LV microscope (JEOL, USA) with acceleration voltage from 0.3 to 30 kV and thermionic electron gun with W filament. FTIR spectra were obtained from a Tensor 27 (Bruker, Germany) using a Golden Gate Single Reflection diamond ATR cell and a standard spectral resolution of 4 cm^{-1} in the spectral range of $4000\text{--}500\text{ cm}^{-1}$.

Adsorption experiments. The adsorption experiments were carried out at a $450\text{ mg}/\text{Nm}^3$ D4 initial concentration, 100 mg of adsorbent material, and room temperature. Flasks were stirred at 700 rpm for 6–9 h to ensure equilibrium. During the adsorption experiments, the samples were analyzed for D4 concentration by gas chromatography. Each sample was injected into a Nexis GC-2030 gas chromatograph (Shimadzu, Japan) with a flame ionization detector (FID) to measure the concentration of siloxane D4. The SH-Rxi-5ms Shimadzu capillary column (15 m x 0.25 mm inner diameter x 0.25 μm film thickness) was used. The inlet oven and detector temperatures were set at 150, 110, and 250 °C, respectively. Helium was used as carrier gas at a constant flow rate of 1.5 mL/min and 83.3 kPa. The injected volume was 0.5 mL with split ratio 5.0; the duration of the method was 1.4 min. The adsorption capacity was determined by mass balance as follows:

$$q = \frac{(C_o - C)V}{m} \quad \text{Eq. (1)}$$

where q is the adsorption capacity (mg/g), C_0 is the D4 initial concentration (mg/Nm³), C is the D4 concentration over time (mg/Nm³), V is the volume (m³), and m is the adsorbent mass (g).

Life cycle assessment implementation

Goal and scope definition of the product system. The LCA of the DUT-4 production process on a laboratory scale was carried out as per ISO 14044 [24]. The system boundary for DUT-4 includes five stages: mixing, synthesis, cleaning, solvent exchange, and drying (Figure 1). In this analysis, the environmental burdens associated with the laboratory equipment construction used in the production of DUT-4 were not considered for two reasons: on the one hand, because it has been reported that its contribution to the environmental impact is less than 2% [25], and on the other, to maintain consistency with other LCA studies on the production of adsorbent materials on a laboratory scale (Sepúlveda-Cervantes et al., 2018; Loya-Gonzalez et al., 2019; Luo et al., 2021).

Each of the different DUT-4 synthesis strategies was considered as study scenarios:

- Scenarios DUT-4(DMF) and DUT-4(W): include the stages of mixing, synthesis, cleaning, and drying.
- Scenarios DUT-4(DCM) and DUT-4(H): consider mixing, synthesis, cleaning, solvent exchange, and drying.

These scenarios are represented in the system boundaries, as shown in Figure 1. The functional unit (FU) was defined as the production of 1 g of DUT-4 produced on a laboratory scale. The FU was established on a mass basis, according to other LCA studies of adsorbents materials production (e.g., activated carbon and MOF-74 [21], [22]).

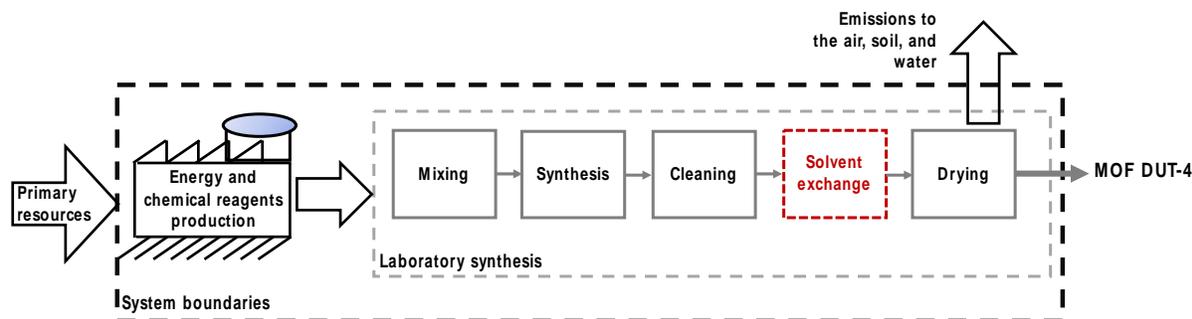


Figure 1. System boundaries for the production of DUT-4.

Data collection and inventory. The Life Cycle Inventory (LCI) was obtained by collecting inventory data from the laboratory logs, analytical procedures, and material-energy balances. A detailed description of data collection and sources is provided in the Supporting Information (SI). All experimental values are based on at least quadruplicate measurements with a coefficient of variation less than 4%.

The system inputs considered in this study include chemical reagents and energy demands (in the form of electricity). The LCI for these resources was taken from the Ecoinvent v3.3 database [26] (Table S3). The energy consumption in the synthesis stage was calculated with an energy balance that considers sensible heat and Teflon liner and autoclave reactor heating (Eq. S1). The cleaning and solvent exchange stages include the separation of the solvent by centrifugation. The energy consumption in these stages was calculated by the rotational kinetic energy equation (described in detail in Section S.2). Finally, the energy consumption in the drying stage was obtained by calculating the heat energy required to remove the solvent per unit mass of DUT-4 [27] (a detailed explanation is provided in Section S.3).

The corresponding system outputs were the final MOF DUT-4 product and emissions related to solvent evaporation in the drying stage. The solvent emissions were estimated by the differences

between the weights of DUT-4 samples before and after being dried in an oven at 120 °C for 4 h. The wastewater generated in the cleaning stage was disposed of as per our university's hazardous waste management program [28]. Therefore, the environmental impacts of the final disposal of this waste were not considered in the LCI, as reported by Loya-González et al. [20] and Sepúlveda-Cervantes et al. [21].

Life Cycle Impact Assessment. The model used in the Life Cycle Impact Assessment (LCIA) was the ReCiPe 2016 method [29], considering midpoint and endpoint indicators. The LCIA was implemented through the LCA software SimaPro 7.3.3 (Pre Consultants, Amers-foort, the Netherlands).

RESULTS AND DISCUSSIONS

Physicochemical characterization

The FTIR spectrum of DUT-4(DMF), DUT-4(DCM), DUT-4(H), and DUT-4(W) showed similar adsorption bands (Figure 2). The band in the range 1693–1668 cm^{-1} in each of the spectra corresponded to the stretching vibration of ($\nu(\text{C}=\text{O})$) of the carbonyl group, which is indicative of the coordination of the linker to the metal ion [29]. The band in each spectrum at 1614–1598 cm^{-1} corresponded to asymmetric stretching vibrations of the carboxylate group ($\nu_{as}(\text{C}-\text{O})$) [30]; the bands in the range 1434–1415 cm^{-1} corresponded to symmetric stretching vibrations of the carboxylate group ($\nu_s(\text{C}-\text{O})$), and the peaks observed at 989–985 cm^{-1} are related to the bending of the bridging groups $\delta(\text{O}-\text{H})$ [31]; the bands between 792 and 783 cm^{-1} in each of the spectra corresponded to flexions into the aromatic plane [32], [33], and the bands between 586–561 cm^{-1} in the four spectra were associated with the stretching vibrations of the aluminum atom with

oxygen atoms ($\nu(\text{Al-O})$) [34]. Additionally, in the DUT-4(W) spectrum, the band at 1294 cm^{-1} was associated with the ($\nu(\text{C-O})$) stretching vibration, and the bands at $921\text{--}914\text{ cm}^{-1}$ were due to the ($\delta(\text{O-H})$) bend [35].

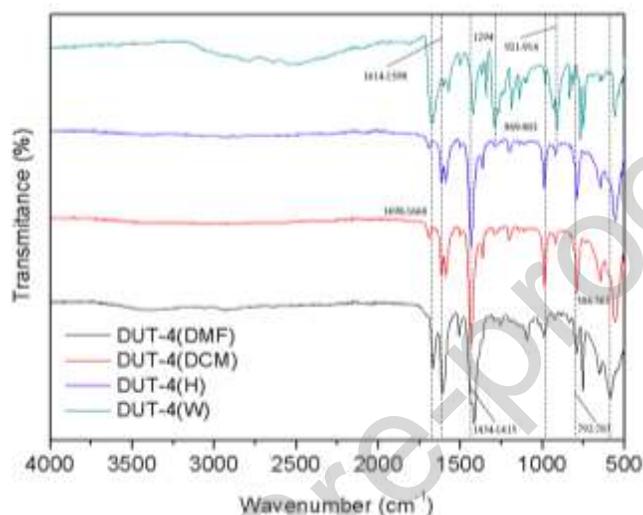


Figure 2. FTIR/ATR spectra for DUT-4(DMF), DUT-4(DCM), DUT-4(H), and DUT-4(W).

Solid-state ^{27}Al MAS NMR spectroscopy was used to determine the local chemical environment and the coordination state of the metal sites. Here, the ^{27}Al MAS NMR spectra for DUT-4(DMF), DUT-4(DCM), DUT-4(H), and DUT-4(W) were obtained (Figure 3). The primary resonating signal of all the materials studied corresponded to 6-fold coordinated aluminum sites ($\text{Al}^{[6]}$) [36], [37], with three overlapped signals in the chemical shift range between -20 to 10 ppm as reported by Volkringer et al. [38] for the Al-MIL-100 structure. According to Vyalikh et al. [39], differences in aluminum sites are due to coordination with distinct types of OH groups; i.e., each aluminum site is coordinated to different OH-groups that participate in intralayer and interlayer hydrogen bonds, causing changes in the chemical environment. Altogether, the NMR spectra for DUT-4 demonstrate the presence of octahedral aluminum sites in the MOF structure.

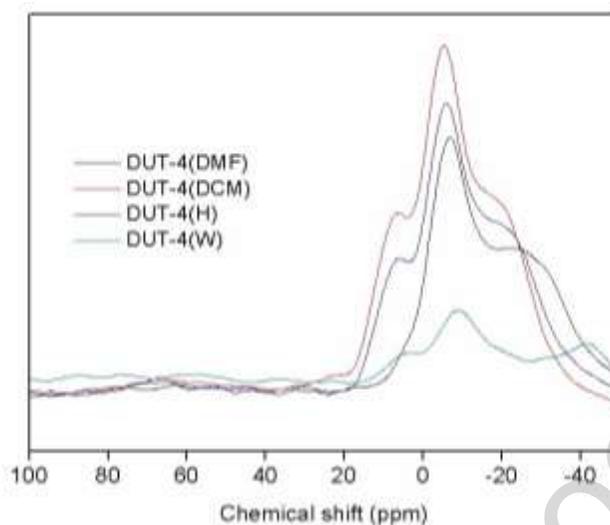


Figure 3. ^{27}Al MAS NMR Spectra for DUT-4(DMF), DUT-4(DCM), DUT-4(H), and DUT-4(W).

The diffraction patterns of as-synthesized samples of DUT-4 by solvothermal synthesis show characteristic peaks at 6.95° , 13.91° , and 21.04° , corresponding to (101), (110), and (113) Miller indices, respectively, and an orthorhombic symmetry according to Senkovska et al. [23]. A significant increase in the relative intensity of the diffraction Bragg peaks was observed on the XRD pattern of DUT-4(DCM) and DUT-4(H) compared to DUT-4(DMF). The calculated crystallinity percentages were 70.82 %, 89.26 %, and 88.74 % for DUT-4(DMF), DUT-4(DCM), and DUT-4(H), respectively. These results suggest that the use of low surface tension solvents instead of DMF improves the crystallinity of the MOF and prevents structural collapse [40]. On the other hand, the hydrothermal synthesis of DUT-4(W) allowed to obtain a structure with 89.89 % crystallinity but non-isostructural to DUT-4 (Figure 4). The higher intensity peaks of the DUT-4(W) phase were 16.39° and 27.74° , which are similar to the organic linker 2,6-naphthalene dicarboxylic acid [41]. It has been reported that water molecules can prevent the coordination between the organic linkers and the ion atoms by hydrogen bonding interactions with the organic linkers [42].

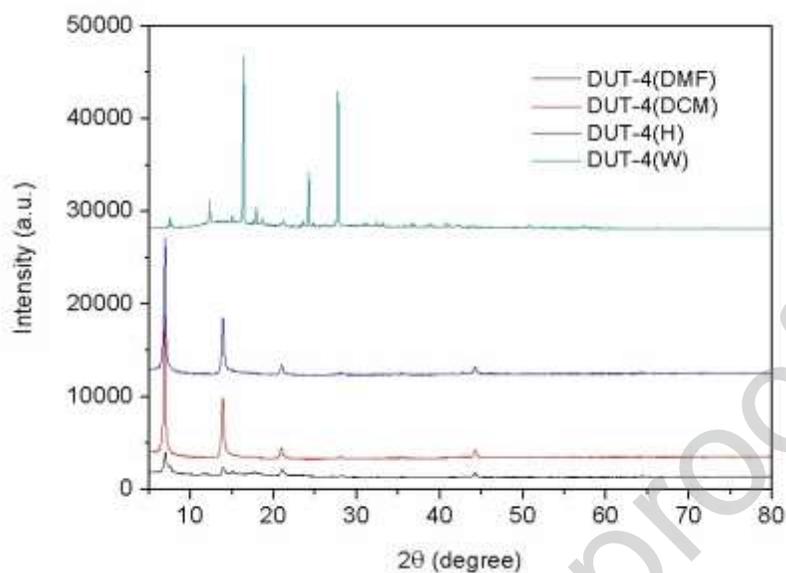


Figure 4. XRD pattern obtained from DUT-4(DMF), DUT-4(DCM), DUT-4(H), and DUT-4(W) powders.

The specific surface area of the synthesized DUT-4(DMF) had a similar value ($1348 \text{ m}^2/\text{g}$) to that reported by Senkovska et al. [23] ($1308 \text{ m}^2/\text{g}$). According to Howarth et al. [43], the solvent exchange with low surface tension solvents helps to achieve the highest possible surface area and porosity. Accordingly, a solvent exchange of DMF for CH_2Cl_2 was carried out to obtain the DUT-4(DCM) material, although a slight reduction of 12 % of the A_s was observed ($1184 \text{ m}^2/\text{g}$). To overcome this reduction on the A_s , DUT-4(DCM) was subjected to a second solvent exchange process where DCM was exchanged for C_6H_{14} , and the as-synthesized material was named DUT-4(H). The specific surface area of DUT-4(H) ($1335 \text{ m}^2/\text{g}$) was very similar to that obtained for DUT-4(DMF). Thus, high specific surface areas were obtained by solvothermal synthesis, irrespective of the solvent exchange. The total pore volumes for DUT-4(DMF), DUT-4(DCM), and DUT-4(H) were 1.71 , 1.48 , and $1.46 \text{ cm}^3/\text{g}$, respectively. A hydrothermal synthesis was carried out to use a greener solvent such as water instead of the toxic DMF solvent.

However, a low specific surface area was obtained ($1.78 \text{ m}^2/\text{g}$), as well as low total pore volume ($0.003 \text{ cm}^3/\text{g}$). Usually, water-based MOF has low porosity in comparison with MOF obtained by solvothermal synthesis [44].

The particle size of the materials obtained by solvothermal synthesis depended on the solvent used in the drying stage. When low surface tension solvents were used (DCM, 29.5 and H, 18.8 dyn/cm), a small particle size was obtained. For instance, DUT-4(DCM) and DUT-4(H) particle size was lower than 500 nm . Conversely, when a high surface tension solvent such as DMF (37.9 dyn/cm) was used, the particle size of DUT-4(DMF) was greater than $1 \mu\text{m}$ (Figure 5). Similar results were obtained for the hydrothermal synthesis (H_2O , 72.8 dyn/cm), where particles of different sizes exceeding $3.25 \mu\text{m}$ were found. The formation of larger agglomerates during drying of the DUT-4(DMF) and DUT-4(W) was due to the capillary forces overcoming the repulsive forces between the particles; therefore, the particles came closer to each other [45,46].

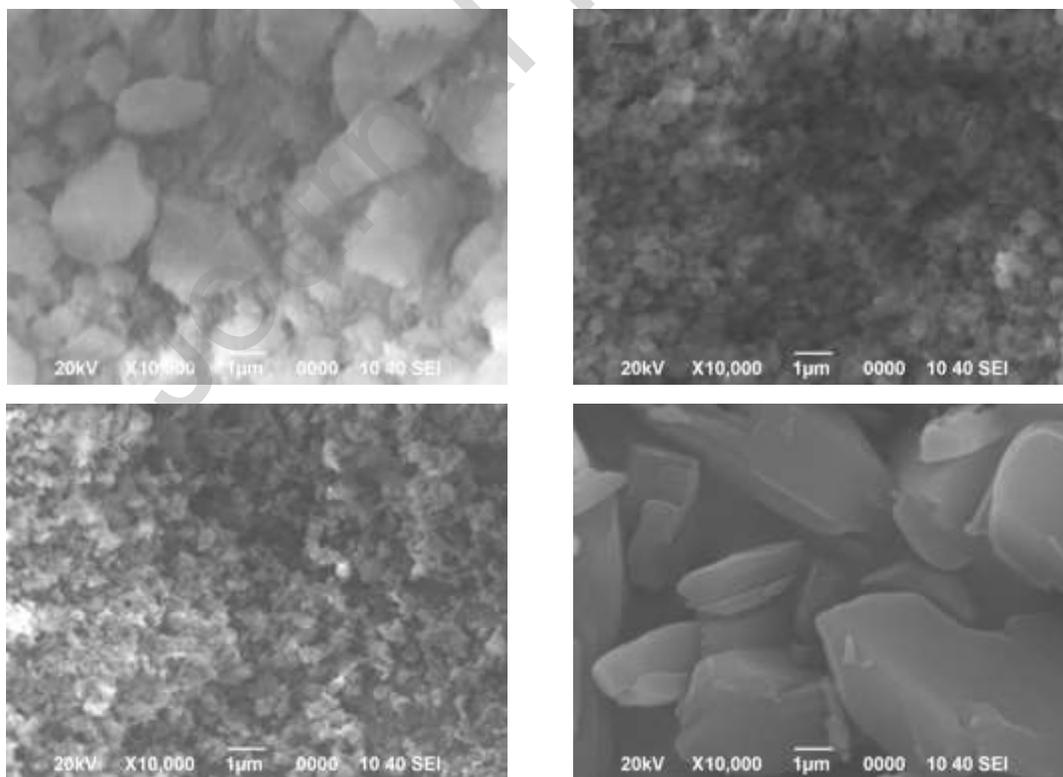


Figure 5. SEM image for a) DUT-4(DMF), b) DUT-4(DCM), c) DUT-4(H), and d) DUT-4(W).

In summary, according to the FTIR and NMR analysis, the spectra of the materials obtained by solvothermal and hydrothermal synthesis show the characteristic absorption bands of the functional groups of the organic linker and the chemical shifts related to the six-fold coordinated Al, respectively. The four synthesized materials had a degree of crystallinity of about 80 %, but only the materials obtained by solvothermal synthesis were isostructural to DUT-4. In addition, high specific surface areas with values higher than 1100 m²/g were obtained by solvothermal synthesis. Meanwhile, the hydrothermal synthesis generated a low specific surface area and low total pore volume caused by a high surface tension solvent. Similarly, the solvent used on the drying stage affected the particle size of the studied materials. That is, low surface tension solvent leads to a small particle size. The trend on the particle size was DUT-4(H)≈ DUT-4(DCM) <DUT-4(DMF) <DUT-4(W) which is similar to the trend of the surface tension of solvents: C₆H₁₄ (18.8 dyn/cm) <Cl₂CH₄ (29.5 dyn/cm) <DMF (37.9 dyn/cm) <H₂O (72.8 dyn/cm).

Adsorption. The adsorption experiments were carried out at an initial concentration of 450 mg/Nm³ of siloxane D4 at room temperature. The kinetic adsorption of the DUT-4 materials was rapid, reaching equilibrium at about 4 h (Figure 6). The equilibrium adsorption capacity for DUT-4(DMF), DUT-4(DCM), and DUT-4(H) was 9.80 mg/g, which is 1.4 times greater than the adsorption capacity of AC (A_s 1240 m²/g) reported in our previous work under the same experimental conditions [47]. The siloxane adsorption during the first hour was higher for DUT-4(DCM) than for DUT-4(H), which is related to the adsorption kinetics rate. Thus, a simple approach was made to quantify the adsorption kinetics rate by calculating the slope of the first experimental points (from zero to one hour). According to the experimental data, the adsorption rate followed the trend of DUT-4(DCM) <DUT-4(DMF) <DUT-4(H) with values of 7.09, 6.54,

and 5.08 mg/g·h, respectively. On the other hand, the adsorption capacity of DUT-4(W) was 1.80 mg/g, reaching equilibrium in 2 h, and was five times less than the adsorption capacity of the rest of DUT-4 adsorbents, associated with its low specific surface area (1.78 m²/g).

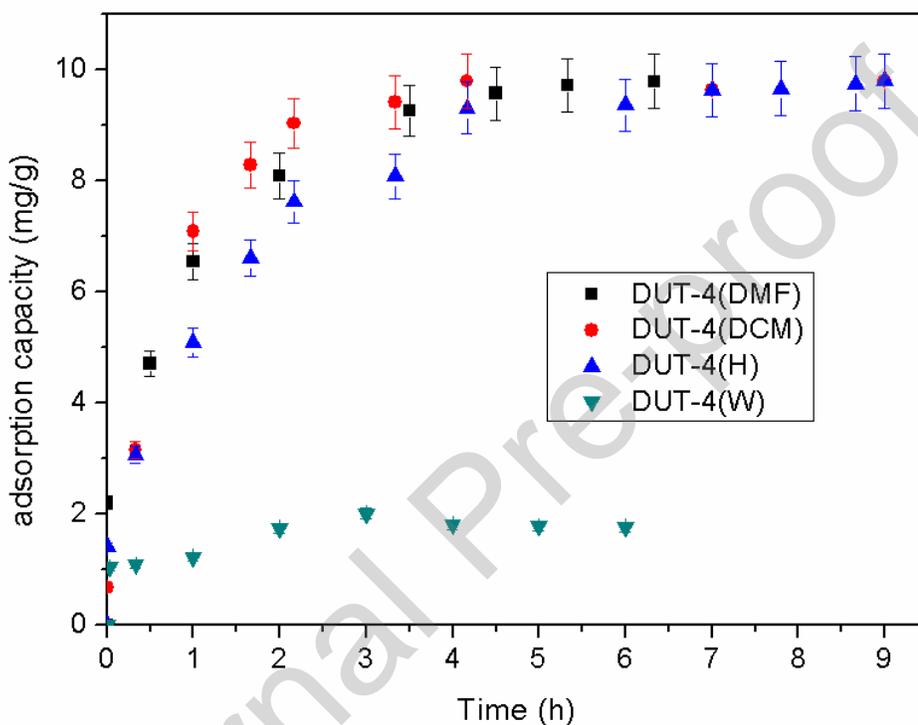


Figure 6. Kinetics adsorption for DUT-4(DMF), DUT-4(DCM), DUT-4(H), and DUT-4(W) at the initial concentration of D4 of 450 mg/Nm³ and room temperature. Error bars represent standard deviation of quadruplicate measurements.

Life Cycle Inventory of DUT-4 production. The input and output flows in the production of DUT-4 are detailed in Table 1. All experimental data were reported as mean values from quadruplicate measurements with a coefficient of variation less than 4%. According to these data, the use of chemical reagents to produce DUT-4 generated the highest environmental impact with a single score between 88.6 and 245 mPt (79.1 and 91.1 % of total environmental damage),

while the electrical energy consumption generated a single score between 2.12 and 24.7 mPt, except for Scenario DUT-4(W), where the electricity consumption generated 31.6 mPt while the use of chemical reagents caused 0.66 mPt. Thus, the production of chemical reagents comprises the activities with the most significant environmental damage. Similar results were reported by Loya-González et al. [20] and Sepúlveda-Cervantes et al. [21] who found that, for the single score indicator (determined through the ReCiPe 2008 method [48]), the production of chemical inputs represents between 93 and 83-93 % of the total environmental damage in the production of activated carbon from agro-industrial waste, respectively. Furthermore, Hjaila et al. [49] found that the production of phosphoric acid contributes in more than 90 % to the midpoint indicators of human toxicity and terrestrial acidification (evaluated through the CML 2 Baseline 2000 method) for the production of activated carbon from olive-waste cakes.

Table 1. Inventory data for DUT-4 production.

FLOW	VALUE	UNITS/FU
Inputs		
Electricity		
<i>Synthesis stage (for all scenarios)</i>	211	Wh
<i>Cleaning and solvent exchange stages</i>		
Scenario DUT-4(DMF)	70	Wh
Scenario DUT-4(DCM)	90	Wh
Scenario DUT-4(H)	80	Wh
Scenario DUT-4(W)	160	Wh
<i>Drying stage</i>		
Scenario DUT-4(DFM)	2	Wh
Scenario DUT-4(DCM)	4	Wh
Scenario DUT-4(H)	2	Wh
Scenario DUT-4(W)	9	Wh
Chemical reagents		
<i>Synthesis stage</i>		
N, N-Dimethylformamide:		
Scenario DUT-4(DMF)	65	mL

Scenario DUT-4(DCM)	103	mL
Scenario DUT-4(H)	111	mL
Scenario DUT-4(W)	162	mL
2,6-Naphthalene dicarboxylic acid:		
Scenario DUT-4(DMF)	0.565	g
Scenario DUT-4(DCM)	0.897	g
Scenario DUT-4(H)	0.963	g
Scenario DUT-4(W)	1.406	g
Nonahydrate aluminum nitrate:		
Scenario DUT-4(DMF)	1.130	g
Scenario DUT-4(DCM)	1.793	g
Scenario DUT-4(H)	1.926	g
Scenario DUT-4(W)	2.812	g
<i>Cleaning stage</i>		
N, N-Dimethylformamide:		
Scenario DUT-4(DMF)	130	mL
Scenario DUT-4(DCM)	207	mL
Scenario DUT-4(H)	222	mL
Deionized water:		
Scenario DUT-4(W)	325	mL
<i>Solvent exchange stage</i>		
Dichloromethane:		
Scenario DUT-4(DCM)	207	mL
Scenario DUT-4(H)	222	mL
Hexane:		
Scenario DUT-4(H)	222	mL
Outputs		
Emissions		
<i>Drying stage</i>		
Scenario DUT-4 (DMF), dimethylformamide	2.7	g
Scenario DUT-4(DCM), dichloromethane	9.8	g
Scenario DUT-4(H), hexane	4.5	g
Scenario DUT-4(W), water	4.03	g

FU: functional unit.

Environmental impacts of DUT-4 production. The environmental impact assessment per FU for each scenario of DUT-4 production is illustrated in Figure 7. Scenario DUT-4(H) has the highest environmental impact score at 269 mPt (single score) due to the environmental impact in the cleaning and solvent exchange stages where three types of solvents were used: DMF, DCM,

and hexane. The use of these solvents also increases the cleaning stage's energy demand (Table 1) because the use of each solvent requires centrifugation. Altogether, solvent production contributes to 245 mPt in Scenario DUT-4(H), where DMF production represents 61.5 % of the environmental impact score, while DCM and hexane solvent production accounts for 33.3 %, and 5.2 % of the impact score, respectively. The use of these three solvents in Scenario DUT-4(H) led it to be the leader in all the environmental impact indicators (Figure S2). Due to the fact that same values of adsorption capacities (9.8 mg/g) were obtained by the three adsorbents DUT-4(DMF), DUT-4(DCM), and DUT-4(H), it is possible to propose a cleaner and greener DUT-4 production by avoiding additional solvents such as DCM and H. In this manner, principles 3, 4, and 5 of green chemistry are fulfilled [50].

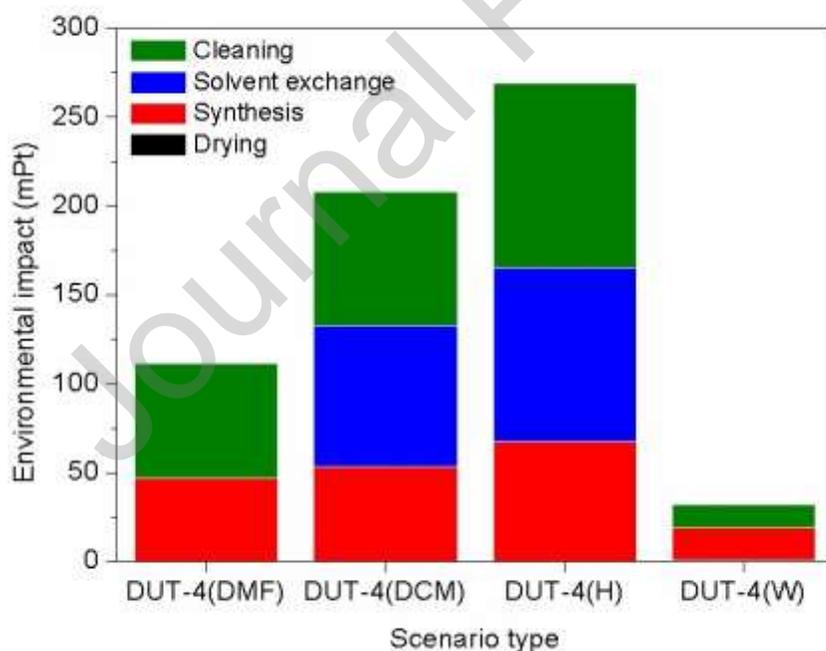


Figure 7. Environmental impact of each scenario of DUT-4 production through ReCiPe 2016 endpoint method.

Scenario DUT-4(DCM) has similar behavior to Scenario DUT-4(H), but a lower environmental impact (211.07 mPt) since it uses 29 % and 7 % less DMF and DCM solvents, respectively, and hexane is not used (Table 1). The production of DUT-4 only uses DMF as the solvent, and its environmental impact is 112 mPt (less than half of Scenario DUT-4(H)). The solvent used determines the environmental profile of these adsorbents. Similar results were found by Grande et al.[22], who evaluated the LCA of the MOF CPO-27, concluding that solvents used in the synthesis and the cleaning stages have the most significant environmental damage. The authors reduced the environmental impact up to 100 times through water-based synthesis since water is non-toxic, stable, cheap, and readily available [44].

In Scenario DUT-4(W), deionized water as the solvent cause minimum environmental damage, 32 mPt. In this Scenario, the electricity used in the synthesis and cleaning stages (Table 1) accounts for 97 % of the environmental indicator. México's energy primary source for electricity production is 87 % fossil sources (62 % crude oil, 20 % natural gas, 4 % coal, and the remaining condensates) [51].

As shown in Figure 8, the main environmental impact category indicator in all Scenarios of DUT-4 production is fossil depletion (10.71–109.14 mPt); this is mainly due to solvent production. In terms of fossil depletion midpoint indicator, the solvent used in each Scenario has impacts of 1.86×10^{-4} , 0.28, 0.53, and 0.75 kg oil eq for Scenarios DUT-4(W), DUT-4(DMF), DUT-4(DCM), and DUT-4(H), respectively; and an electricity consumption ≤ 0.08 kg oil eq for all scenarios (Table S5).

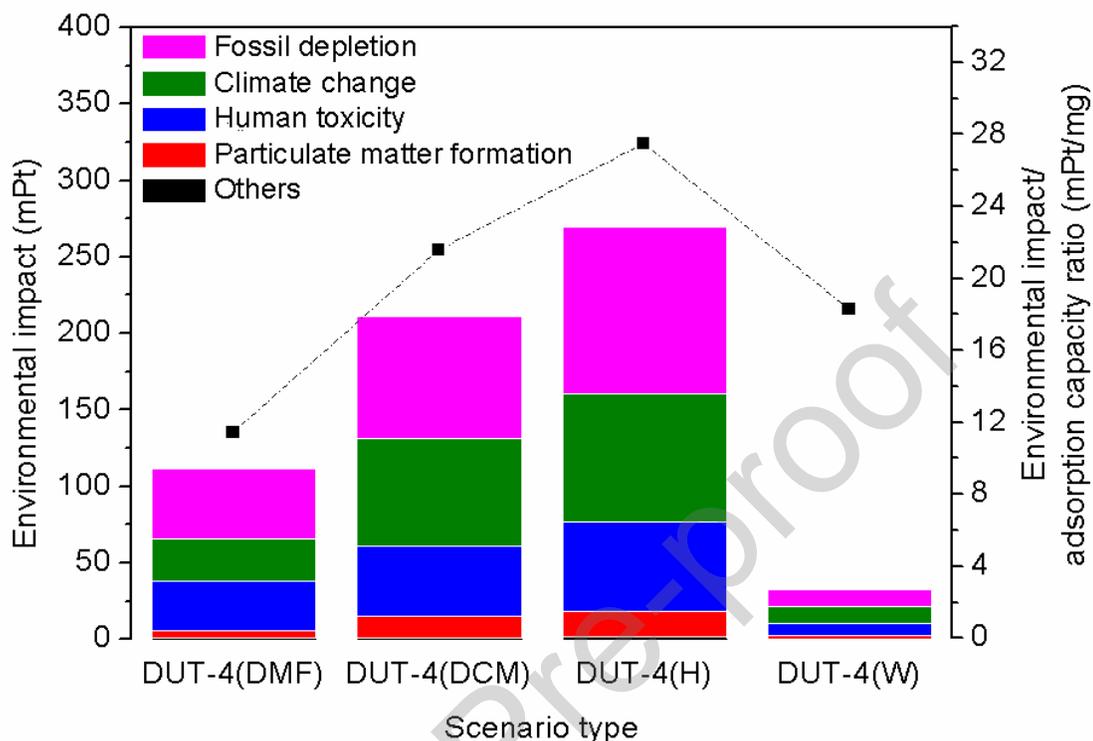


Figure 8. LCA for different DUT-4 production scenarios through endpoint using SimaPro software.

The second most representative indicator is climate change (11.34–83.10 mPt). Regarding the midpoint indicator, the GHG emissions account for 0.25–2.02 kg CO₂ eq (Table S4), mostly associated with carbon dioxide and methane emission. As in the case of fossil depletion indicator, solvent production is the activity with the most incidence in GHG emissions, 7.23x10⁻⁴, 0.45, 1.50, and 1.83 kg CO₂ eq for Scenarios DUT-4(W), DUT-4(DMF), DUT-4(DCM), and DUT-4(H), respectively, while electricity consumption generated ≤0.24 kg CO₂ eq (Table S5).

The human toxicity indicator in Figure 8 ranges from 7.48–58.70 mPt, equivalent to 0.01–0.42 kg 1,4-DB eq. Similarly, solvent use is the main activity of this environmental damage. For solvent production, pouring barium into water represents 81.4–84.7 % of this indicator, and

emitting selenium into the air accounts for 3.1–4.4 %, while the electricity consumption generates <2.6 % in each scenario. The particulate matter formation indicator (2.59–16.72 mPt) comes mainly from the air emissions in solvent production: PM_{2.5} (1.44–4.20 mPt), sulfur dioxide (0.64–5.41 mPt), and nitrogen oxides (0.32–4.30 mPt).

Similar results were obtained by Loya-González et al. [20] and Sepúlveda Cervántes et al. [21], where the leading environmental indicators were fossil depletion (~55 and 42 %, respectively), climate change (~33 and ~36 %, respectively), and particulate matter formation (~11 and ~10 %, respectively).

It is possible to observe that the substitution of DMF solvent for water during the synthesis of DUT-4(DMF)—Scenario DUT-4(W)—decreases environmental damage, but this substitution changed the physicochemical properties of the original MOF, resulting in low siloxane adsorption capacity. This matter should be analyzed from a techno-environmental perspective.

A techno-environmental impact factor—environmental impact/adsorption capacity ratio—was calculated for the four different DUT-4 production scenarios (right axis in Figure 8). The DUT-4(H) adsorbent production has the highest significant environmental impact/adsorption capacity ratio among all four DUT-4 scenarios. In contrast, the DUT-4(DMF) production scenario has the lowest environmental impact/adsorption capacity ratio. These results can be explained by taking into account that DUT-4(DMF) and DUT-4(H) have the same adsorption capacity, but the latter has a higher environmental impact caused by the two solvent exchange stages. Instead, the DUT-4(W) production scenario with a green solvent has a higher environmental impact/adsorption capacity ratio than DUT-4(DMF) production. This result can be explained considering that DUT-4(W) has the lowest siloxane adsorption capacity (1.8 mg/g); thus, to achieve similar adsorption

than the rest (9.80 mg/g), it is necessary to produce five times more of this material. This fact could lead to economic savings to foster greater sustainability in removing siloxanes from biogas. Therefore, from an environmental and technical point of view, DUT-4(DMF) is the best scenario to produce the siloxane adsorbent since the ratio obtained was 53, 42, and 63 % lower than DUT-4(DCM), DUT-4(H), and DUT-4(W), respectively.

CONCLUSIONS

In this study, the synthesis of DUT-4 was carried out by four different routes to improve its physicochemical characteristics for higher siloxane D4 adsorption. In addition, the environmental impacts of the different routes were evaluated by the life cycle assessment methodology.

According to the physicochemical analysis, only the solvothermal synthesis produced materials isostructural to DUT-4 and favored high specific surface areas with values higher than 1100 m²/g. The experimental data demonstrated DUT-4 to be a suitable candidate for use as an adsorbent to remove siloxane from gaseous streams such as biogas. The life cycle assessment emphasizes that using DMF, DCM, and hexane increases environmental damage, mainly in the indicators of fossil depletion, climate change, and human toxicity. Therefore, the synthesis of DUT-4(W) was the one with the lowest environmental impact. However, DUT-4(W) presented the lowest siloxane adsorption capacity compared to DUT-4(DMF), DUT-4(DCM), and DUT-4(H). Finally, based on the environmental impact/adsorption capacity ratio, Scenario DUT-4(DMF) production is the most convenient since lower adsorbent mass is required to remove siloxane, which reduces the environmental impact of the adsorption process.

ASSOCIATED CONTENT

Supporting Information

PDF files containing details of the calculation of the energy balance, estimation methods, environmental impact categories, description of the indicators of fossil depletion, and climate change.

AUTHOR INFORMATION

Corresponding Author

* Nancy Elizabeth Dávila-Guzmán

Phone number: 52-8183294000, ext. 3475

Fax number: 52-8183294000, ext. 6282

E-mail: nancy.davilagz@uanl.edu.mx

* Pasiano Rivas García

E-mail: pasiano.rivasgr@uanl.edu.mx

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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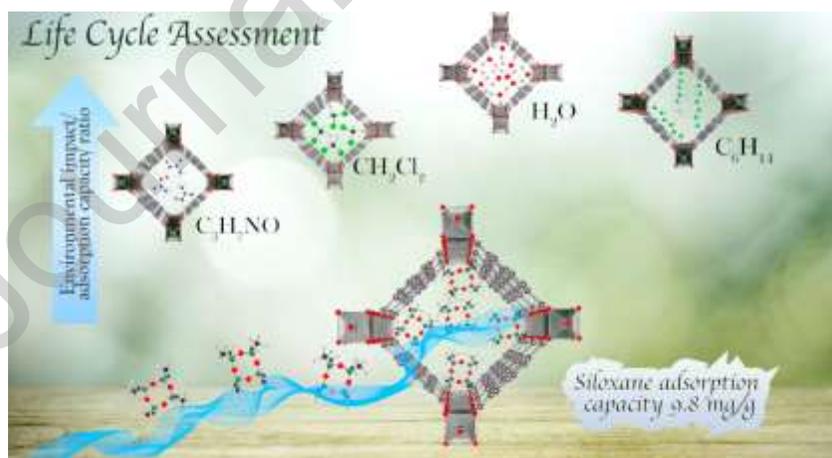
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Graphical abstract:



Synopsis: Search of sustainable routes for the synthesis of metal-organic frameworks for clean energy applications.

CRedit authorship contribution statement

Sandra Pioquinto-Garcia: Investigation, Writing-Original draft, Formal analysis; **Nancy Davila-Guzman:** Conceptualization, Methodology, Writing-Review & Editing, Project administration, Funding acquisition; **Pasiano Rivas-Garcia:** Conceptualization, Formal analysis, Review & Editing; **Juana María Rosas:** Methodology, Formal Analysis; **Margarita Loredo-Cancino:** Validation, Formal analysis; **Sylvain Giraudet:** Formal analysis, Review & Editing; **Eduardo Soto-Regalado:** Review & Editing, Methodology.

Journal Pre-proof

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof

Highlights:

- The solvothermal synthesis produced materials isostructural to DUT-4 with high surface areas.
- DUT-4 is suitable for the adsorption of siloxane from gaseous streams such as biogas.
- Cleaning and solvent exchange stages have the highest environmental impact according to LCA.
- The hydrothermal synthesis of DUT-4 has the lowest environmental impact and adsorption capacity.
- The synthesis of DUT-4(DFM) has the lowest environmental impact/adsorption capacity ratio.

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