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Chapter

Adsorption-Based Atmospheric Water Harvesting: Technology Fundamentals and Energy-Efficient Adsorbents

Muhammad Sultan, Muhammad Bilal, Takahiko Miyazaki, Uzair Sajjad and Fiaz Ahmad

Abstract

Nowadays, atmospheric water harvesting (AWH) became very essential to provide fresh potable water. This technique is in practice since 1900 (US661944A) by Edger S. Belden. Atmospheric water is a source of freshwater with 13000 trillion liters availability of water at any time and can be utilized in overcoming water shortage, especially in arid and rural areas. It holds up the water molecules in the form of vapors and accounts for adding 10% of all freshwater present on the earth. Mainly, the two most common methods have been used for the extraction of atmospheric water. First, the ambient air is cooled below the dew point temperature, and second in which the moisture in atmospheric air is adsorbed/absorbed using desiccant materials. Conventional vapor compression, thermoelectric cooling, dew, and fog water harvesting based systems/technologies possess some limits in terms of energy requirements, less efficiency, and high cost. However, the adsorption based AWH technology is relatively cheaper, environment friendly, and can be operated by a lowgrade thermal energy source. The limited availability of commercial instruments to harvest atmospheric water using adsorbents indicates a lack of fundamental studies. The fundamental research on water adsorption, adsorption kinetics, regeneration conditions, and water collecting surface designs has not gained as much interest as required in the field of atmospheric water harvesting. In this regard, this book chapter discusses and presents the progress in the field of adsorbent materials and system designs along with the future directions to accelerate the commercialization of this technology.

Keywords: adsorption, desiccant dehumidification, atmospheric water harvesting, energy-efficient adsorbents, thermal energy, condensation

1. Introduction

Globally, water scarcity is considered one of the prime issues in the upcoming decades. Almost 2.1 billion people are lacking access to clean and fresh water [1]. **Figure 1** shows the water-stressed areas in the world. Middle East, Asia, South America, and some parts of Africa face water scarcity. Therefore, many studies

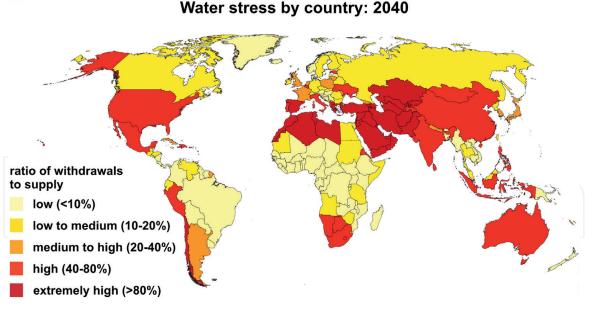


Figure 1.

World map showing the water-stressed areas by 2040 reproduced from [2].

have been investigated to supply enough water with cheaper, and portable methods [3, 4]. These methods include desalination, wastewater treatment, sewage recycling, and water harvesting from the atmosphere. The energy consumption in desalination systems is very high that is almost 50% of the cost, and make this technology inappropriate in most situations [5]. Also, seawater desalination is not suitable for remote areas and has many environmental problems. Thus, portable systems with less energy consumption are needed. Atmospheric water harvesting can be considered as a potential resource of fresh water in remote areas [6]. For this purpose, many researchers have introduced innovations for water production from humid air technology. This can be done by many ways i.e., using vapor compression cycle (VCC) [7–10], thermoelectric cooling (TEC) [11, 12],

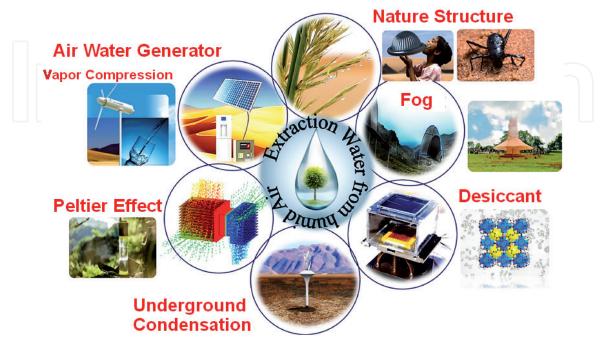


Figure 2. Summary of various technologies for water production from humid air available in the literature [28].

absorption/adsorption refrigeration [13, 14], wind power with VCC [15], using solar chimneys [16, 17], using membranes [18, 19], and using adsorbent materials [20–27]. Figure 2 summarized the various technologies investigated in the literature for producing water from the humid air. The purpose of all these technologies is to produce water and are using worldwide depending on the conditions and the requirements. Among all these technologies, desiccant based atmospheric water harvesting (AWH) shows a great potential to extract enough amount of drinkable water with less energy consumption [6]. The adsorption based AWH is possible in dry and desert regions with the lowest relative humidity. This technology utilizes renewable energy sources (solar, wind, and low-grade biomass) which ultimately lead towards the cheapest and most efficient systems. This chapter focuses on the fundamentals and principles of adsorption based AWH. The progress and perspectives and associated adsorption based AWH systems are also discussed in this study. Moreover, energy-efficient desiccant materials along with the recently developed new generation MOFs for AWH are also highlighted in this study. The main purpose of this chapter is to introduce the importance of AWH by employing various efficient desiccant materials.

2. Atmospheric water harvesting

2.1 Conventional AWH

Atmospheric water harvesting could be considered as a huge renewable source of water that can provide enough amount of water, but unfortunately is ignored [29]. Conventional water harvesting was started first when a Russian forester built a stone condenser during 1905 and 1912 and was considered as the early Greek dew condenser [30, 31]. Ziebold tested with this type of condenser and named as "the aerial wells", but unfortunately, this project was failed and the expected amount of water was not produced due to the low thermal conductivity and low heat capacity [32]. In 1957, a review was carried out on the absorption of water by the plants [33]. Since then several studies have been carried out focusing on the fog and dew harvesting by the plants and animals [34].

2.2 Modern AWH

Modern AWH shifted towards the innovations, methods, and technologies that can provide a significant amount of water in remote areas [35]. As mentioned earlier in the introduction section, various new methods have been proposed for AWH i.e., VCC, TEC, using membrane and adsorbent materials. Among these, the fog water was first collected with the help of nets in 1956 [36]. Shi et al. replaced these traditional meshes with vertically arranged wires to avoid the problems of clogging [37]. Dew water collection considered as the alternative approach because it is not majorly affected by climatic conditions and can provide water in most of the ambient environment [38]. A lot of advancements have been done in the designs of active condensers after the commercialization of mechanical refrigerators in the 1980s. The desiccant based dew water harvesting was taken into consideration in the Nineteenth century, in which the various desiccant materials capture the moisture from the atmosphere during the night, and then releases the moisture in vapor form during the day. This method has been proved the most energy-efficient and reliable technology because it employs solar energy and can provide water anywhere and anytime in the world.

3. Water vapor parameters in atmospheric air

Atmospheric air is a mixture of nitrogen, oxygen, and argon gas, and water vapors with varying contents. The relative humidity (Φ), absolute humidity (ω), and the dew point temperature (T_d) are considered as the most essential parameters of the air which can be used as the source of water. The relative humidity (Φ) represents the ratio of the partial pressure of water vapor (P_w) to the saturation pressure (P_s), while the absolute humidity (ω) represents the maximum amount of water that can be extracted from the air. The relative humidity can be expressed using (Eq. (1)) found in the literature [39, 40].

$$\Phi = \frac{P_w}{P_s(T)} \tag{1}$$

where, Φ represents the relative humidity, P_w denotes the partial pressure of water vapor, and P_s represents the saturation pressure. The relation between relative humidity, absolute humidity, temperature, and total air pressure can be described using (Eq. (2)) found in the literature [40].

$$\Phi = \frac{\omega P}{\left(0.622 + \omega\right) P_s(T)} \tag{2}$$

The dew point temperature (T_d) can be determined from (Eq. (2)) by solving for T at $\Phi = 1$ for given air pressure and absolute humidity. The water vapor saturation pressure (P_s) at any temperature (T) can be described using (Eq. (3)), while the total air pressure (P) can be described using (Eq. (4)) found in the literature [40].

$$P_{s}(T) = 610.94 \exp\left(\frac{17.625T}{243.04 + T}\right)$$
(3)

$$P = P_a + P_w \tag{4}$$

Total air pressure (P) is the sum of the partial pressure of dry air (P_a) and the vapor pressure of water in the air (P_w). The moist air enthalpy can be described using (Eqs. (5)–(7)) given in the literature [40].

 $H = H_a + \omega H_{wv} \tag{5}$

$$H_a = C_{p,a}T \tag{6}$$

$$H_{wv} = H_{wv} \left(0^{\circ} C\right) + C_{p,wv} T \tag{7}$$

where H_a term represents the enthalpy of dry air, H_{wv} term represents the enthalpy of the presence of water vapor, and $C_{p,a}$ denotes the heat capacity of air (kJ kg⁻¹ C).

4. Principles of adsorption based AWH

Adsorption based AWH is unique in its way that it utilizes the desiccant materials to capture water vapors from the air and shows higher thermal efficiencies as

compared to the traditional AWH systems. The main advantage is that the desiccant materials can be regenerated by solar thermal energy and the condensation process can occur at ambient conditions [41, 42]. Figure 3 shows the adsorption based AWH process which consists of two stages. In the first stage, the desiccant material in contact with the ambient air at night which adsorbs the water vapors. In the second stage, the desiccant material is packed into a closed system where a significant amount of heat is provided to regenerate the desiccant material. Due to the regeneration process, the material desorbs the water vapors, and the collected vapors will be condensed into liquid form. With this approach, the AWH can be possible in low relative humidity areas. A lot of advancement has been done in the material designs, and system developments. Figure 4 shows the dual-stage AWH device mechanism and prototype introduced in the literature [44]. A novelty in this device was that two adsorbent layers were used to improve the water production per day. The latent of condensation from the upper stage was used for the desorption purpose of the bottom stage. With this approach, the thermal efficiency can be improved, and this system can become more suitable for daily purposes. AQSOA Z01, zeolite material was experimentally tested and showed that a prototype can harvest up to 0.77 L/m^2 /day with an 18% increase as compared to the single-stage AWH device [44]. The results found that a temperature of 90°C on the solar absorber area can give a maximum water production for AQSOA Z01.

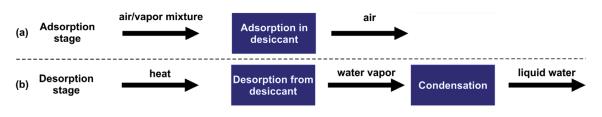


Figure 3.

Adsorption-based AWH process consists of two stages. (a) Adsorption stage (water vapors from the ambient air adsorbed in the adsorbent). (b) Desorption stage (water vapors desorbed from the adsorbent and condensed into liquid form) [43].

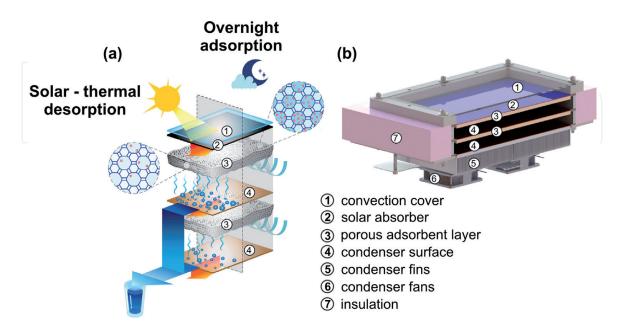


Figure 4.

Illustration of dual stage adsorption based AWH device. (a) Mechanism of dual stage adsorption based AWH in which adsorption process occurs during night when ambient air in contact with the adsorbent layer, while the desorption process occurs during day when device is closed, and heat is supplied to regenerate the adsorbent layer. (b) Dual stage AWH prototype consists of convection cover, solar absorber, adsorbent layer, and condenser [44].

5. Progress and perspectives in adsorption based AWH

Adsorption based AWH is a vital technology that can provide cost-effective water in arid areas. The vapor concentration in this technology can be achieved through desiccant materials which ad/absorb and desorb the water vapors from the air [45]. In this context, efficient desiccant materials are a key research priority and various materials have been developed. First, it was believed that the solid desiccant AWH systems can extract enough amount of water but requires a large amount of material which makes these systems very expensive [46]. Also, the operating costs of air blowers to circulate the air for both adsorption and desorption purposes make this system less attractive. However, the development of next-generation MOFs, nano-porous organic materials, and various composite desiccant materials shows great potential for AWH systems. Figure 5 shows the recent progress in adsorption based AWH systems. Ideal desiccant material should possess the required properties of stability, hydrophilicity, and pore diameter. Adsorption capacities and densities are of great importance in any practical application [51, 52]. The desiccant materials with type IV and type V isotherms are most suitable for this application [43]. During the adsorption process, the materials adsorption capacity should linearly increase with relative humidity, while in the desorption process, the materials desorption capacity should drop steeply with the increased temperature. In this regard, progress has been made and Kallenberger et al. developed a composite material by incorporating the calcium chloride into an alginate-derived matrix [53]. The water uptake capacity of this material was almost linear with relative humidity and when adsorption temperature increases to 65°C, the water uptake capacity drops which shows that the desiccant material can be regenerated at low temperatures. Also, recently developed MOFs show this type of flexibility to harvest enough amount of water at the lowest relative humidity conditions [27, 54]. After the desorption process, the inlet air of the condenser is the outlet air of the desorber. It is worth noting that both the desorption and condensation temperature

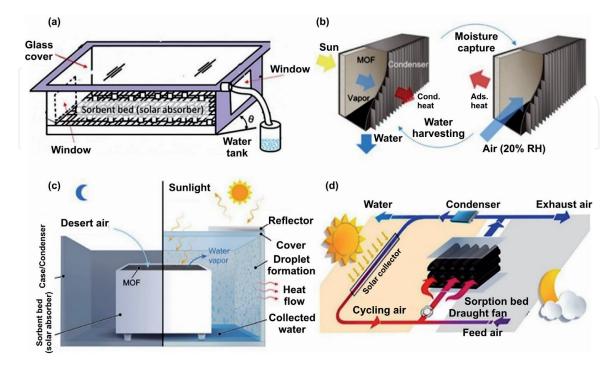


Figure 5.

Adsorption based AWH systems published in the literature. (a) Solar glass desiccant box type system [47]. (b and c) MOFs based AWH systems [48, 49]. (d) Packed columns desiccant matrix based AWH system mechanism [50].

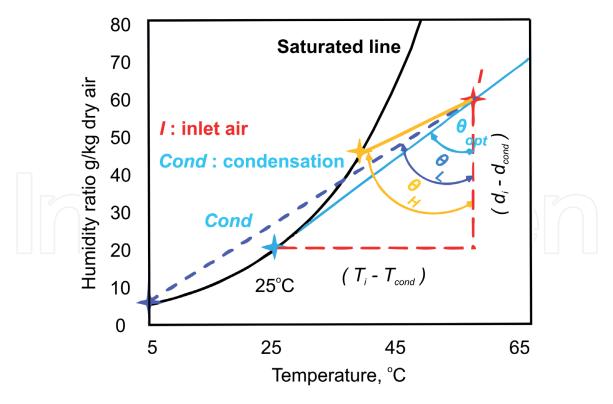


Figure 6. *The optimal condensing temperature on the psychrometric chart developed in the literature* [46].

should be carefully chosen to balance the specific water production per day per unit collector area (SWP), and the specific energy consumption per unit mass water production (SEC). In this regard, Tu et al. developed a powerful tool to determine the proper desorption and condensation temperature [46]. **Figure 6** shows the optimal condensing temperature on the psychrometric chart in which the inlet air of the condenser is denoted by I (Ti, di), and the condensation states of the humid air are denoted by the stars on the saturated line. The tangent of the angle (θ) and SEC can be described using (Eqs. (8) and (9)) given in the literature [46].

$$\tan\theta = \frac{T_{i} - T_{cond}}{d_{i} - d_{cond}}$$

$$SEC = C_{p} \left(\frac{\varepsilon_{T}}{\varepsilon_{d}}\right) \times \tan\theta + h_{fg}$$
(9)

It is noted that when the line through the point I (Ti, di) is tangent to the saturated line, then the angle (θ) is at the smallest value, and therefore the condensing temperature at given inlet conditions for a minimum value of SEC can be obtained at the tangent point. An appropriate heat source and airflow rate can be chosen to find the optimum outlet air conditions of the desorber by using this tool.

6. Energy-efficient desiccant materials for AWH

6.1 Silica gel and hygroscopic salts based AWH materials

Energy efficient materials must have high capacity of adsorbing and desorbing water from the air [55]. Heidari et al. investigated a novel desiccant based

evaporative cooling system for production of water [56]. The results showed that the silica gel-based system can harvest up to 585 L of water during a week. Milani et al. investigated a small scale air cooled silica gel based wheel dehumidifier for extraction of water from the atmosphere [57]. It was found that the system can generate more than 5.2 L of water per day in the ambient conditions of Sydney. A simulation model on TRNSYS was also built and found that the system can generate a cumulative of 18.5kL of water in the ambient conditions of Abu Dhabi, 10kL of water in London, and 13.8kL for the ambient conditions of Sydney. Similarly, various desiccant materials based on the hygroscopic salts were also investigated to produce water from humid air. Table 1 shows the silica gel and hygroscopic salts-based materials used in atmospheric water harvesting systems. Hamed et al. investigated a system based on sandy bed impregnated with calcium chloride for atmospheric water harvesting [59]. The system was exposed to ambient air to absorbs the water vapors in the night and the desiccant material was covered with the glass layer where regeneration process will occur, and water vapors condensed into liquid form. It was found that the system can provide 1 L per m² of water per day. Wang et al. investigated a semi open system with a novel composite sorbent of LiCl with active carbon felt (ACF) for water production from humid air [61]. The system was tested at different experimental conditions and found that 14.7 kg, 13.6 kg, and 12.5 kg of water was obtained at conditions of 85%, 75%, and 65% relative humidity, respectively.

6.2 Zeolites based AWH materials

Zeolites are the family of porous crystalline and hydrated aluminosilicates that are widely used as the adsorbents in many applications. These materials can extract water from air at low relative pressures due to their affinity with water [62]. As zeolite materials have a framework structure, a high temperature is required to regenerate and desorb the water vapors. **Table 2** shows the summary of some potential zeolite materials with efficient adsorption capacities. Furukawa et al. studied the zeolite 13X and found that it can harvest water up to 0.40 g/g at low relative pressures [63]. The adsorption properties of Li-X zeolite and Na-X were investigated and found that these materials can be employed to extract water from air [64]. The results found that Li-X and Na-X can extract up to 0.244 g/g and 0.192 g/g respectively. The kind of ion in this type of zeolites not only influences the amount of adsorbed water but also the energy densities and heat of adsorption. Despite the high performance, the energy requirements for desorption purpose restricts the zeolite materials to be used in AWH systems [52].

Adsorbent	Material	Quantity	Water harvesting capacity	Reference
Silica gel	Desiccant wheel		585 L during a week	[56]
Hygroscopic salts 	CaCl ₂ /cloth		1.5 L/m ² day	[58]
	CaCl ₂ /cloth sand	1 kg	2.32 L/m ² day	[26]
	CaCl ₂ /sand	1 kg	1 L/m ² day	[59]
	LiCl/sand		90 mL/day, 115 mL/day	[24]
	CaCl ₂ /saw wood/ vermiculite		40–140 mL/kg/day	[60]
	LiCl/active carbon felt	40.8 kg	14.7 L	[22]

Table 1.

Summary of various silica gel and hygroscopic salts based desiccant materials for atmospheric water harvesting found in the literature.

Adsorbent	Material	Water harvesting capacity	Reference	
Zeolite	Zeolite 13X	0.40 g water/g zeolite	[63]	
_	Li-X-Zeolite	0.244 g water/g zeolite	[64]	
	Na-X	0.192 g water/g zeolite	[64]	
_	AQSOA type zeolites	0.1–0.3 kg water/kg zeolite	[65]	

Table 2.

Zeolite based desiccant materials for atmospheric water harvesting found in the literature.

6.3 MOFs based AWH materials

MOFs have been researched for their water capture properties and they were found to be highly promising and energy efficient materials. Several members of the MOF family showed unprecedented water uptake property [63]. Specifically, zirconium MOFs made from Zr6O4(OH)4(-CO2)n secondary building units and carboxylate organic linkers showed very interesting properties in water adsorption [66]. MOF-841 was investigated and showed the maximum water uptake and maintained its structure over 80 adsorption-desorption cycles [63]. A similar trend was observed in other zirconium MOF named as MOF-801 which showed a water uptake at 10% relative humidity. Motivated by these results, MOF-801 based device was built and tested in Arizona, desert [49]. The device was consisted of two boxes, the inner box was open and holds the MOF material while, the outer box has a lid. The outer lid was open at night to allow the MOF-801 to in contact with ambient air and hold the water molecules in its pores and then the lid was closed in day and device was exposed to sunlight to regenerate the MOF material. This device was delivered 200-300 mL of water/ kg of MOF/day at 20-40oC temperature and 5–40% relative humidity. This device showed remarkable results and proved as a first device in the history to extract water from the desert air. **Table 3** shows the water harvesting capacities of potential MOFs. It can be seen that Co₂Cl₂BTDD material delivered 0.82 g of water/g of MOF under 5–30% relative humidity conditions [68]. It was found that the pore diameter of this material was above the critical diameter for water capillary action which enabled water uptake at the limit of reversibility. Figure 7 shows the framework structures of some potential MOFs used in AWH systems. The key in all MOFs is the framework structure which allow to trap water from low relative humidity conditions. The water harvesting through MOFs was moved to next level after the development of MOF-303 based device which showed extraordinary results at low relative humidity conditions and also exhibit adsorption and desorption cycles each on the scale of minutes [54]. This device was first tested in a laboratory and later in Mojave Desert at conditions of 10% relative humidity and 27°C and it delivered 0.7–1.0 L of water/kg of MOF/day [54]. It is clear from the discussion that MOFs can be considered as the potential and energy efficient materials for AWH. With these MOFs based AWH systems, not only clean water can be harvested in any climate but also to make this concept more mobile and dispensed [66].

6.4 Other AWH materials

Other adsorbent materials for AWH that have been interested and investigated in the last decade are nano porous super gels and super hygroscopic gels [72–74]. The main factors of these type of materials include the effective capturing of water molecules, high efficiency storage, and fast water desorption abilities under different climatic conditions [28]. **Figure 8** shows the nano-porous super hygroscopic hydrogel employed to harvest water from highly humid atmosphere zones [73]. This hydrogel was made up of Zn and O atoms in a unique ratio of 1:1.1.

Adsorbent	Material	Relative humidity (%)	Water harvesting capacity	Reference
Metal–Organic Framework	MOF-801	20	2.8 L	[27]
	MOF-303		0.175 L/kg	[67]
	MOF-841	5–35	44 wt%	[63]
	Co ₂ Cl ₂ BTDD	5–30	0.82 g/g	[68]
	UiO-66	40	0.052 g/g	[69]
	Banasorb-22		0.08 g/g	[70]
	Cr-soc-MOF-1	70	1.95 g/g	[71]
	HSO ₃ -UiO-66		0.038 g/g	[69]
	IRMOF-1		0.11 g/g	[70]

Table 3.

Metal–organic framework based desiccant materials for atmospheric water harvesting found in the literature.

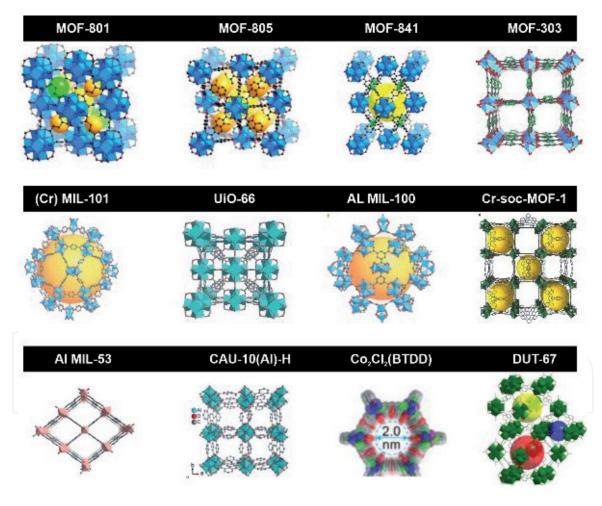


Figure 7. Illustration of MOFs structures used in AWH systems.

It was found that this synthesized hydrogel has a high-water uptake of over 420% of its own weight. A steep increase in water absorption at high relative humidity of over 80% was shown by the hydrogel which makes it suitable for extraction of water from the humid air. The hydrogel showed the excellent stability for more than 1000 absorption/desorption cycles. It was concluded from the calculations that the absorption cycles of 15 min and desorption of 5 min could give the

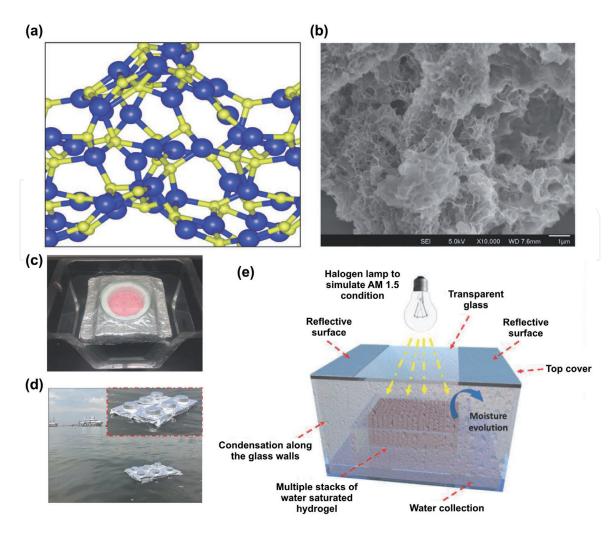


Figure 8.

Nano-porous super hygroscopic hydrogel-based AWH. (a) The hydrogel is made up of Zn:O ratio 1:1.1 (blue balls for zinc atoms, yellows balls for oxygen atoms). (b) SEM image of the hydrogel showing porous network. (c-d) The prototype developed for the absorption characteristics of the hydrogel by floating on the sea surface. (e) Schematic of the AWH system based on super hygroscopic hydrogel reproduced from [73].

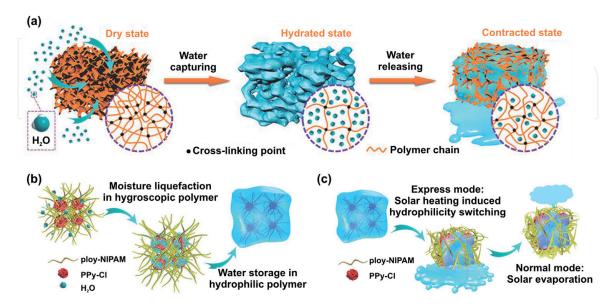


Figure 9.

Super moisture-absorbent gel-based AWH. (a) Illustration of the AWH process (moisture captured by the SMAG and releases water under room temperature). (b) Schematic showing the moisture absorption enabled by the SMAGs. (c) Schematic showing the express and normal modes for water harvesting reproduced from [72].

maximum fresh water of over 14 L/kg of hydrogel/day. Similarly **Figure 9** shows the illustration of super moisture-absorbent gel water harvesting process [72]. The super absorbent gel consists of poly-NIPAM framework which ultimately expands the internal area of the gel and serves as a pathway for water during desorption process. It was found that this super absorbent gel in saturated condition can directly release 50% of the absorbed water within 15–20 min once it is slightly heated to 40oC (denoted the "express mode"). After this phase, the water can be collected via condensation process (denoted the "normal mode"). The super moisture absorbent gel showed two water releasing modes and both can be powered by solar radiation. The super gel-based prototype was also investigated, and it was found that it can produced about 20 and 55 L of water in 60% and 90% relative humidity, respectively. These hydrogels-based systems can be considered as the low energy consumption and cost-effective.

7. Conclusions

The supply of freshwater to a rapidly growing world population is a great societal challenge. In this regard, several technologies have been developed and currently in use worldwide, but the advancements of additional methods for freshwater generation is very crucial to effectively address the global water scarcity. For this purpose, this chapter highlights the importance of adsorption based AWH which utilizes the desiccant materials to capture water vapors from the atmosphere and condenses into liquid form. The important water vapor parameters in ambient air are discussed in this study. The fundamental principles of adsorption based AWH are reviewed, moreover, the progress and perspectives in this technology also explained from the viewpoints of newly developed desiccant materials and the modified AWH systems designs. The study explores the energy efficient desiccant materials which are already employed in AWH systems. From the literature, it was found that the recently developed MOFs are promising due to their flexible nature and tailorable architectures and can harvest water from the atmospheric air at low relative humidity conditions. Some newly developed hygroscopic gels are also showing great potential to utilized in AWH systems. It was found that the temporal and spatial restrictions for AWH and as well as the energy requirements can also be reduced if the appropriate adsorbents are selected. The adsorption based AWH systems ensures no bulky equipment, more environment-friendly and cost effective. Thus, this study presents a comprehensive knowledge on AWH through adsorbent materials.

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Conflict of interest

The authors declare no conflict of interest.

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