

Article MIL-160 as an Adsorbent for Atmospheric Water Harvesting

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Abstract: Nowadays, the rapidly growing population, climate change, and environment pollution put heavy pressure on fresh water resources. The atmosphere is the immense worldwide and available water source. The Adsorptive Water Harvesting from the Atmosphere (AWHA) method is considered a promising alternative to desalination technologies for remote arid regions. The development of novel adsorbents with advanced water-adsorption properties is a prerequisite for practical realization of this method. Metal-organic frameworks (MOFs) are a novel class of porous crystalline solids that bring a great potential for AWHA due to their extremely high specific surface area, porosity, and tailored adsorption properties. This work addresses MIL-160 as a water adsorbent for AWHA. The water-adsorption equilibrium of MIL-160 was studied by volumetric method, the isosteric heat of adsorption was calculated, and finally, the potential of MIL-160 for AWHA was evaluated for climatic conditions of the deserts of Saudi Arabia, Mongolia, the Sahara, Atacama, and Mojave as reference arid regions. MIL-160 was shown to ensure a maximum specific water productivity of 0.31–0.33 gH2O/gads per cycle. High fractions of water extracted (0.90–0.98) and collected (0.48–0.97) could be achieved at a regeneration temperature of 80 °C with natural cooling of the condenser by ambient air. The specific energy consumption for water production varied from 3.5 to 6.8 kJ/g, which is acceptable if solar heat is used to drive the desorption. The AWHA method employing MIL-160 is a promising way to achieve a fresh water supply in remote arid areas.

Keywords: adsorptive water harvesting from the atmosphere; metal–organic frameworks; MIL-160; water vapor adsorption; specific water productivity; specific energy consumption

1. Introduction

Climate change leading to the desertification of a vast area, environmental pollution, and a rapidly growing world population make the fresh water supply one of the major issues of our time [1]. Although the worldwide resources of fresh water are quite abundant $(1\cdot10^5 \text{ km}^3)$, most parts of them are in the form of hard-to-reach glaciers and deep underground water. The rest (rivers, lakes, and shallow underground water) is distributed very unevenly, which puts enormous pressure on water resources in arid regions. Nowadays, 1.5 billion people are facing portable water scarcity, and by 2025 this number is expected to grow to 3 billion. The most water-scarce regions include North Africa, the Near and Middle East, Northern China, India, Eastern Australia, Mexico, northeastern Brazil, and the west coast of South America [2,3].

At the same time, the total amount of moisture in the Earth's atmosphere—about 13,000 km³—significantly exceeds the world's requirements [4,5]. Due to its worldwide availability, interest in atmospheric water harvesting has been observed since ancient times. Artificial springs and ponds were described in [6] that accumulated moisture from the air during dewfall. Currently, water harvesting from the air is considered a promising method for water supply in arid and inland regions [7]. There are two basic types of atmospheric water extraction: passive, which does not require additional energy input (rainwater, fog, and dew collection), and active, which can operate only with an external



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). input of electric or thermal energy. The active method can be based on: (i) the air cooling below its dew point to condense water [8], and (ii) the sorption of moisture by solid [9,10] or liquid desiccants [11,12].

The Adsorptive Water Harvesting from the Atmosphere (AWHA) method is founded on the absolute humidity in arid regions, which is comparatively stable during the day. The air temperature and, consequently, the relative humidity opposite vary greatly. [13]. The AWHA process involves two main stages: (i) the adsorption of moisture on an adsorbent at night when relative humidity is high, and (ii) the desorption of water from the adsorbent during the day driven by an external heat source (e.g., solar heat) with subsequent vapor condensation on a cold surface [14]. The main performance indexes of the AWHA are the specific water productivity (SP) per cycle, or the ratio of <the mass of water collected>/<the adsorbent mass>, and the specific energy consumption (SEC), equal to <the energy input>/<the mass of water collected>. Considering a quite low moisture content of 4-15 g per 1 m³ of air in arid regions [15–18], hundreds of cubic meters of air have to be passed through the adsorbent to extract several liters of water. This emphasizes the primary importance of the efficiencies of water extraction during adsorption and collection during the desorption/condensation stages. These efficiencies can be expressed as fractions: $\delta_{ex} = \langle \text{amount of water adsorbed} \rangle / \langle \text{amount of vapor passed through the} \rangle$ adsorber> of water extraction, and δ_{col} = <amount of water collected>/<amount of water desorbed> of water collection [13].

The performance of AWHA is closely related to the used adsorbent, or, to be more precise, to the harmonization of its properties with the climatic conditions of the region where the process is implemented. A thermodynamic analysis showed that to enhance the performance of AWHA, the adsorbent should have adsorption centers with different affinities for water [13]. Adsorption sites with a strong affinity for water vapor effectively adsorb moisture at low relative pressure during the adsorption stage, and ensure high efficiency of water extraction. Adsorption sites with weak affinity easily release vapor during desorption at high relative pressure, and promote high water collection efficiency. The affinity should be distributed over a wide range, corresponding to the climate conditions of the region where the AWHA is realized. Such an adsorbent exhibits a divariant adsorption equilibrium, with uptake rising between relative humidity (*RH*) values, corresponding to the adsorption and desorption stages.

A number of adsorbents have been proposed for AWHA, including common porous solids like silica gel [19,20], crystalline alumino-phosphate (zeotype) AQSOA Z01 [21], composite sorbents involving hygroscopic salts embedded inside solid matrix [10,14,22,23]. A low water-adsorption capacity of silica gels and a high regeneration temperature of conventional zeolites have restricted the practical realization of AWEA. Several advanced zeotypes possess S-shaped adsorption isotherms, and can be regenerated at a low temperature. However, an analysis showed that their adsorption properties did not match the climatic conditions of the arid regions very well. Their drawbacks were a quite low amount of water exchanged under conditions of the AWHA cycle in arid regions (below 0.23 g/g, see Section 3.3.1) and expansive synthesis [24]. The "salt/matrix" composites possess a large adsorption capacity and variable adsorption properties. However, their use in open AWHA systems may be obstructed by the potential leakage of the salt solution, which is formed during the moisture adsorption, from the pore space [25]. This could lead to the adsorbent degradation and the adsorber corrosion.

Metal–organic frameworks (MOFs) are a novel family of crystalline compounds that consist of metal ions or clusters and bridging polydentate organic linkers. MOFs are characterized by one-, two-, or three-dimensional frameworks with a large fraction of voids [26–28]. Due to their extraordinarily surface area and pore volume, and the presence of both hydrophilic and hydrophobic parts, MOFs possess unique adsorption properties such as a large water-adsorption capacity and a great diversity of water-adsorption isotherms. [29,30]. Furthermore, the possibility to control MOFs' adsorption properties by modifying both organic linkers and inorganic clusters makes it possible to tailor the

MOFs with required sorption properties and hydrolytic stability [31,32], which inspired high hopes for enhancement of AWHA performance [33].

Seo et al. [34] first proposed mesoporous MIL-100 and MIL-101 as desiccants for AWHA. Since then, the study of AWHA employing MOFs has been attracting steadily increasing interest [4,13,35,36]. For a humid climate at the relative humidity of ambient air RH > 40-50%, MIL-100(Cr) and MIL-101(Cr) are promising adsorbents that display a high working capacity of up to 1.2 mL/g [37]. A Co₂Cl₂BTDD designed for AWHA was able to deliver 0.82 mL/g of water under moderately humid conditions at RH = 30% [38]. The performance of MOFs as adsorbents for arid climates is essentially lower. Kim et al. [39] showed that at the ambient RH = 20%, potentially ~0.2 mL/g per cycle can be harvested with MOF-801 by utilizing solar thermal energy to drive desorption. A microporous MOF-303 has recently been developed and tested at AWHA [40], and the water harvester operating for several cycles per day generated 0.7 and 1.3 L/kg per day at 10 and 32% relative humidity, respectively. MIL-160(Al) was suggested as a promising adsorbent for AWHA regions with arid climates [13]. Chang et al. [41] evaluated the potential of application of MIL-160(Al) as a material for water harvesting in a bench-scale fixed-bed unit, and demonstrated its capable of maximum water productivity of 305 L/(day·ton) at regeneration and condensation temperatures of 80 °C and 10 °C, respectively.

This research focuses on the study of MIL-160 as an adsorbent for the AWHA process and evaluation of its potential under climatic conditions of extremely arid regions (the Mojave and Sahara Deserts, Chile, Algeria, the central part of Saudi Arabia, and Mongolia). The performance characteristics of AWHA employing MIL-160 were estimated in terms of the specific consumption of thermal energy for the water production, the specific mass of the water harvested, and the fractions of water extracted from the air and water collected. These fractions are important performance indexes, as they determine the specific electric energy consumption for air blowing through the fixed-bed adsorber, which can be significant due to a small moisture content in the atmosphere in arid regions.

The structure of MIL-160 is formed by inorganic AlO_6 octahedra, which form ciscorner-sharing chains linked via carboxylate groups of the ligand (2,5-furandicarboxylic acid) (Figure 1) [42]. It possesses both strong and weak adsorption sites, which allows AWHS to promote high efficiencies of water extraction and collection.



Figure 1. Scheme of the MIL-160 structure: helical inorganic chains formed by AlO6 octahedra (**left**); channels in framework constructed from inorganic chains linked via carboxylate groups of the 2,5-furandicarboxylic acid (**right**). AlO₆ octahedra (light gray), atoms C (black), O (red).

2. Materials and Methods

2.1. Sample Synthesis

MIL-160 was synthesized by a hydrothermal method according to a slightly modified procedure described in [42]. 2,5-furandircaboxilic acid (4.680 g, 30 mmol, >99%), AlCl₃·6H₂O (7.240 g, 30 mmol), and NaOH (1.212 g, 30 mmol) were dissolved in distilled H₂O (60 mL) with stirring using a magnetic stirrer (~500 rpm) for 15 min. The obtained mixture of reagents was placed in a Teflon container inside a 100 mL cylindrical stainlesssteel autoclave and heated at temperature T = 120 °C for 24 h in a convection oven. After cooling down to the ambient temperature, the mixture was separated from the solution with a small-pore paper filter using a water-jet pump and washed with hot water to remove the unreacted organic ligand. Finally, the obtained white solid precipitate was activated at 150 °C for 15 h under continuous evacuation.

2.2. Characterization

The structure of the obtained MIL-160 sample was confirmed by PXRD analysis using a Bruker D8 ADVANCE diffractometer with an XRK-900reaction chamber. The measurements were carried out using CuK_{α} -radiation ($\lambda = 1.54$ Å) in scanning mode ($2\theta = 5-60^{\circ}$), with a step width of $2\theta = 0.02^{\circ}$ and an accumulation time of 10 s at each point.

IR-spectra were recorded on an Agilent Cary 660 FT-IR spectrometer using an attenuated total reflection (ATR) attachment, the 025-2018 MIRacle ZnSe Perf Crystal Plate, at 25 °C in the 500–4000 cm⁻¹ range.

The BET surface area, the micropore volume, and total pore volume of the synthesized MIL-160 were determined by low-temperature nitrogen adsorption at 77 K using a Quantachrome Nova 1200e gas sorption analyzer. The samples were degassed in a vacuum at 150 °C for 3 h before measurement of N₂ sorption isotherms. The specific surface area was calculated by the BET analysis of the adsorption branch of the isotherm in a relative pressure range of 0.01–0.025. The total pore volume was obtained from the amount of N₂ adsorbed at a relative pressure close to unit $P/P_0 = 0.99$. The micropore volume was calculated using the statistical thickness analysis of the isotherm adsorption branch and de Boer's t-method. The pore-size distribution was calculated using the Dubinin–Astakhov method.

2.3. Water-Adsorption Equilibrium

The water-adsorption isotherms of MIL-160 were measured by a volumetric method at T = 50, 35, and 20 °C and in the water-vapor pressure range P = 0.8–40.0 mbar. Before the measurements, a preliminary degassing was carried out at 80 °C for 3 h under continuous evacuation (the residual pressure was 0.1 mbar) for drying the MIL-160 sample. The dry sample weight m₀ was 0.50216 ± 0.00002 g. Afterward, the sample was cooled down to a fixed temperature, which was controlled by a thermostat connected to the adsorber with an accuracy of ±0.1 K. The temperature was measured with a K-type thermocouple placed at the bottom of the adsorber. Then, the measuring cell with the adsorbent was connected to the buffering vessel filled with water vapor, which resulted in a jump in water-vapor pressure over the sample. The vapor pressure was measured using an MKS Baratron[®] Type 626a pressure sensor with an accuracy of ± 0.01 mbar. The vapor-pressure jump initiated the adsorption, which led to a gradual decrease in the pressure. The sample was maintained at a fixed temperature for 1–4 h to reach equilibrium. The amount of water vapor sorbed (Δw (g/g)) was calculated from the temporal pressure dependence P(t) using the ideal gas equation:

$$\Delta w(t) = \frac{M_{\rm H2O}V}{m_0 RT} (\Delta P(t)) \tag{1}$$

where M_{H2O} —the water molar mass, V—the system volume, —the universal gas constant, and T—the steam temperature. Subsequently, based on the data obtained, a set of water-sorption isotherms w(P) of the MIL-160 sample was calculated.

3. Results and Discussions

3.1. Structure Characterization of as-Prepared MIL-160

The texture characteristics of MOF-801 determined from the N₂ sorption isotherm at 77 K (Figure 2a) belonged to the I-type according to the IUPAC classification, and the hysteresis loop was absent, which is typical for microporous solids. The synthesized MIL-160 possessed the specific surface area $S_{BET} = 830 \text{ m}^2/\text{g}$ and the total pore volume $V_p = 0.40 \text{ cm}^3/\text{g}$, which agreed with the literature data [42]. The micropore volume V_{μ} coincided with the V_p . Hence, the synthesized MIL-160 was microporous without mesoor macropores. The pore-size distribution obtained by the Dubinin–Astakhov method (Figure 2b) demonstrated a narrow peak in the micropore-size region. As shown in the curve obtained, the average pore diameter is 0.42 nm, which is consistent with the data presented in [42].



Figure 2. N_2 adsorption (solid symbols) and desorption (open symbols) isotherms (**a**) and pore-size distribution using DA model (**b**) of MIL-160.

The XRD pattern (Figure 3a) of the synthesized sample was consistent with that reported in the literature [42,43]. The FT-IR spectrum of the prepared MIL-160 sample (Figure 3b) agreed well with the literature data [41,43–45]. The characteristic bands with high intensity were attributed to asymmetric (1649 cm⁻¹) and symmetric stretching (1405 cm^{-1}) vibrations of carboxylate groups, along with the C=C bonds' stretching vibrations of the furan ring at 1583 cm⁻¹ [41,44,45]. The strong band at 630 cm⁻¹ corresponded to the vibrations of the Al–O bond in the MIL-160 structure [41]. The peaks in the range of 1000–1300 $\rm cm^{-1}$ could be attributed to the asymmetric and symmetric stretching vibrations of the C–O–C in the furan rings [41]. A band at 782 cm⁻¹ ascribed to the out-of-plane deformation vibrations of C-H bonds in the furan ring also was observed [44]. The broad band around 3500 cm^{-1} was assigned to the vibrations of the water molecules adsorbed from the ambient air, while the weak peak around 3200 cm⁻¹ represented the vibration of bridging hydroxyl groups μ -OH in the metal-oxide clusters AlO₆ [41,44]. It is worth noting that the lack of a band at 1700 cm⁻¹ indicated the absence of residual free 2,5-furandicarboxylic acid in the pore-synthesized MIL-160 [44,45]. Thus, the characterization of the synthesized MIL-160 by XRD, nitrogen adsorption, and FTIR analysis verified its genuine structure and high purity.



Figure 3. XRD patterns (**a**) of the synthesized MIL-160 (2) and the curve calculated from CIF-file (1); FT-IR spectra (**b**) of MIL-160.

3.2. Water-Vapor Adsorption on MIL-160

The isotherms of water adsorption on the MIL-160 were S-shaped curves (Figure 4) showing a small water uptake (0.02 g_{H2O}/g_{ads}) at low pressures, followed by a steep increase in uptake up to 0.25–0.30 g_{H2O}/g_{ads} in a narrow pressure range, which depended on the temperature. Upon further increase in vapor pressure, the uptake gradually rose to 0.34 g_{H2O}/g_{ads} , which was somewhat smaller than the specific volume of micropores $V_{\mu} = 0.40 \text{ cm}^3/\text{g}$. This indicated that a fraction of the pore space in the vicinity of hydrophobic sites (organic linker) remained unoccupied by water molecules.



Figure 4. Isotherms of water adsorption on the MIL-160 at T = 50 °C (red), 35 °C (blue), and 20 °C (black).

Based on the obtained data on water adsorption equilibrium on MIL-160, isosteres of water adsorption were plotted in $\ln(P) - 1/T$ coordinates (Figure 5a). The isosteric heat ΔH_{ads} of the water adsorption was calculated according to the Clausius–Clapeyron equation:

$$\ln P = Q_{a\partial c} / (RT) + \text{Const}$$
⁽²⁾



Figure 5. Water adsorption isosteres (**a**) and isosteric enthalpy ΔH_{ads} (**b**) for the MIL-160.

The adsorption heat $Q_{a\partial c}$ varied in the range of 49 to 52 ± 1 kJ/mol at w = 0.05-0.25 g/g (Figure 5b). The obtained values of adsorption heat somewhat exceeded the latent condensation heat of water $\Delta L = 43.9$ kJ mol⁻¹ at 303 K, which pointed to a moderately strong interaction of water molecules with the MIL-160's surface.

Experimentally measured water adsorption isobars on the MIL-160 presented as a function of the Polanyi adsorption potential $\Delta F = -RT \ln[P/P_0(T)]$, where *P* is the partial vapor pressure, *P*₀ is the saturation vapor pressure at temperature *T*, merged into one characteristic curve $w(\Delta F)$ (Figure 6). This meant that the water adsorption equilibrium of the MIL-160 obeyed the Polanyi principle of temperature invariance [46]. The characteristic curve $w(\Delta F)$ was approximated by an empiric equation:

$$w = \frac{A\Delta F + B}{1 + e^{(-k_1 - (\Delta F - x_{01}))}} + \frac{C}{1 + e^{(-k_2 - (\Delta F - x_{02}))}}$$
(3)

with the fitting parameters $A = -1.321 \cdot 10^{-3}$, $B = 1.451 \cdot 10^{-2}$, C = 0.321, $k_1 = -10.00$, $k_2 = -1.470$, $x_{01} = 6.875$, and $x_{02} = 6.268$.



Figure 6. Characteristic curve of water adsorption on the MIL-160 (symbols) and the fitting curve (solid line). Dashed lines indicate the values of adsorption potential, corresponding to the weakest (ΔF_{weak}) and strongest (ΔF_{str}) adsorption sites. The blue area shows the ΔF range for the boundary conditions of the AWHA cycle in Riyadh-Old during the dry season (July).

3.3. Performance of AWHA Employing MIL-160

3.3.1. Specific Water Productivity

The characteristic curve $w(\Delta F)$ was used to evaluate the performance of AWHA employing MIL-160 for climatic conditions of several arid regions located on different continents (Figure 7). The Mojave Desert in North America; the Atacama in Chile, South America; Tamanrasset in Algeria; the Sahara Desert; Riyadh-Old in the central part of Saudi Arabia; and Noyon in Mongolia were selected as reference regions, characterized by their extremely arid climates. The climatic data (the average temperatures T_n and T_d , and the average relative humidity RH_n and RH_d during night and day, respectively) were collected from the Meteonorm Global Climate Database. They were used to calculate the values of adsorption potential ΔF_{ads} and ΔF_{re} (Table 1), corresponding to the boundary conditions of adsorption and desorption stages, respectively:

$$\Delta F_{\rm ad} = -RT_{\rm n}[\ln P_{\rm am}/P_0(T_{\rm n})] \tag{4}$$

$$\Delta F_{\rm re} = -RT_{\rm re} \left[\ln P_{\rm am} / P_0(T_{\rm re}) \right],\tag{5}$$

where T_{re} is the regeneration temperature.



Figure 7. Selected reference regions with extremely arid climates [47].

Table 1.	Climatic	data	for	the	selected	regions.
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Desien	$T_{\mathbf{n}}$, °C	<i>RH</i> _n , %	$T_{\mathbf{d}\prime} ^{\circ}\mathbf{C}$	<i>RH</i> _d , %	P _{am} , mbar	ΔF_{ad} , kJ/mol	$\Delta F_{\rm re}$, kJ/mol ($T_{\rm re}$ = 80 $^{\circ}$ C)		
Kegion -	January								
Riyadh-Old	12.5	55.9	16.3	45.1	8.3	1.3	11.9		
Sahara	11.1	33.0	14.9	27.2	4.5	2.5	13.7		
Noyon	-13.0	55.6	-9.1	41.7	1.3	1.3	17.4		
Atacama	5.3	73.0	9.4	55.5	6.5	0.7	12.6		
Mojave	3.0	26.3	7.6	17.9	6.8	1.5	14.1		
June/July									
Riyadh-Old	32.6	20.2	36.7	16.5	10.1	4.1	11.3		
Sahara	26.9	25.8	30.4	21.2	9.3	3.4	11.5		
Noyon	8.6	25.8	13.7	16.4	2.9	3.2	15.0		
Atacama	-1.7	33.1	5.1	20.0	1.8	2.5	16.4		
Mojave	21.6	26.3	27.5	17.9	6.9	3.3	12.6		

The characteristic curve of water adsorption on the MIL-160 demonstrated that the strongest adsorption sites adsorbed water vapor at $\Delta F_{\text{str}} \approx 9.0$ –10.0 kJ/mol (Figure 6), which was lower than $\Delta F_{\text{re}} = 11.3$ –17.4 kJ/mol at $T_{\text{re}} = 80$ °C in all the reference regions (Table 1). Thus, the retained water could be desorbed completely at a quite low temperature of 80 °C, allowing usage of a simple solar collector for the adsorbent regeneration.

The maximum specific water productivity SPmax per cycle can be achieved in the AWHA process if water retained in the adsorbent during the adsorption stage is completely removed and collected during the desorption/condensation stage. The productivity SPmax was calculated from the characteristic curve (Figure 6) as the uptake variation $\Delta w = w_{\text{max}} - w_{\text{min}} = w(\Delta F_{\text{ad}}) - w(\Delta F_{\text{re}})$. In all the selected regions, MIL-160 exchanged $\Delta w = 0.31-0.33 \text{ g}_{\text{H2O}}/\text{g}_{\text{ads}}$ at $T_{\text{re}} = 80$ °C, which surpassed respective values for various adsorbents, both traditional and novel (Figure 8).



Figure 8. Amount of water exchanged under climatic conditions of Riyadh-Old during the dry season for various adsorbents.

3.3.2. The Fractions of Water Extraction and Collection

Along with the specific water productivity, the fractions δ_{ex} of water extracted from the air during adsorption and δ_{col} of water collected during condensation are also the crucial performance indexes of AWHA. They determine the volume of air to be passed through the adsorber, for harvesting a unit mass of water, and consequently, the energy demand of the system for the air blowing.

The fractions of water extracted δ_{ex} and collected δ_{col} in a simple fixed-bed flowing adsorber (Figure 9a) with MIL-160 as the adsorbent can be evaluated as [13]:

$$\delta_{\text{ex}} = (P_{\text{am}} - P_{\text{out.ad}})/P_{\text{am}} = 1 - P_{\text{out.ad}}/P_{\text{am}}$$
(6)

$$\delta_{\rm col} = [P_{\rm out.re} - P_0(T_{\rm d})]/P_{\rm out.re} = 1 - P_0(T_{\rm d})/P_{\rm out.re}$$
(7)

where P_{am} —the partial pressure of water vapor in the ambient air; $P_{out.ad}$ —the water vapor pressure in the outlet air during adsorption stage; $P_{out.re}$ —the water vapor pressure in the outlet air during regeneration stage; and $P_0(T_d)$ —the pressure of saturated water vapor at a day temperature of ambient air T_d .



Figure 9. Scheme of a fixed-bed flowing adsorber (**a**) and distribution of water uptake (**b**,**c**) and vapor partial pressure (**d**) along the adsorber.

Here, we assumed that the adsorption front thickness ΔL in a fixed-bed adsorber was negligible in comparison with the adsorber length $L >> \Delta L$ (Figure 9a–c). In this case, the dynamic adsorption capacity w_d of the adsorbent equaled the equilibrium capacity w(P,T). Until the concentration front was inside the bed, the outlet vapor pressure $P_{\text{out.ad}}$ during adsorption equaled the equilibrium pressure over the dry adsorbent (Figure 9d). The strongest adsorption centers of the MIL-160 adsorbed water vapor at $\Delta F_{\text{str}} \approx 10.0 \text{ kJ/mol}$ (Figure 6). Consequently, the outlet vapor pressure $P_{\text{out.ad}}$ during the adsorption stage could be calculated as:

$$P_{\text{out.ad}} = P_0(T_n) \exp(-\Delta F_{\text{str}}/RT_n)$$
(8)

The δ_{ex} values evaluated according to Equations (6) and (8) varied from 0.90 for Riyadh-Old to 0.96 for the Atacama regions during the dry season (Figure 10). During the humid season, δ_{ex} was even higher due to the increase in *RH* of the ambient air (Figure 10), and reached 0.96–0.98 for the selected regions. Consequently, the affinity of the strongest adsorption sites MIL-160 to water vapor provided effective extraction of water vapor from the ambient air. That promoted a reduced air volume blown through the adsorber to extract a unit volume of water, and consequently, lowering energy consumption for the air purging.

During the regeneration stage, the outlet air was in equilibrium with the adsorbent, saturated with water up to w_{max} right after the adsorption stage (Figure 9c,d). The weakest adsorption sites adsorbed water vapor at $\Delta F_{\text{weak}} \approx 3.0 \text{ kJ/mol}$ (Figure 6). Consequently, at $\Delta F > \Delta F_{\text{weak}}$, these sites released adsorbed water, and the outlet vapor pressure $P_{\text{out.re}}$ during the desorption stage could be calculated as:

$$P_{\text{out.re}} = P_0(T_{\text{re}})\exp(-\Delta F_{\text{weak}}/RT_{\text{re}})$$
(9)

It should be noted that for the dry season, the $\Delta F_{ad} > \Delta F_{weak}$ for all regions except Atacama (Table 1). This meant that the weakest adsorption sites remained unsaturated with water during the adsorption stage, and maximum uptake in the cycle equaled $w = w(\Delta F_{ad})$. Accordingly, for the dry season, the pressure $P_{out.re}$ was calculated using the following expression:

$$P_{\text{out.re}} = P_0(T_{\text{re}})\exp(-\Delta F_{\text{ad}}/RT_{\text{re}})$$
(10)

Figure 10. Water-extraction fraction δ_{ex} for the AWHA system based on MIL-160.

Then, the fraction δ_{col} was evaluated as a function of temperature T_{re} using Equation (7). If the condenser was cooled by the ambient air at T_d , δ_{col} values for the selected regions varied in the range 0.48–0.95 and 0.88–0.97 during the dry (July) and humid (January) seasons, respectively, at $T_{re} = 80$ °C (Figure 11). The increase in the regeneration temperature enhanced the water collection fraction: at $T_{re} = 100$ °C, the collection fraction rose to 0.77–0.97 and 0.95–0.98 for the dry and humid seasons, respectively. On the contrary, lowering the regeneration temperature to 70 °C resulted in a dramatic reduction of this fraction, particularly for the dry season, down to 0.15–0.9. This showed the necessity of an external heat source for the water desorption, which could be solar or waste heat.

Figure 11. Effect of the regeneration temperature on the water-collection fraction δ_{col} of the AWHA system based on MIL-160 during the dry (**a**) and humid (**b**) seasons, with the condenser cooled by the ambient air.

Another efficient method of increasing the fraction δ_{col} is a decrease in the condensation temperature T_{con} . A tank with a heat exchanger located underground or a condenser connected to a heat pump or adsorptive chiller can be used as a condenser [48,49] instead of that cooled by the ambient air. Figure 12 shows that reducing T_{con} from $T_d = 36.1$ °C to 10 °C allowed the growth of δ_{col} from 0.48–0.77 to 0.90–0.95 at $T_{re} = 80–100$ °C under the climatic conditions of Riyadh-Old during the dry season.

Figure 12. Effect of the condensation temperature on the water-collection fraction δ_{col} of the AWHA system based on MIL-160 during the dry season (July) for the Riyadh-Old region.

Thus, the calculated δ_{ex} and δ_{col} values showed a high performance of the AWHA system employing MIL-160 as an adsorbent. This MOF possessed both strong and weak adsorption sites, exchanged up to 0.33 g_{H2O}/g_{ads} under climatic conditions of the selected arid regions, and provided high fractions $\delta_{ex} = 0.90-0.98$ and $\delta_{col} = 0.48-0.97$ at $T_{re} = 80-100$ °C.

3.3.3. The Specific Energy Consumption

An important performance index of the AWHA system is the specific consumption of thermal energy SEC for the water production, which can be calculated as:

$$SEC = Q_{sp,re}/(\Delta w \cdot \delta_{col}) = [\Delta w \cdot Q_{ads} + (C_{pad} + w_{ads} \cdot C_{pH2O}) \cdot (T_{re} - T_{ad})]/(\Delta w \cdot \delta_{col}), \quad (11)$$

where $C_{pad} = 1.63 \text{ J/(g·K)}$ is the specific heat of MIL-160 at 80 °C [50]), $C_{pH2O} = 4.19 \text{ J/(g·K)}$ is the specific heat of water at 80 °C, and $Q_{ads} = 2.84 \text{ kJ/g}$ is the average isosteric heat of adsorption in the range $w = 0.05-0.30 \text{ g}_{H2O}/\text{g}_{ads}$.

For the selected regions during the dry season, the SEC ranged from 3.7 to 6.8 kJ/g_{H2O} at a regeneration temperature of 80 °C (Figure 13). The SEC was affected by the water-collection fraction δ_{col} (Equation (11)). Accordingly, during the humid season (January), SEC decreased to 3.5–3.8 kJ/g_{H2O} due to a higher water-collection fraction δ_{col} . The decrease in condensation temperature was another way to reduce SEC. Thus, when the condenser was cooled to 10 °C, SEC for the Riyadh-Old region was reduced to 3.6 kJ/g_{H2O} as compared to 6.8 kJ/g_{H2O} for the condenser cooled by the ambient air at temperature T_d (Table 2), owing to an appropriate increase in the water-collection fraction δ_{col} .

Table 2. SEC for water production in the AWHA process employing MIL-160 in the Riyadh-Old region at $T_{re} = 80$ °C (dry season).

$T_{\rm con} = T_{\rm d} = 33.1 ^{\circ}{\rm C}$	$T_{\rm con}$ = 20 °C	$T_{\rm con}$ = 10 °C
6.8	4.1	3.6

These SEC values were higher than the heat of water vaporization (2.26 kJ/g_{H2O} at 100 °C). Therefore, the energy consumption for AWEA was higher than the energy consumption for conventional water desalination. However, taking into account that in arid regions, solar heat is usually available in abundance and can be used for adsorbent regeneration, the obtained SEC-values for water production were quite acceptable. Accordingly, the AWEA method employing MIL-160 as an adsorbent is promising for arid regions remote from other sources of water.

Figure 13. SEC for water production in the AWHA process employing MIL-160 as an adsorbent at $T_{re} = 80 \degree C$ and $T_{con} = T_{d}$.

4. Conclusions

In this paper, the water-vapor adsorption on MIL-160 was studied, and the assessment of the feasibility of MIL-160 for the AWHA process in arid climatic regions was carried out. The water-vapor adsorption isotherms were S-shaped curves with a maximum uptake of 0.34 g/g. The isosteric heat of water adsorption equaled 49–52 \pm 1 kJ/mol at a water-uptake range of 0.05 to 0.25 g/g. Under conditions of several arid regions, namely Riyadh-Old (Saudi Arabia), the Sahara Desert, the Mojave Desert, Atacama (Chile), and Noyon (Mongolia), a high maximum specific water productivity of $0.31-0.33 g_{H2O}/g_{ads}$ per cycle could be achieved with MIL-160. Employing MIL-160 allows a fraction of water extracted $\delta_{ex} = 0.90-0.98$ during the adsorption stage. The fraction of water collected varied in the range of 0.48–0.76 and 0.85–0.97 during the dry and humid seasons, respectively, at $T_{\rm re} = 80 \,^{\circ}{\rm C}$ with natural cooling of the condenser by ambient air. Further increase in the fraction of water collected could be achieved by lowering the condensation temperature to 10 °C and increasing the regeneration temperature to 100 °C. The specific energy consumption for water production varied from 3.5 to 6.8 kJ/g. This is quite acceptable if solar heat, available in abundance in arid regions, can be used to drive the desorption. The AWHA method employing MIL-160 is a promising way to achieve a fresh water supply in arid areas remote from coast-line.

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