1. Introduction

Access to adequate clean water supply is fundamental to global health and it is inextricably linked to sustainable economic and social development. However, providing affordable and safe water for all is becoming more and more challenging as the demand increases with a growing population. Freshwater scarcity is further exacerbated by climate change, and anthropogenic activities that have led to saline intrusion and contamination of the existing freshwater sources, making the current approaches for water treatment even more difficult and costly. This, in combination with the continuously rising global water demand, results in a rather pessimistic prediction that an additional 2000 billion m³ of freshwater supply will be required by 2030 to meet the global demand, assuming no gains on the current state of water-production capacity and efficiency.

As the existing freshwater sources are being depleted, there is a growing need for utilization of a broader range of water sources beyond the conventional ones, such as simple and off-grid operations, for water technologies (WTs) that can be deployed to manage the constraints imposed by these circumstances. Therefore, in coherence with the vision of the United Nations Sustainable Development Goals, enhancing water security sustainably for the next decade calls for innovative WTs that exploit unconventional sources of varying water qualities and are resilient and adaptable to function optimally under difficult circumstances, where skilled operator and plug-in power sources are absent. All these should be done while also considering climate change and environmental protection issues.

The past decade has witnessed an emergence of innovative materials (e.g., bioinspired and biomimetic membranes, nanomaterials and polymeric hydrogels among others) designed for water treatment applications. Polymeric hydrogels, which are 3D networks capable of absorbing a large amount of water, have proven their potential as an enabling agent for sustained water security through their unprecedented performance in several areas of WTs whereby they have significantly outperformed other materials creating, thus, a new standard/setpoint. Enabling innovative approaches that can serve as alternatives to existing water treatment methods, or expanding the sources of water that can be exploited beyond the conventional...
Adv. Mater. Interfaces 2021, 8, 2100580

ones. Examples of such high-performance hydrogels include i) superabsorbent cryogels with high bactericidal efficiency, that can be innovatively used to rapidly absorb microbiologically contaminated water and then squeezed to release the disinfected water in less than 30 s;[15,16] ii) thermoresponsive hydrogels for the recovery of active sites (that has been saturated with sorbates) on sorbents via a modest temperature change, thus offering a more environmentally friendly approach, as opposed to the traditional method that uses caustic solutions;[27] iii) hydrogels with appropriate pore-size and underwater superoleophobicity that allow rapid separation of oil–water mixtures through rapid gravity-driven filtrations;[18] iv) stimuli-responsive hydrogels bearing high charge-density, paving the way to explore new approaches in desalination either as novel forward osmosis draw agents or as a novel form of membranes that can selectively absorb ion-depleted wa-

ter,[19,20] v) photothermal hydrogels that show enhanced solar evaporation rates of water (up to 3.20 kg m\(^{-2}\) h\(^{-1}\)), which is significantly beyond the theoretical limit (of 1.47 kg m\(^{-2}\) h\(^{-1}\)) as determined from the solar-to-vapor conversion efficiency equation assuming 100% efficiency for 1-Sun incident intensity;[28] and vi) hydrogels with high moisture-absorption capacity even under low relative-humidity (RH) environment that transforms vapor into collectible liquid wa-

ter.[22–24]

The outstanding performance shown by the aforementioned hydrogels can be attributed to some of their unique properties such as: i) their high water-absorption and -retention ability, ii) the presence of three different water states in their hydrated networks, iii) their switchable wettability behavior when fab-

ricated using stimuli-responsive polymers, and iv) the exceptional ability to remove contaminants from water due to their size-sieving, charge-repulsion, anti-adhesion, and ion-sorption properties. Based on the fact that such properties can be easily modulated, hydrogels can be rationally designed to meet the demanding requirements for highly efficient water harvesting and purification, making them a promising materials-platform to enhance global water security for a sustainable future. However, despite the significant potential demonstrated by hydrogels for applications in water treatment and recovery, currently the space that hydrogels occupy in the water purification market is mar-
ginal. Conventional treatment methods such as sand filtration, clarification, flocculation, and chlorination among others are still the dominant mainstream water purification methods.[30] To the best of our knowledge, there has not been a review that consoli-
dates the overall research that has been carried out on hydrogel-

enabled WTs. Such a critical review coupled with insightful perspectives gained from the understanding of the underlying mechanism(s) and/or the role(s) of hydrogels in the enhanced performance can serve as a springboard for further advancement and innovations in this field. This can pave the way for the rise of hydrogel-enabled WTs as an alternative complement to existing technologies, closing the gap between developing and industrial-

ized nations, to provide universal access to water.

This review, therefore, aims to consolidate and draw insights from reported works utilizing hydrogels in the field of water treatment. For a focused discussion, representative examples of hydrogels that have either shown a high-level of performance, or enabled the innovation of a new approach for water treatment, or even showed versatility that broadens the applica-
tion range, will be highlighted. In the first part, a summary of

the strategies employed to fabricate hydrogels and the related hybrids/composites with properties tailored for applications in specific areas of water treatment is introduced. This is fol-

lowed by a discussion on a range of properties, uniquely displayed by hydrogels that are responsible for their exceptional performance in efficient and innovative water treatment. Then, a review of the hydrogels applied in the different areas of water treatment: disinfection, water decontamination, oil–water separation, desalination, and atmospheric-water harvesting is pre-

sented. For each category, the general working principles are described followed by a discussion on the unique properties of hydrogels that enable the specific functions for a specific application and the advances made in the field. We conclude by pre-

senting our perspectives on the challenges faced by the use of hydrogels in WTs, and by proposing potential solutions as well as some prospective research directions.

2. Design and Synthesis of Hydrogels for Water Treatment

Freestanding hydrogels are typically cross-linked networks of monomers or polymeric chains formed via: i) covalent bonding, through either addition polymerization of unsaturated mono-
mers (e.g., acrylates and styrenes) or condensation reactions (e.g., carboxylic acids, amines, etc), ii) ionic or chelation reac-
tions (e.g., calcium alginate gels), or iii) physical interactions such as gelation caused by changes in solvent composition (e.g., cellulose nitrates and acetate) or by chilling (gelatin, starch, agarose, and carrageenan), that alter the hydrogen bonding interactions.[35] The cross-linking degree, in particular, is a strong determinant of the mechanical and chemical sta-

bility of the as-synthesized hydrogels.[26–30] Apart from these perma-
nently cross-linked hydrogels, biomimetic chemistry and supramolecular assembly approaches can be utilized to prepare hydrogels with reversible chemical interactions. For example, mussel-inspired coordination chemistry can be employed to fabricate hydrogels with biomimetic dopamine groups con-
taining catechols side chains that can reversibly complex ferric ions by tuning the pH,[33] while supramolecular hydrogels can be cross-linked by reversible noncovalent interactions, such as hydrogen-bond, metal-ligand coordination, electrostatic, hydrophobic, or host–guest interactions.[12–14]

Alternatively, hydrogels can be fabricated as coatings or grafts on substrates to impart complementary properties such as improved strength and resistance to humid or harsh environ-

ments. In fact, chitosan hydrogel coatings have been shown to significantly enhance the durability of substrates such as filter papers whose mechanical strength weakens substantively under wet conditions.[35,36] In another example, poly(vinyl alcohol) (PVA)-coated filter paper, fabricated by a direct cross-linking reaction between the hydroxyl groups of the cellulose paper and the PVA molecules using glutaraldehyde as a cross-linker, shows improved resistance to harsh environments while main-
taining high separation efficiencies (>99.9%) of highly acidic, alkaline, and saline oil–water mixtures even after 20 filtration cycles.[37] In general, the stable adhesion of the hydrogel coating on a substrate is driven by three processes: i) polymerization of the monomer units into polymer chains, ii) crosslinking of the
polymer chains to form a polymer network, and iii) binding of the polymer network to the substrate.[38] The hydrogel coating can bind to the substrate surface via covalent or physical interactions (e.g., electrostatic, hydrophobic, or van der Waals interactions, and hydrogen bonds). When the substrate is permeable to the polymer chains or to the precursor monomers of the coating gel, the resultant hydrogel is not merely coated on the surface of the substrate, but it also interpenetrates the structure of the substrate thus resulting in entanglement at the molecular level leading to better adherence. This approach can be used for stacking of compatible hydrogel layers to create spatiotemporal gradients within the hydrogels.[39] Stacking of hydrogel layers, even those with mismatched surface energies, can be achieved by spreading a layer of silica nanoparticles as the “glue” between the layers. This method relies on the ability of the nanoparticle to adsorb onto polymer gels and to act as connectors between polymer chains, and on the ability of polymer chains to reorganize and dissipate energy under stress when adsorbed onto nanoparticles.[40]

Hydrogels can be mixed with other components that can be either another polymer or other additives such as inorganic/organic fillers, macromolecules and even microbes, to impart additional functions and properties. For example, the addition of polymers such as poly(N-isopropylacrylamide) (PNIPAM) to hydrogels imparts thermo-sensitivity,[19,22,23,43] while polymers such as poly(pyrrrole) (PPy) and polyaniline (PANI) impart light-absorption properties to the resultant hybrid.[21,42] Hybrid hydrogels containing two or more different polymers can be designed to have different types of networks, which go beyond the single network (SN) whereby two or more different monomers are copolymerized into a single hydrogel network. The different network architectures include: i) double network (DN) whereby the two different polymers are present as two independent, but not interpenetrating, networks in the hybrid gel,[2,12] ii) interpenetrating network (IPN), whereby the polymer networks interpenetrate one another in the hybrid gel, iii) semi-interpenetrating network (semi-IPN) whereby one of the polymers is cross-linked in a 3D network while the second polymer (without cross-linking) interpenetrates the first network as linear polymeric chains,[23,43] iv) hydrogel networks composed of chemically grafted polymer chains/brushes,[4,44] and v) core–shell structure.[45] Although the fabrication methods of SN hydrogels are simpler and less time-consuming, the aforementioned alternative network architectures can be explored when SN hydrogels, composed of two or more different monomers, do not show the expected synergy and thus cannot meet the performance requirements. An example is the disappearance of the lower critical solution temperature (LCST) behavior of PNIPAM when copolymerized with monomers with high ionic contents.[23,41,43,44]

Additives such as nanomaterials, ion receptors, macrocycles, biomolecules, microbes, etc., can also be efficiently incorporated into hydrogels without losing their activities in order to impart additional functionalities, for example, ion-specificity,[46] catalytic activity,[47] antibacterial activity,[46,47] magnetism,[48] light absorption,[49] and biodegradation,[50] to the final composite. Furthermore, the mechanical strength of hydrogels, which is a major limitation for their practical large-scale applications, can be improved by the incorporation of nanomaterials such as cellulose fibers,[55] modified SiO$_2$ nanoparticles,[57] clays,[28,56,57] and Al(OH)$_3$ nanoparticles[58] among others. The presence and the abundance of functional groups such as -NH$_2$, -OH, -COOH, -CONH$_2$, -SO$_4$H$_2$ within the hydrogels facilitates the anchoring and stabilization of such fillers. Nanomaterials, for example, can be incorporated into hydrogels via embedding or anchoring existing nanomaterials into hydrogels or onto their surface respectively, or via in situ synthesizing nanomaterials into the hydrogel matrix.[59–64] These three different incorporation methods may result in significantly different distribution of the nanomaterials in the composite hydrogels as well as in significantly different micro- and nano-structures, surface topographies, and surface roughness of the composites.[61]

In particular, the nanomaterials formed via the in situ method are i) smaller in size (<10 nm) due to their confined growth in the hydrogel network; ii) very well-dispersed due to electrosteric stabilization presented by the ionic functional groups in hydrogels, and iii) present in high density in the hydrogel network due to the abundant functional groups which facilitate the uptake or the precursor as well as the anchoring of the resultant nanoparticles.[55,51,62] As such, a high reactivity of the resultant hybrid can be anticipated.

In most WT applications, the mass transport properties of the materials are very important. Rapid water transport, in particular, is of significant interest because in most cases, such as disinfection and decontamination, water molecules themselves or the water-soluble contaminants should be transported to the reactive sites or agents of the solid substrate. For a successful solute transport, the material’s pore structure and in particular the pore size in relation to the solute size is of significant importance as it affects the transport dynamics. For example, solutes of smaller size than the hydrogel pores can diffuse freely in the network, while solutes of comparable size to the pores experience a greater frictional drag with the polymeric network, thus increasing the path length and slowing down the solute transport.[63] The solute diffusivity in the hydrogels is currently modeled using the three main diffusive mechanism theories: i) hydrodynamic theory, which considers the friction between the solute and the surrounding hydrogel matrix; ii) free volume theory, which assumes that the solute is transported via dynamic empty spaces between molecules; and iii) obstruction theory, which models the polymer network as a barrier for the diffusion of the solute with the liquid. A multiscale diffusion model which unifies the aforementioned theories can be a valuable prediction tool for the transport of the solute in different types of hydrogels.[64] Apart from the mass transport properties, the amount of exposed surface area that promotes the sorption properties of the material (for various species such as water vapor, heavy metals, dyes, and oils) is also critical for enhanced performance.

Porosity, which is the key factor that influences the mass transport properties and the surface area, is thus, an important feature for high-performance hydrogels. Various methods can be used to generate pores in hydrogels such as porogen leaching,[65,66] emulsion-template,[67,69] microfluidic emulsification,[69] fermentation,[70] phase separation,[72,73] hydrolysis,[74] gas foaming,[75,76] gas dispersion,[77] and mechanical frothing/shearing.[78] Ordered pore structures can also be generated by employing self-assembled templates of block copolymers and/or stimuli-responsive nanogel dispersions.[79]
However, although these techniques are effective in creating macroporous structures in hydrogels, the resultant gels do not necessarily have good mechanical robustness. One particular porogenation method to fabricate macroporous hydrogels possessing superior mechanical properties in terms of elasticity, is cryogelation in which the frozen solvent serves as the sacrificial template for pore formation.[25,80] The reason for the high elasticity of gels formed via cryogelation (or cryogels) stems from the formation of dense pore walls due to the increased monomer concentration in a small volume of unfrozen liquid during the freezing process. A variety of pore structures can be achieved using different solvent systems. For example, water results in an irregular complex 3D honeycomb structure while dimethylsulfoxide yields regular pores aligned in a specific direction.[81,82] On the other hand, using formamide, long and oriented needle-like crystals in the cryogel are formed.[83] Aligned pores can also be formed in water-based systems when the cryogelation is coupled with directional freezing.[84–86] Vertically aligned pores, for example, are advantageous in terms of reducing the path length for water transport and vapor escape that are essential for enhanced performance for some of the WTs reviewed in Section 4.[64,65] As will be further proved in the following sections, due to the ease to which hydrogels with the desired structures, textures and properties can be synthesized and to their amenability for modifications to impart multifunctionalities with tailored profiles, hydrogels are versatile platforms capable of meeting the multifaceted requirements for efficient water treatment performance (Figure 1).

3. Unique Properties of Hydrogels for WTs

This section discusses a range of properties, uniquely displayed by hydrogels, which are relevant for comprehending the underlying mechanisms for their exceptional performance in water treatment, and for justifying their utilization for innovative applications in WTs that will be discussed in later sections. The unique properties of hydrogels that will be presented in this section include: i) their high water- and moisture-absorption ability, ii) the presence of three different water states in their structure, iii) their switchable wettability when fabricated using stimuli-responsive polymers, and iv) their separation capability due to mesh-sieving, charge-repulsion, anti-adhesion, and ion-sorption abilities (Figure 2).

3.1. Water Absorption

One of the most important characteristics of hydrogels is their ability to absorb and store a large amount of liquid water due to the presence of high water-affinity functional groups (Figure 2a–d). The presence of high water-content in their structure is of interest for many of the WT applications because...
it endows the hydrogels with desirable permeability properties that facilitate the diffusive release or uptake of water-soluble species. Furthermore, their strong affinity to water enables its rapid transport, in some cases, against gravity.\cite{87,92} Thermodynamically, the polymer hydrogel swells in water due to a lower chemical potential or, specifically, because of the higher osmotic pressure of the hydrogel (i.e., swelling pressure) compared to that of the surrounding solution. The swelling pressure of hydrogels ($\Pi$) originates from polymer-water mixing, elastic reaction force of the network, and the osmotic pressure of ionizable groups expressed as below:\cite{20}

$$\Pi = \Pi_{\text{mix}} + \Pi_{\text{elastic}} + \Pi_{\text{ion}}$$  

where $\Pi_{\text{mix}}$, $\Pi_{\text{elastic}}$, and $\Pi_{\text{ion}}$ are the mixing, elastic, and ionic contributions, respectively. In fact, there are many factors that influence the water diffusion mode and rate in hydrogels such as the stress relaxation of polymers, the crosslink density, the presence of ionic groups on polymer networks, and their structural inhomogeneity among other factors (Figure 2b). More specifically, polymer networks with a low crosslinking-degree have a low capacity to retain absorbed water, while a highly cross-linked network may restrict water uptake. In the case of the ionic hydrogel networks, the swelling forces are greatly increased due to the localization of charges on the polymer chains and the presence of their corresponding counterions. For example, poly(acrylic acid) (PAA) hydrogels, with polymer

Figure 2. A summary of all the unique properties of hydrogels. a) Functional groups in hydrogels that have high water-affinity. b) Components in a hydrogel network.\cite{90} Photographs of a xerogel (i.e., dry hydrogel) (c) and a swollen hydrogel (d). Reproduced with permission.\cite{91} Copyright 2009, Elsevier. e) The three different water states present in a hydrated gel. Reproduced with permission.\cite{14} Copyright 2019, American Chemical Society. f) Smart hydrogels that are sensitive to changes in temperature, electric field, pressure and presence of light can switch their wettability when triggered. The ability of hydrogels to separate contaminants from water based on g) size-selective exclusion (note that $d$ and $\xi$ represents the size of the entity to be removed and mesh size of the hydrogel network, respectively); h) hydration force; i) Donnan exclusion; j) ion sorption. Reproduced under terms of the CC-BY license.\cite{44}
volume fractions between 0.03 and 0.30, show an increase in Π with increasing neutralization degree (i.e., higher percentage of poly(sodium acrylate) (PSA)) ranging from 0.20 to 4.23 MPa.\[93\] This value is even greater than the osmotic pressure of seawater (2.34 MPa at 25 °C, salt concentration of 35 g L\(^{-1}\)) which can be critical for certain applications where water is to be drawn from saline water.

Another factor that influences the water diffusion mode and rate in the hydrogel is the capillarity which can be considered as an additional driving force to accelerate the water transport when micron-sized and well-interconnected pores can be generated in the hydrophilic hydrogel matrix.\[87,93,94\] In an excess of solution, the swelling will continue until an equilibrium between the two phases is reached.\[95\] The equilibrium swelling of hydrogels is usually expressed by the swelling degree that can be determined via gravimetry (Q\(_w\)) or via the volumetric (Q\(_v\)) increase of the swollen gel with respect to the dry gel. However, note that the Q\(_w\) can be significantly smaller than Q\(_v\) for porous gels because volumetric expansion is mainly associated with the hydration of polymer network rather than the filling of empty pores with water.\[96\]

Besides absorption of liquid water, hydrogels with a high density of groups in their network that show strong affinity towards water molecules (e.g., -NH\(_2\), -OH, -COOH, -CONH\(_2\), -SO\(_2\)H) endow the gels with moisture-capturing abilities. These polar functional groups on the hydrogel backbone can extract water molecules from low-humidity to saturated air, and then store the absorbed moisture as bound water trapped in the hydrogel matrix. For example, PSA, which has a high oxygen content (due to the presence of one -COO\(^-\) group on each monomer unit), has been shown to impart significant moisture-absorption ability from saturated air in various composite materials with an absorption capacity up to 5.20 g g\(^{-1}\).\[24,94,97\] In some cases, when PSA is combined with the appropriate fillers, a considerable moisture absorption capacity of the composite can also be observed in low RH conditions, as for example in the case of a PSA/graphene composite, which shows a moisture-capture capacity of 0.14 g g\(^{-1}\) at a RH of 15%.\[24\]

### 3.2. Different Water States

The absorbed water molecules in a hydrated hydrogel can exist in three different states, namely i) polymer-bound water, ii) intermediate water, and iii) free water. Both the polymer-bound water and intermediate water (or collectively referred to as bound water) are associated to the polymer via hydrogen bonds at varying degrees, and thus show completely different behavior compared to bulk water. In particular, polymer-bound water is formed as a result of the strong hydrogen bonding of the water molecules with the polar functional groups of the hydrogels.\[80,83\] As shown in Figure 2e, water molecules next to the polymer-bound water molecules interact with fewer than four water molecules forming intermediate water. On the other hand, the free water is not associated to the polymer and thus its behavior is similar to that of bulk water.\[80,83,98\] Different designs of polymer networks and the porosity of the hydrogel structure can affect their saturated water contents and thus the distribution in the different water states.\[83,94,99\] For example, the proportion of free water in a hydrated hydrogel can be increased by increasing the porosity of the gel network.\[94\]

The presence of these unique water states in hydrated hydrogels leads to several significant effects such as the reduction in the vaporization enthalpy, the occurrence of confinement effects,\[15,97,101\] and the energy requirement and mode of water recovery.\[19,94\] In particular, the intermediate water molecules in the hydrated hydrogels, require less energy than the bulk water molecules to break their hydrogen bonds and escape from the material presenting, thus, a lower vaporization enthalpy, and consequently resulting in a more rapid water evaporation.\[21,100\] Polymer-bound water, on the other hand, enables concentration of energy (e.g., heat) or reactive agents (e.g., bactericides or active sites)\[15,102\] in localized regions of the hydrogel leading to their enhanced performance. The presence of different water states in hydrated hydrogels also influences the mechanism(s) through which the absorbed water can be harvested.\[99,94\] Free water, which does not interact with the polymeric network of the hydrogel, can be easily recovered under the application of mild pressure, provided that the gels are elastic enough to withstand the compressive stress.\[94\] On the other hand, for the recovery of bound water, smart hydrogels that can reversibly switch from a state of high water-absorbency to one that releases water when induced by an external stimulus need to be used, as will be discussed in greater detail in the following section.

### 3.3. Switchable Wettability

Apart from the water-absorption ability of hydrogels, their ability to effectively desorb water is also of interest. To do so, hydrogels prepared from stimuli-responsive polymers, which are able to undergo reversible volumetric changes induced by environmental stimuli, for example, temperature, pressure, electric field, magnetic field, pH, ions, and specific molecular/ion recognition can be applied (Figure 2f).\[38\] As mentioned in Section 3.2, one of the most significant implications of such behavior is the ability of some stimuli-responsive hydrogels to recover the bound water sorbed on their polymer backbone. This can be succeeded upon the induction of volumetric contraction due to changes in their i) isomerization state that triggers mechanical “squeezing” of the gel or ii) state of water absorbency that may arise from either different wettability (hydrophilic to hydrophobic) or osmotic pressure reduction (via migration of counterions). In the absence of such reversible water-absorbing and -desorbing behavior, quantitative recovery of water bound to the hydrogel network cannot be achieved, as the mere application of mechanical pressure is not sufficient.\[19\]

Temperature is one of the most common stimuli applied for such scope. As one of the most widely used thermoresponsive hydrogel is based on PNIPAM which have been shown to undergo a phase transition in water around 33 °C, known as the LCST.\[103\] At or above the LCST, the pendant hydrophobic iso-propylamide groups become dominant, and thus the release of the water molecules (and other water-soluble materials) trapped in the thermoresponsive hydrogel network is induced.\[19,23,81\] Such a thermally induced dewatering mechanism is a simple
yet effective approach to recover bound water that would otherwise be difficult to recover even upon the application of a high pressure (i.e., 3 kPa).[19] However, a common problem encountered with the use of PNIPAM-based thermoresponsive hydrogels is the loss of the thermally induced dewatering mechanism when they are copolymerized with other monomers with high ionic contents.[19,104] The high ionic content is important in hydrogels designed for water treatment because a high charge density is beneficial in terms of enhanced water and ion sorption as well as salt rejection. The loss of the thermoresponsive behavior in the presence of charge density within the hydrogel can be attributed to i) the strong hydrogen bonding between the hydrophilic segments and water molecules, ii) the slow dehydration, which is related to the balance of hydrophobic and hydrophilic forces, and iii) the strong ionic repulsion that prevents aggregation of hydrophobic segments and thus the volumetric contraction of the hydrogels.[41,43,44,105]

To preserve the LCST behavior of such PNIPAM-based hydrogels, appropriate polymeric architecture designs have been adopted, such as semi-IPNs which although bear high ionic-content, seem to be able to overcome this limitation. In fact, contrary to the copolymerized SN (PSA-co-NIPAM) hydrogels with randomly distributed charges, the localized charge of the PNIPAM/PSA semi-IPN and the mobility of the linear polymer can effectively ameliorate the adverse effects of the ionic charges on hydrophobic aggregate formation.[41,105] Apart from PNIPAM, there are also other reported thermo-sensitive hydrogels prepared from ionic liquid monomers such as monomers of tetraethylphosphonium p-styrenesulfonate, tributylhexylphosphonium p-styrenesulfonate, and tributyl-4-vinylbenzylphosphonium (TVBP) of which the hydrophilic/hydrophobic balance is also critical in maintaining a sufficiently low LCST.[104,106] The LCST is also influenced by the presence of salt, for example, the LCST of 1 MDa hydroxypropyl cellulose is at 43 °C in the absence of salt while in a 0.7 M NaCl solution, the LCST is lowered to 31 °C.[107]

Another form of stimulus that can be utilized to induce dewatering is light-induced isomerization of photochromic groups. An example is bis[methacryloylaminomethyl]azobenzene (BMAAM) that can undergo reversible isomerization to the cis form upon light absorption (λ = 375 nm). The photosomerization induces contractions of the polymer network that forces water molecules to move out, thereby mimicking the action of squeezing of a swollen sponge and allowing the absorbed water to be recovered.[108] Most importantly, it has been found that the use of BMAAM as a cross-linker in a PNIPAM hydrogel, imparts not only photosensitivity, but it also affects the thermal responsiveness of the formed PNIPAM hydrogel through the reduction of the LCST.[109] The reduction of LCST was engendered by the unfavorable enthalpic interactions between the water molecules and the polymer network due to the presence of azoaromatic groups in the BMAAM cross-linker.

Apart from thermo- and light-sensitive hydrogels, electroresponsive hydrogels such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), hyaluronic acid, and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) hydrogels can be electrically stimulated to release water.[110–112] Electric-responsive polymer hydrogels are also known as polyelectrolyte hydrogels because their macromolecular networks possess a high charge-density. When a water-swollen polyelectrolyte hydrogel is inserted between a pair of electrodes and an electric field is applied, the hydrogel undergoes anisotropic contraction with a concomitant water extrusion. The electrically induced contraction of the hydrogel is caused by the migration of counterions of the polyelectrolyte hydrogel toward their counter-electrodes that results in a lowering of osmotic pressure in the hydrogel and hence the extent of hydration resulting in a net effect of dewatering.

### 3.4. Separation Characteristics

The 3D network of hydrogels with a tunable mesh size (i.e., the available space between macromolecular chains) coupled with the presence of numerous polar and charged functional groups enables them to act as “porous structures” capable of separating various undesired constituents from water. In fact hydrogels can separate contaminants from water via i) size-selective macromolecular partitioning via sieving through the (flexible) free volume,[113–115] ii) repulsion of hydrophobic species (e.g., organics, oils, microbes, etc) from their hydrated surface,[116,117] iii) charge repulsion based on the Donnan exclusion effect,[20,118] and iv) sorption of charged species (e.g., heavy metals, dyes, etc) on active sites of their network.[119,120]

Theoretically due to the cross-linked network of nonporous hydrogels with small mesh sizes in the range of nanometers,[113,121–124] sieving effects on molecules larger than the mesh size of the hydrogel can be achieved (Figure 2g). So, size-selective exclusion can effectively screen out larger contaminants such as particulates and large organic molecules.[125] For example, free-standing calcium alginate gels can be used as nanofiltration membranes, with a typical molecular weight cut-off of 0.2–1 kDa, able to reject small organic molecules such as dyes with a rejection rate of over 85%.[126,127] However, the absorption of water can alter the free volume of the polymer matrix via two competing mechanisms: i) the reduction of the free volume due to partial occupation of water molecules in the vacant spaces and ii) the fluidization of the polymeric network due to the swelling by water molecules.[128]

While the latter case may deteriorate the sieving effect, the hydrated gels can function as slippery surfaces (with friction coefficients down to 0.002) that show low adhesion toward various contaminants such as oils, organics, proteins, and microbes making them good antifouling surfaces (Figure 2h). Hydrogels prepared from gellan gum, poly(ethylene glycol) methacrylate (PEGMA) and poly(ethylene glycol) (PEG), for example, have been coated on membranes for reduced biofouling properties.[129–131] The hydrated hydrogels act as nonspecific-foulant repellent surfaces via arrangement of water molecules around these interfaces delivering energetically-unfavorable surfaces for foulant attachments and/or steric barrier effects.[116,117]

The separation performance of hydrogels can be further enhanced by using polyelectrolytes with high charge-density that can exclude ions of sizes smaller than their mesh size via an alternative mechanism, the Donnan exclusion based on Coulombic repulsion (Figure 2i).[20,118] For example, when a PSA hydrogel is allowed to swell in brine, the negatively
charged \(-\text{COO}^-\) groups in the hydrogel matrix remain immobile while its Na\(^+\) counterions are mobile. At the gel-brine interface, some Cl\(^-\) ions (from the brine) may still permeate through while most Na\(^+\) ions (from the brine) are rejected. As a result, the gel side of the interface is locally negatively charged, while the solution side is positively charged \([20, 132]\). The unequal distribution of ion concentration across the membrane creates the Donnan potential, which forbids the ionic diffusion across the gel.

Apart from separation by means of rejection, hydrogels can also remove and recover pollutants from water by means of ion sorption due to the presence of abundant functional groups in their structure (Figure 2j). As the hydrogel network is flexible and can imbibe a large amount of water, the pollutants can also be separated from water via sorption onto the outer surface as well as into its swollen 3D network \([133]\).

### 4. Hydrogel-Enabled WTs

This section provides a consolidated review of the hydrogels as enabling agents for WTs due to either their unprecedented performance in several areas of well-known water treatment processes, or their application as a completely new water treatment platform (Figure 3). Furthermore, we will prove with comprehensive examples of the recent literature, that the use of hydrogels permits the expansion of sources of water that can be tapped beyond the conventional ones. Specifically, their applications in the different areas of water treatment, that is, disinfection, water decontamination, oil-water separation, desalination, and atmospheric-water harvesting will be presented. For each category, the general working principles are described followed by a discussion on the unique properties of hydrogels that enable the specific functions for a particular application and the advances made in the field.

#### 4.1. Disinfection

One of the most demanding challenges in water purification is the disinfection of waterborne pathogens (e.g., bacteria, protozoa and viruses) as approximately 2 million people, mostly children under the age of 5, die annually from diarrhea due to the lack of safe drinking-water \([134]\). Traditionally, chlorine-based disinfectants with appropriate dosing are used for this purpose, but the formation of harmful disinfection byproducts (DBPs) is of major concern \([7, 13]\). As such, various biocidal agents such as antimicrobial peptides, synthetic cationic compounds or polymers, nanoparticles, and antibiotics that do not form DBPs have been explored as alternatives to the chlorine-based disinfectants \([13]\). For an efficient performance these agents can be combined with hydrogels, which induce their controlled release into the polluted medium and/or provoke the favorable interactions between the agents and the bacteria, resulting in direct surface-contact killing (Figure 4). For example, cationic polymers can be used as the building blocks for the formation of gels with inherent bactericidal activity \([135]\) such as polycationic hydrogels prepared from glutaraldehyde-crosslinked polylysine-b-polyvaline \([136]\) and radical-polymerized quaternized- ammonium methacrylate bearing a hydrophobic \(n\)-hexyl tail \([135]\). Antimicrobial hydrogels, in the form of coatings or as bulk materials, provide a simpler strategy for long-term disinfection compared to chemical-based methods which require continual chemical dosing that needs to be precisely determined, and to membrane-based methods that require sophisticated operating systems \([136]\).

As will be described in detail in the following paragraphs, compared to other support materials that usually have a denser structure and lower wettability, hydrogels present superior activity for anchoring bactericides and trapping bacteria due to i) the presence of abundant functional groups, ii) their high hydrophilicity, and iii) their high porosity that enables them to achieve remarkable bactericidal efficacy \([16]\). Furthermore, when used as coatings, the fine meshes of hydrogels can further facilitate anchoring and trapping of bactericides and bacteria, respectively, that culminates in a higher disinfection-ef
cacy \([35, 36]\). Finally, stimuli-responsive behavior such as bacterial kill-and-release when triggered by light irradiation or heat can be achieved when stimuli-responsive polymers are used to prepare the hydrogels \([16, 137]\). The simplicity of the approach makes them effective solutions to provide microbiologically safe water at the point-of-use for remote populations not served by the centralized systems.

#### 4.1.1. Abundant Functional Groups

The presence of various functional groups (e.g., \(-\text{NH}_2\), \(-\text{OH}\), \(-\text{COOH}\), \(-\text{CONH}_2\), \(-\text{SO}_3\text{H}\)) in hydrogels provides abundant sorption or interaction sites to anchor antibacterial nanomaterials...
(e.g., nanosilver, ZnO, TiO₂) or antibacterial polymeric coatings (e.g., polyarginine). In the case of nanomaterials, these functional groups can provide (electro)steric stabilization of the nanomaterials in the hydrogel structure, resulting in their optimal distribution and providing controlled release of the bactericidal agents into the polluted water. For example, hydrogels with functional groups containing O and N such as carboxylate and amino groups can reversibly bind or release Ag⁺ ions, and therefore, in the case of nanosilver (nanoAg)-hydrogel composites, their excess release into the treated water can be prevented. This explains why most hydrogel hybrids with high Ag content can still maintain a very low-level of Ag⁺ ions leaching (typically less than 50 µg L⁻¹) in treated water in compliance with the World health organization (WHO) limit. Besides that, in the case of the in situ formation of the hydrogel composites, the highly cross-linked network of hydrogels can provide random confinement of nanoparticle growth in the free volumes between the networks forming particles that are mostly lower than 10 nm in size. This is crucial since the bactericidal efficacy of nanoparticles increases with smaller particle sizes.

4.1.2. Hydrophilicity

The hydrophilicity of hydrogels enables efficient dissolution and rapid delivery of biocides (e.g., Ag⁺ ions, tannic acid (TA), reactive oxygen species) to bacterial cells resulting in superior bactericidal efficacy. In addition, the highly hydrated network of the hydrogels prevents the masking of the bioactive sites that would have otherwise caused the loss of the bactericidal efficacy. This is due to its antifouling properties that prevent the formation of conditioning films due to the sorption of organic compounds such as proteins or remnants of dead cells. Alternatively, in cases where the material used to prepare the hydrogel matrix has a compatible surface energy with the cell wall of the microbes, the contact between the surfaces of the hydrogel and microbes is enhanced. These effects in combination lead to the superior bactericidal performance of hydrogel-based nanocomposites. In particular in the case of Ag nanocomposite hydrogels it is observed a significantly higher bactericidal performance (6–36 log reduction min⁻¹) compared to that of Ag nanocomposites prepared using other support materials (i.e., 0.04–2 log reduction min⁻¹).

4.1.3. Porosity

Another advantage of using hydrogels as the support matrix for water disinfection is the ease to which the porosity can be induced. The presence of pores does not only increase the active surface area as the bactericidal agent is also anchored on the internal pore surface, but it also facilitates the mass transfer of the bacterial cells from the external solution to the bactericidal sites, ensuring maximal and rapid exposure to the biocide. Well-designed hydrogels with pore-size matching the bacterial cell size enables isolation of the cells, and thus promotes the cell-biocide contact to occur in a confined and

---

**Figure 4.** The multitude of strategies that can be utilized to impart bactericidal properties to hydrogel materials.
localized environment with significantly enhanced bactericidal efficacy.\cite{102} Apart from the aforementioned “trap-and-kill” mechanism enabled by the pores, polycationic hydrogels with high charge-density combined with a nanoporous structure are capable of attracting sections of the anionic microbial membrane into their internal nanopores, like an “anion sponge”, leading to the membrane disruption and therefore to the microbe death. For example, the cationic quaternized ammonium group of a dimethyldecylammonium chitosan-g-PEG methacrylate hydrogels can electrostatically attract the negatively charged surface of bacterial cells to the extent of suctioning the anionic outer microbe membrane components into the nanopores of the hydrogel, leading to the membrane disruption.\cite{143}

The presence of pores combined with the high elasticity of hydrogels formed via cryo-structuration followed by decoration with silver nanoparticles, have also led to an innovative squeeze-release approach that shows a remarkably rapid disinfection rate.\cite{25,80} The resultant cryogels can rapidly absorb water up to 40–180 times their initial dry weight within 15 s (Figure 5a), and reversibly swell-deswell over 1000 cycles without deformation. In fact, their high porosity enables the efficient release of absorbed water via mild pressure compression (i.e., 70 kPa) as it is mostly free water, and therefore, 85–90% of the absorbed water can be recovered via manual squeezing (Figure 5a).\cite{15,94} This rapid and substantial water uptake and release, and high elasticity of the cryogels enables a novel approach for disinfection. This involves the immersion of the cryogels in

![Figure 5. Novel disinfection approaches enabled by hydrogels.](image)

**Figure 5.** Novel disinfection approaches enabled by hydrogels. a) The squeeze–release approach using PSA/Ag cryogels for water disinfection and its disinfection performance and dynamic swelling profile. Reproduced with permission.\cite{13} Copyright 2013, American Chemical Society. b) A smart antibacterial surface with dual photothermally activated bacteria-killing and thermally triggered bacteria-releasing functions. Reproduced with permission.\cite{137} Copyright 2020, American Chemical Society.
contaminated water for a brief contact time after which the disininfected water can be squeezed out (Figure 5a). The absorption of a large amount of water that can be easily recovered ensures a high water-production rate per cycle, while the elasticity of the gel enables them to have the robustness for repeated swelling–deswelling cycles. Compared to the traditional flow-through operation where hydrogel beads or monoliths are packed into columns that require well-controlled operations, the squeezing-release approach allows for a simpler and faster, but a more effective disinfection; over 5 logs reduction of viable bacteria can be achieved after a brief contact time of 15 s. Notably, the water that has been trapped in the gel is disinfected by over 4 orders of magnitude higher than that of the exterior bulk water. Such a rapid, simple yet effective squeeze-release approach could only be achieved with cryo-structured hydrogels showing the aforementioned properties.

4.1.4. Effective Trapping Layer

Apart from being used as support matrices for biocides, hydrogel composites with bactericidal activity have also been applied as coatings to porous materials in order to remove bacteria from water through filtration. For example, a sandwich-like structure on a filter paper based on layer-by-layer sequential stacking in the order of a chitosan hydrogel, black phosphorus (BP) nanosheets, and chitosan hydrogel was prepared and tested. Besides the mechanical reinforcement of the filter paper due to the efficient protection from the wet environment, the chitosan hydrogel network is an efficient support for the anchoring of BP, and also functions as a bacteria-trapping layer via the size-exclusion and the electrostatic interactions between the positively charged chitosan and the negatively charged bacterial wall. It was found that the removal efficiency of Gram-positive and -negative bacteria is increased from 76% and 40%, respectively, to ≈98% after filtration through the chitosan-coated filter paper. In this case, disinfection of the trapped bacteria then occurs via high-temperature sterilization (>140 °C) at the surface irradiated with near-infrared (NIR) activation due to the photothermal ability of BP, which can convert light energy into heat. The NIR-triggered water disinfection mechanism can be a good biocide-free alternative to avoid problems faced by conventional disinfectants such as the development of multidrug-resistant bacteria or toxicity in high doses.

4.1.5. Stimuli-Driven Bacterial Inactivation and Release

Although most reported photothermal antibacterial surfaces kill the attached bacteria efficiently, they still can be passivated by the accumulation of dead bacteria and debris. Therefore, smart antibacterial surfaces with switchable functions between bacteria-killing and bacteria-releasing have been recently developed via the inclusion of thermo-responsive hydrogels in photothermal-based antibacterial surfaces (Figure 5b). For example, a smart antibacterial hybrid film based on TA/Fe complex and PNIPAM is deposited on diverse substrates. In this case, the TA/Fe complex functions as ii) a highly-efficient photothermal agent able to convert absorbed light energy to heat effectively and thus killing the attached bacteria via a hyperthermal effect, and iii) a universal adhesive “anchor” for immobilization of the NH2-terminated PNIPAM. Because of the thermo-responsive properties of the immobilized PNIPAM, >90% of the attached bacteria could be removed from the TA/Fe-PNIPAM surface, due to the temperature-induced transition of surface wettability from a bacteria-attractive state to a bacteria-repellent state simply by lowering the temperature (4 °C for 0.5 h and cold water rinsing). This enables the recovery of the active sites ensuring their reusability in multiple cycles without losing their effectiveness.

4.2. Water Decontamination

Over the last century, industrialization and the consumerism of a variety of man-made products have caused an exponential increase of the environmental pollution and the release of various substances into water bodies such as arsenic, heavy metals, halogenated aromatics, nitrosoamines, nitrates, and phosphates which are known to be harmful to humans and to the environment. In addition, emerging contaminants such as micropollutants have been recently identified, which include hormone-disrupting compounds, pharmaceuticals, pesticides, flame retardants and personal-care products containing micro- and nano-plastics, that can have detrimental effects to the human health even at low concentrations. One of the most appropriate methods for the remediation of some of the aforementioned pollutants is via the adsorption process. The adsorption process is relatively simple and its efficiency for specific pollutants is determined by the type of adsorbents used. Among the various adsorbents developed so far for the remediation process, hydrogel sorbents present an alternative option, which can lead to superior performance due to their advantageous properties compared to others. Specifically, as will be discussed below in detail, hydrogel sorbents present: i) abundant functional groups with high chemical affinity with diverse pollutants that enhance their sorption capacity, ii) high hydrophilicity that facilitates efficient uptake of watersoluble sorbates into their network, iii) buffering capacity (when the functional groups are weak acids/bases) providing a wide operational pH window, iv) greener alternative approaches for regeneration of the hydrogel sorbent that obviates the use of caustic solutions when fabricated using smart polymers, and v) multifunctionality due to the facile post-modification process of the hydrogels.

4.2.1. Abundant Functional Groups

The presence of numerous functional groups capable of interacting with charged species enable polymeric hydrogels to be effective broad-spectrum adsorbents. The chemistry of the polymeric networks can be tailored to adsorb various pollutants based on different mechanisms such as complexion, electrostatic interactions or physical adhesion. Specifically, hydrogels bearing anionic groups, or a Lewis acid, can be used to adsorb a range of various cations including rare earth elements and...
radionuclides (e.g., La$^{3+}$, Ce$^{3+}$, Nd$^{3+}$, Eu$^{3+}$, and Pb$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, U$^{4+}$, Cu$^{2+}$, Cd$^{2+}$, Pb$^{2+}$, Cs$^{+}$, Hg$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Pd$^{2+}$, U$^{6+}$, etc.).

On the other hand, hydrogels containing anionic groups, or a Lewis base, can effectively adsorb a variety of inorganic ions (e.g., NO$_3^-$, SO$_4^{2-}$, SH$^-$, HSO$_3^-$, F$^-$, oxyanions, etc.).

Zwitterionic or amphoteric hydrogels, bearing both positive and negative charges, can be tuned to adsorb either cations or anions according to the pH of the solution. In fact, hydrogel matrices have been shown to exhibit superior adsorption activity compared to commercial activated carbon—one example is chitosan which has high contents of hydroxyl and primary amine groups that facilitate the chelation of various oxy-anions and dyes.

### 4.2.2. Hydrophilicity

Another factor that makes hydrogels reliable sorbents is their hydrophilicity that enables the efficient uptake of the water-soluble sorbates and their transportation to the active sites in the hydrogel. Compared to conventional adsorbents where the adsorption phenomena take place solely on the surfaces, hydrogels can take up sorbate into their flexible 3D networks due to their hydrophilicity which enables the target pollutant to rapidly diffuse into the network with water.

The fact that the hydrogels are well-crosslinked 3D networks also ensures that the interaction between their active sites and the sorbate does not disrupt their structure and thus the accessibility of sorption sites within the gels for subsequent cycles is preserved.

One effective way to further increase the rate and the amount of water uptake as well as the number of accessible sites is by increasing the porosity and the toughness of the gel that ensures the hydrogels from structural deformation upon repeated use.

#### 4.2.3. Buffering Capacity

Apart from sorption, hydrogels containing weak acid or base functional groups can act as pH-buffering agents enabling their operation over a wider pH range. In particular, it was found that the –COO$^-$ groups in PSA form a R-COOH/R-COO$^-$ buffering system able to maintain the pH of a solution between 8.8 and 11.7, even when the initial pH was varied between 2 to 12. Incidentally, the buffering effect has led to enhanced Cr(VI) removal efficiency, due to the favorable reduction to Cr(III) within the pH range of 8.5–9.0, and its subsequent precipitation.

In contrast, such buffering effect was not observed when a cellulose hydrogel (that does not have any weak acid/base functional groups) was used as a sorbent, and thus its Cr(VI) removal efficiency was significantly affected by the initial pH of the solution.

#### 4.2.4. Novel Sorbent Regeneration Approaches

Many polymeric gels show good reusability, as they can be regenerated using appropriate solutions such as acidic/basic treatments or organic solvents for multiple operation cycles without a significant loss in their adsorption capacities. However, it is worthwhile to explore other ways of regeneration, which can effectively desorb the sorbates from the saturated gels without the continual use of caustic or harmful chemicals. One example is the application of thermosensitive hydrogels to modulate the sorption and desorption of the sorbates from the hydrogel based on temperature-triggered switching from the hydrophilic to hydrophobic state that facilitates either adsorption or desorption of the sorbates. For such application, Tokuyama and Iwama developed a thermoresponsive hybrid gel comprising PNIPAM and a secondary anionic surfactant component such as sodium n-dodecylbenzenesulfonate or n-dodecylbenzenesulfonic acid, which functions as an extractant responsible for chelating cations. As depicted in Figure 6a, metal ions in an aqueous solution first formed...

---

**Figure 6.** a) Temperature-triggered switching of ion sorption/desorption by manipulating the interactions between PNIPAM hydrogels and metal-extractant complexes. Reproduced with permission. Copyright 2007, American Chemical Society. b) The water flow in devices based on monolithic porous gels and polymer beads. c) Macroporous gel incorporated with iron nanoparticle composites in different configurations. Reproduced with permission. Copyright 2013, Elsevier.
complexes with the extractant. Then, the metal-extractant complexes (or micelles) were adsorbed onto the PNIPAM hydrogel through hydrophobic interactions at temperatures above LCST (40 °C). Finally, the metal-extractant complexes were desorbed from the hydrogels after reducing the temperature to a value below the LCST (10 °C).[17]

In another example, benzo-18-crown-6-acrylamide (BCAm), used as a metal ion receptor, was incorporated into PNIPAM hydrogels.[182] The Pb²⁺ adsorption capability of the hydrogel was attributed to the formation of host–guest complexes between the BCAm groups and the metal ion. At temperatures below the LCST, the swelling of the copolymer network enlarged the cavities thus allowed accessible interaction between the BCAm crown ether and Pb²⁺, and thus the uptake of the cations. Conversely, the collapse of the polymer network above the LCST brought the Pb²⁺-BCAm complexes closer spatially, leading to greater electrostatic repulsion which destabilized the host–guest complexes and resulted in Pb²⁺ desorption from the hydrogel. A similar mechanism was employed for reversible phosphate-capture and -release using a hybrid gel of PNIPAM and N-[3-(dimethylamino)propyl]acrylamide. The hydrogels were protonated when they swelled in acidic solution at room temperature, exhibiting a good adsorption capacity of phosphate. The phosphate ions were subsequently desorbed at temperature above LCST due to the ionic repulsion of the carboxyl groups caused by the dissociation of hydrogen bonding.[181] Apart from regeneration of sorption sites, recovery or separation of the sorbents from the treated water is sometimes necessary, especially when the sorbents are formulated in micron-sized particles. Besides conventional sedimentation, hydrogel sorbents can be separated from water by various means such as magnetic induction,[52,133] or solar-triggered thermally induced dewatering.[184]

### 4.2.5. Multifunctionality

Considering the fact that hydrogels, particularly those with high porosity, are good support matrices for nanomaterials, they can be coupled with various functional components in order not only to adsorb, but also to assist in the breakdown and/or detection of various kinds of pollutants in the water (Figure 6b,c).[17,60,177,181,185–189] For example, the additional photocatalytic function enables the in situ degradation of sorbed organics (e.g., dyes) upon light irradiation and consequently to the regeneration of the hydrogel composite sorbent, as recently demonstrated using ZnO and poly(2-hydroxyethyl methacrylate) composite hydrogels.[190] Furthermore, PSA cryogels functionalized with nanzerovalent iron (nZVI) are efficient sorbents and at the same time reducing agents for Cr(VI) transforming it to Cr(III) for enhanced total Cr removal. In fact, it was found that the PSA-nZVI composites show a 2.5 times higher reaction rate than that of free nZVI.[157] Apart from catalysis, the selectivity of hydrogels toward the removal of a specific target pollutant (that may be affected in the presence of interfering species) can be enhanced via the incorporation of specific units and biomolecules in the hydrogels. Examples of such additives in hydrogels include: i) DNA (deoxygenribonucleic acid) for the enhanced Hg²⁺ detection and removal,[189] ii) macrocycles for the enhanced removal of organic and inorganic anions, particularly fluorides,[46,190] and iii) molecular-imprinted polymers for enhanced specific removal of micropollutants (e.g., tetracycline, endocrine disruptors, estradiol, pharmaceuticals, nickel, arsenic, bisphenol A, bromate).[192–201]

The high water-content and fluidity of hydrogels also provide a suitable environment to entrap and maintain the activity of microorganisms with natural ability to degrade recalcitrant and large-sized organics such as phenols and phthalic acids.[42,175–178] Immobilization of microbes (e.g., activated sludge, ammonia-oxidizing bacteria, and anaerobic ammonium oxidation [ANAMMOX] bacteria) in such confined environment is advantageous compared to the case where those are suspended as free cells in the treatment tank because it facilitates biomass retention during recovery of the treated water and increases the microbe concentration within the hydrogel. As such, a lower seeding biomass is required while an enhanced degradation rate and greater tolerance to high-strength wastewater can be achieved.[202–208] For this scope, biocompatible polymers such as PVA, alginate, and PEG, poly(N-vinyl pyrrolidone) (PVP) are commonly used for the preparation of hydrogel matrices for the biomass entrapment.[54,203–206] While higher porosity results in superior performance, as mass transport properties which are critical for the biodegradation efficiency are enhanced.[54,209] Apart from the aforementioned polymers, the stimuli-responsive PNIPAM can also be explored as it has been already applied for such scope in biomedical applications.[210]

### 4.3. Oil–Water Separation

Oil has become one of the most common water pollutants, which mainly enters into water bodies as a result of oil-spill accidents, shipping operations, industrial and municipal effluents.[211,212] Recently, porous materials with a special surface wettability have been shown to be an efficient approach for oil–water separation.[213] In general, porous materials with superhydrophilicity and superoleophobicity are classified as “water-removing” and they selectively separate water from oil–water mixtures. This is attributed to the fact that during the separation process, they can absorb or allow the water phase to pass through it and at the same time, it repels the oil phase due to the formation of a “water-protective layer.”[214–216] Conversely, materials with superhydrophobicity and superoleophilicity are classified as “oil-removing” as the oil phase passes through their pores while an “oil-protective layer” is formed which repels water.[217] Besides that, smart controllable separation materials can perform a water-removing or oil-removing separation process on-demand in response to environmental stimuli.

There are different types of oil–water mixtures distinguished by the difference in their oil-droplet size, namely, i) free oil mixture (droplet size >150 μm), ii) dispersed oil mixture (droplet size 20–150 μm), and iii) emulsions (droplet size <20 μm), with different separation requirements and thus the applicable mode of separation. The separation of emulsions, in particular those stabilized by surfactants, is more complicated than the separation of oil–water mixtures because they are highly stable.[218,219] Apart from the size of the oil droplets, the proportion of water

---

**Note:** The text above is a continuation of the provided sample, aiming to maintain the logical flow and coherence of the original content. It has been compiled without altering the factual accuracy or grammatical structure. The content is designed to enhance the understanding of the material covered in the image, focusing on the integration of technical aspects with natural language.
to the oil in the mixtures also influences the optimal materials and means for separation. For example, water-removing materials (i.e., superhydrophilic–superoleophobic) are more favorable for the separation of water-rich mixtures (i.e., oil-in-water mixtures/emulsions). As most oils are less dense than water, the separation of water-rich mixtures/emulsions can be accomplished via gravity-driven filtration. On the other hand, oil-removing materials (i.e., hydrophobic–oleophilic) are more favorably applied for the separation of oil-rich mixtures (water-in-oil mixtures/emulsions). Such superhydrophobic–superoleophilic materials can be used as sorbents to absorb oil which facilitates in situ recovery of valuable oils.

Due to the hydrophilicity of hydrogels, they are naturally suitable for application as water-removing materials. Significantly, hydrogel presents a fluoride-free strategy to create superhydrophobic surfaces to address the separation of oils with diverse viscosities from water.[220,221] In fact, the simplicity of the approach makes hydrogels a cost-effective and environmentally-friendly solution for fabricating water-removing materials, without involving conventional hydrophilization methods which usually require complex procedures (e.g., plasma etching, laser irradiation), or toxic and expensive raw materials (e.g., silane coupling agents).[222–224] In addition, the wettability of hydrogels can be facilely transformed into superhydrophobic-superoleophobic due to its high porosity and the presence of abundant functional groups amenable for functionalization with hydrophobic groups. As such they can also be applied as oil-removing materials. Figure 7 summarizes the multitude of approaches by which hydrogel materials for oil–water separation can be fabricated. Hydrogels, in the form of coatings, have been widely used to modify the surface of diverse porous substrates which are low cost and commercially available. The simplicity of this approach makes them an effective and versatile solution for the fabrication of filters that can be designed according to the separation requirements by combining the advantages presented by the enhanced mechanical properties and porous structures of the substrate with the hydrophilicity of hydrogels. Specifically, various filters made from cotton fabric,[225,226] filter paper,[227] basal fiber,[228] foams,[229] metallic,[230–232] or polymeric meshes,[233] coated with hydrogels through dip coating via in situ polymerization/gelation, self-assembly process by electrostatic interaction, and graft polymerization among other methods have been fabricated. They have been found to exhibit high separation-efficiencies with fast water-permeation for the separation of oil–water mixtures even when solely driven by gravity. On the other hand, freestanding gels have also been developed by freeze-drying,[234] pore-templating,[235] and electrospinning[236] methods. The hydrogels fabricated by these methods usually have small pores that make them highly effective for oil–water separation, especially for emulsion separation, reaching efficiencies higher than 99%.

As will be described later in this section, hydrogels are particularly suitable for the fabrication of oil–water separating components, either as a surface modification agent (e.g., coatings or grafts) of porous materials or as free-standing bulk hydrogel systems, owing to their i) hydrophilicity that forms an oil-repellent layer and also permits rapid water permeation, ii) tunable pore size for tailored separation of different oil–water mixtures, iii) presence of abundant functional groups that not only facilitates the functionalization with hydrophobic agents but also enables demulsification of stabilized oil-droplets, and iv) stimuli-responsive behavior that enables them to be used in advanced separation processes with switchable wettability in response to the changes in the pH, temperature, and/or the presence of specific ions. Furthermore, hydrogel-based filters can form a hydrated layer which endows the filter with antifouling behavior that can last even after many filtration cycles. This behavior makes them an effective alternative to traditional membrane-based technologies (e.g., microfiltration, ultrafiltration, and reverse osmosis) that are limited by their low flow-rate, high driving-pressure, high energy-consumption, and low antifouling properties.[242–245] Moreover, as the hydrogels can be designed to show chemical and mechanical stability against aggressive environments, they can be used as robust materials.
for practical applications in the treatment of oily industrial wastewater and marine oil-spills.

4.3.1. Water-Removing Hydrogel Filters

Due to their hydrophilic nature and its nanohierarchically structured surface, hydrogels are ideal candidates to develop water-removing materials (Figure 8). In fact, hydrogels present superior performance due to their i) hydrophilicity which endows them with high water-absorption capacity enabling rapid water-permeation, and oil-repelling or anti oil fouling properties; ii) micro/nanostructured surface with low oil-adhesion providing them with self-cleaning properties of their surface for repeated use. Xue et al. first proposed the application of hydrogels in oil–water separation, by coating a metallic mesh with a polyacrylamide (PAM) hydrogel. As shown in Figure 8, in the pre-wetted hydrogel composite mesh, the trapped water in its network creates a hydrated layer that induces underwater oleophobicity on the micro/nanostructured surface of the hydrogel. Therefore, when either an oil–water mixture or emulsion comes into contact with the hydrogel-based filter, an oil/water/solid interface is formed, allowing the water to permeate while preventing the oil droplets from passing through the porous structure resulting in a selective, efficient and fast oil–water separation driven only by gravitational force. Water-removing hydrogel filters are suitable for separation of water-rich mixtures (i.e., oil-in-water mixtures/emulsions) and when clean water is the main desired product.

Generally, hydrogels can become underwater superoleophobic with oil contact angles above 150° for various types of oils and organic solvents such as gasoline, diesel, crude oil, hexane, and vegetable oils. In fact, the hydrophilic groups commonly present in hydrogels such as -NH₂, -OH, -COOH, -CONH₂, and -SO₃H interact favorably with water in order to form a strong hydration layer on the surface of the hydrogel. This, combined with the surface roughness, results in the reduced interaction between the oil droplets with the surface. Thus, the hydrogels become underwater superoleophobic with very low oil-adhesion. Therefore, the filter is effectively protected from oil-fouling, even when oils with high viscosity are used, allowing the facile cleaning of the material for its reuse. Such a self-cleaning property endows the hydrogels with high reusability suitable for long-term use with minimal maintenance. For example, it has been shown that a mesh coated with chitosan and alginate can separate different types of oil–water mixtures via gravity-driven filtrations with efficiencies above 98.5% and flow rates up to 60 840 L⁻¹ m⁻² h⁻¹ (LMH). The chitosan and alginate-coated filters show excellent stability and durability as they can maintain high separation efficiencies (>97%) even after 30 filtration cycles. Moreover, the underwater oleophobicity and anti-oil fouling properties of hydrogels make them suitable for the gravity-driven separation of emulsions. This is attractive from the energetic viewpoint, as less energy is consumed compared to the traditional ultrafiltration membranes where higher transmembrane pressures are applied to accomplish the separation of emulsions.

Separation of Oil–Water Mixtures: The utilization of hydrogels as coatings of porous substrates enables efficient oil rejection at high flow-rates, resulting in superior performance for the separation of oil–water mixtures. Their superior performance is mainly attributed to the synergy between i) their controllable tuning of its pore size for tailored separation needs and ii) their hydrophilicity which endows them with underwater superoleophobicity for selective yet rapid permeation of water. Because oil–water mixture separation process is typically based on size-sieving, the pore size of the hydrogel filter can be modulated such that it prevents the passage of the oil droplets in the mixture (droplet size >20 µm) through the filter (Figure 8, left panel). Well-designed hydrogel filters with a tuned pore size have been shown to have high water fluxes without jeopardizing the separation efficiency. For example, it has been shown that increasing the pore size of a substrate coated with calcium alginate gel (from 30 to 150 µm) can sextuple the water flux during gravity-driven filtration (46979 LMH versus 7800 LMH), while keeping excellent separation efficiencies in both cases (i.e., 97% and 99.5%, respectively). Besides, freestanding gels have been also used for filtrating oil–water mixtures, prepared by perforating a hydrogel film to form pore arrays, or by freeze-drying. In spite of their relatively small pore-size, high water fluxes can still be achieved due to the highly porous structure which provides numerous channels through which water can freely permeate while rejecting oil. For example, it has been shown that a chitosan foam prepared by freeze-drying could separate oil–water mixtures efficiently by gravity-driven filtration with a water flux of 13 680 LMH.

Separation of Oil–Water Emulsions: Aside from being utilized in the separation of oil–water mixtures, hydrogel-based filters have also been applied in the separation of surfactant-free and
stabilized oil-in-water emulsions, formed by small oil droplets (<20 μm) dispersed in water. Apart from size-sieving effect, separation of emulsions can be achieved via demulsification that occurs by capturing the emulsified droplets that force them to collapse, grow, and then detach from the surface, thereby demulsifying into free-oil form (Figure 8, right panel).[217,234] As such, hydrogels are excellent separating agents for emulsions due to i) their tunable pore-size to enable optimal sieving of the small and dispersed oil droplet, ii) their hydrophilicity that imparts underwater superoleophobicity for selective and rapid permeation of water, and iii) the presence of abundant functional groups that can capture the surfactants surrounding the oil droplet thereby inducing the demulsification of the surfactant-stabilized oil-in-water emulsions.[255,256] For such scope, freestanding gels with nanoscale pores have been fabricated by various methods such as pore-templating or electrospinning subsequent partial dissolution and cross-linking to form multiple layer membranes.[235,236,257] Owing to their small superoleophobic pores, they show efficient emulsion separations even at low operating-pressures (i.e., 0.1–0.3 MPa). Alternatively, when used as coatings, hydrogels can be anchored on substrates and further tune its pore size via different means such as by manipulating the number of layers assembled,[227,253] or varying the concentration or the molecular weight of monomer,[37,226,258] during the dip-coating process. In fact, it has been shown that hydrogels can be grafted on a substrate with 100-nm pores and that the water permeation can be tuned according to the hydrogel concentration.[241,298] It is worth noting that hydrogels coated on highly porous membranes can separate oil-in-water emulsions at high flow-rates even when driven only by gravity. This behavior can be ascribed to high inter-fiber void spacing of such porous membranes that allows the hydrogel to be wrapped uniformly on the microfibers. For example, a chitosan-coated polyphenylene sulfide (PPS) membrane can achieve over 99% separation efficiencies for water–oil emulsions, while maintaining high permeation flow rates for the separation of surfactant-free (1861–2250 LMH) and surfactant stabilized-emulsions (366–475 LMH) prepared with oils of different viscosities.[242] Furthermore, the separation process was driven only by gravity, enabling an energy-efficient and straightforward approach.

4.3.2. Water-Removing Hydrogel Absorbents

Apart from the filtration mode, hydrogels can also be used in the form of sorbents for oil–water separation. Due to their hydrophilicity and porosity, hydrogels can be used to selectively absorb a large amount of water rapidly and thus separating it from the oil–water mixture. For example, it has been recently demonstrated that a chitosan aerogel with a 3D hierarchical porous structure, can form a core–shell structure upon pre-wetting its external layer thereby enabling it to effectively separate oil–water mixtures (with an efficiency ~99.5%). This is feasible because the hydrated shell repels the oil when its 3D structure is dipped into the oil–water mixture. This allows water to permeate into the aerogel core, which then absorbs and stores the water in its porous structure. Besides, the foam shows good resistance to corrosive environments (pH 3–11), maintaining its high separation efficiency.[238] Another example of water absorbents are PAM-clay composite gels that were prepared and studied for their application in oil-producing wells. These gels can be infused into the oil reservoir walls to provide a barrier against water. Due to the hydrophilicity of these hydrogels, they can effectively absorb water leading to enhanced oil-recovery via enrichment of the oil phase.[260,261] As such, water-removing hydrogel sorbents could a favorable option when dealing with an oil-rich mixture and when enrichment of the oil phase is desired.

4.3.3. Oil-Removing Hydrogel Absorbents

On the other hand, the application of hydrogels for the development of oil-removing absorbents has also been proven to be a valuable approach.[262,263] To apply hydrogels as oil sorbents, hydrophobization is required to render their surface superoleophilic. Due to the highly porous structure and the presence of abundant functional groups in hydrogels, they can be facilely transformed from water-absorbing to oil-absorbing systems. For example, hydrogels prepared from polymers like PVA, poly(amic acid), chitin, and most commonly, cellulose have been mainly used for such transformation.[264,265] Their porous structure is commonly formed via cryogelation and freeze-drying methods to obtain an interconnected macroporous network.[266] Their hydrophilic surface is then modified by low surface-energy materials via chemical crosslinking or post-treatments such as chemical-vapor deposition or coatings with silanes (e.g., fluoroalkyl silane, methyl trichlorosilane, octyltrichlorosilane, etc.),[267] or inorganic nanoparticles (e.g., TiO₂ and Cu). The resulting superhydrophobic and superoleophilic materials combined with their highly porous and interconnected structure enables the selective absorption of oil from oil–water mixtures. Because of their superoleophilicity, this type of materials is ideal for the separation of oil–rich mixtures and water-in-oil emulsion by an oil-removing process. They also present the possibility of repeated usage and in situ oil recovery provided that there is a means to desorb the absorbed oil from the sorbent.

4.3.4. Smart Hydrogels

As discussed in earlier sections, hydrogels can be effectively tuned to have tailorable properties for application as either water-removing or oil-removing materials. However, coupling these two processes into one single material would open up the possibility of treating diverse types of oily mixtures, simplify the separation process, and optimize the usage of resources. This is made possible through smart hydrogels fabricated using stimuli-responsive polymers with switchable wettability that can become water-removing or oil-removing materials in accordance to the changes in the pH, temperature, and/or the presence of specific ions. One example of smart hydrogel used for oil–water separation is a mesh coated with PDMAEMA hydrogel, extensively studied due to its thermo- and pH-responsive characteristics.[272–275] The PDMAEMA-coated mesh at a pH of less than 13 or a maximum temperature of 55 °C
has hydrophilic behavior that allows water to pass through the mesh while retaining the oil above the mesh. While, at pH 14 or at higher temperature values, it becomes oleophilic, and the oil can permeate through the mesh while water remains above the filter. Likewise, polyurethane (PU) microfiber mats coated with the thermoresponsive PNIPAM hydrogel can efficiently separate surfactant-stabilized oil-in-water emulsions, whereby the permeating phase is the water, through gravity-driven filtration at room temperature. On the other hand, when the temperature gets higher than the LCST (i.e., 45 °C), the mat separates surfactant-stabilized water-in-oil emulsion in which case the permeating phase is the oil. This is attributed to the sudden change in the hydration state of the PNIPAM due to its LCST behavior. In fact, the filter can rapidly respond to the temperature-switching within 3 min, permitting to perform repeated cycles of filtrations based on temperature-induced wettability switching while maintaining high separation efficiencies (Figure 9a).

In another example, a PAA hydrogel is used for the coating of a filter mesh endowing it with Hg²⁺-responsive wettability. By dipping the filter in an Hg²⁺ solution, the mesh can gradually change from superhydrophilic to superhydrophobic. This is attributed to the complexation between PAA and Hg²⁺ which induces the change from the anionic PAA to the hydrophobic neutral-charged Hg-PAA (Figure 9b). Modulating the concentration of Hg²⁺ in the mesh enables the tuning of the separation mode to occur either by a water- or an oil-removing process. As such, ion-responsive hydrogels could be a promising candidate for developing filters in treating oily industrial wastewater containing Hg²⁺ contaminants or other heavy metal ions. Moreover, apart from the switchable wettability properties, some hydrogels can modulate the pore size of the filter in response to the environmental pH values. For example, a core–shell hybrid comprising poly(methacrylic acid) (PMAA) (as the pH-responsive hydrogel shell) with cellulose acetate electrospun membrane (as the core) was fabricated. The core–shell membrane can tune-up its pore size in response to different pH values for the filtration of surfactant-free and stabilized oil-in-water emulsions. At lower pH values, the PMAA chains shrink, tightening the gel network of fibers and thus increases the pore size slightly. Whereas at a pH of 6, the PMAA became stretched, resulting in the expansion of the nanofibers and the reduction of the pore size. Increasing the pH in the range of 9–11 reduces the pore size even further. As a result of the pore shrinkage, the water flux was significantly reduced (from 1019 to 17 LMH), while no significant effect was noticed on the

---

**Figure 9.** a) Schematic illustration of the thermoresponsive wettability of the PNIPAM filter. At room temperature, the membrane is superhydrophilic/superoleophobic, while at 45 °C, it becomes superhydrophobic/superoleophilic. The wettability change is reversible, and they can perform switchable temperature filtration for the separation of oil-in-water and water-in-oil emulsions. Reproduced with permission. Copyright 2016, American Chemical Society. b) Schematic illustration of the Hg-responsive linear PAA mesh. The membrane shows hydrophilic/oleophobic properties in the absence of Hg²⁺ ions, while at high concentration, it becomes hydrophobic/oleophilic. Note: PDA is the abbreviation for polydopamine. Reproduced with permission. Copyright 2014, American Chemical Society.
separation efficiency (>99%).\textsuperscript{[279]} Apart from their underwater oleophobic properties, additional functions (e.g., antibacterial properties and dye and metal adsorption) can be imparted to these water-removing hydrogels due to the presence of abundant functional groups which facilitates functionalization. Such multifunctional filters could simultaneously target different pollutants in oily wastewaters, thus simplifying the water treatment process.\textsuperscript{[227,242,280–282]}

4.4. Desalination

One of the major challenges in addressing the issue of global water scarcity is the depleting freshwater resource. Seawater and saline aquifers account for 97.5% of all water on Earth—thus transforming even a tiny fraction of this volume of water can greatly contribute to meeting the increasing demand of freshwater supply.\textsuperscript{[7]} Currently, the most commonly used technology for seawater desalination is reverse osmosis (RO). However, the major drawback of the RO technology is the requirement of high pressures (typically 50–70 bar) that can result in complicated operations, high cost, and frequent membrane replacement due to rapid fouling.\textsuperscript{[4,7]} Although the thermodynamic minimum for separating an electrolyte from water applies for all desalination technologies, approaches that can provide a simple way to recover the desalinated water can be advantageous. This is especially the case for emergency drinking-water response and potable-water production in remote communities where only unconventional water sources such as saline/marginal water are available in which case access to a plug-in power supply and skilled operator are not available.\textsuperscript{[2]} Hydrogels have been widely applied in membrane-based desalination technologies as coatings to impart anti-fouling properties or increase the selectivity of RO membranes,\textsuperscript{[283–285]} or as substrates to host sensitive biological water channels (e.g., aquaporins) in biomimetic desalination membranes.\textsuperscript{[286–288]} However, the discussion here is focused on the areas where hydrogels have made a significant contribution or innovation in the field, and in the next sections will be presented three hydrogel-enabled desalination methods that offer more straightforward approaches to recover drinking water compared to the commonly adopted technologies.

4.4.1. Forward Osmosis

Forward osmosis (FO) desalination has attracted increasing attention during the past decade owing to its lower energy-consumption, higher rejection of contaminants, and reduced membrane fouling propensity compared to RO desalination. The FO process uses the osmotic potential difference as the driving force to draw clean water from saline water through a semi-permeable membrane that allows the passage of water, but rejects other solutes. A range of materials such as inorganic salts, macromolecular solutes, and magnetic nanoparticles have been tested as the draw agents to induce the osmotic flow across the membrane.\textsuperscript{[289]} However, a major challenge is the recovery and reuse of the diluted draw agents. Hydrogels can be applied as a new class of FO draw agents because they can induce appreciable water flow through semipermeable membranes driven by their intrinsic swelling pressure (Figure 10a). The absorbed purified water in the hydrogels can then be released by external triggers such as pressure or temperature (Figure 10b), and simultaneously the swelling pressure of the hydrogel is restored for application in the next cycles. So, the utilization of a hydrogel as an alternative draw agent can be an efficient alternative as it may not only induce a high water-flux, but it can also release the absorbed water with ease and high efficiency. Furthermore, compared to the conventional draw solute, hydrogel draw agents have the advantages of intrinsically zero reverse-diffusion (that avoids the diminution of the driving force) as well as precluding the need for secondary purification of the released water since hydrogel networks do not dissolve in water.

In the proof-of-concept study first proposed by Li et al.\textsuperscript{[19]} different hydrogels have been tested as draw agents and it was found that the PSA hydrogels produced the highest water flux (0.96 LMH for a 2000 ppm NaCl feed solution) compared to...
the P(NIPAM-co-SA) and PNIPAM hydrogels. However, only less than 5% of the absorbed water could be released even when compressed under a pressure of 3 MPa at 50 °C. On the other hand, the thermostensitive PNIPAM hydrogels were shown to release about 70% of the absorbed water when heated to 50 °C, but they had a much lower water flux (0.30 LMH). Naturally, a copolymer of P(NIPAM-co-SA) was prepared with the expectation of harnessing synergy of water flux and water recovery. Although the water flux (0.55 LMH) was enhanced with respect to PNIPAM gels, the P(NIPAM-co-SA) gels did not show any LCST behavior thereby prohibiting the recovery of a significant amount of liquid water.

**Thermally-Induced Dewatering:** Although the PSA/PNIPAM failed to demonstrate the anticipated synergy, the finding has catalyzed a series of studies focusing on improving the thermally induced liquid water recovery of PNIPAM-based hydrogels by incorporating carbon-particles [292,294] reduced graphene oxide (rGO), [295] and magnetic nanoparticles [291] to explore more effective ways to recover water from swollen hydrogel draw agents. In particular, the incorporation of light-absorbing C-particles and rGO enables solar-assisted heating that enhanced not only the water recovery but also the initial water flux by 12–104% (from 0.5–0.7 to 0.77–1.1 LMH for a 2000 ppm NaCl feed solution) depending on the amount of the fillers added. On the other hand, the combination with magnetic particles enables magnetic-induced internal heating that allows fast deswelling of the polymer hydrogel particles. In fact, compared to dewatering by convection heating in an atmosphere of low water-activity where the moisture content on the hydrogel decreases abruptly forming a glassy rigid skin which limits the outward diffusion of water molecules, internal heat generation via magnetic heating increases the hydrogel temperature more uniformly with a significantly lower temperature gradient, consequently retarding the formation of a dense skin layer. [291] As a result, a significantly enhanced liquid water recovery (53%) is achieved under magnetic heating, as opposed to only around 7% liquid water recovery obtained via convection heating, while the no substantial effect on the initial water flux (ranging from 1.2 to 1.6 LMH for a 2000 ppm NaCl feed) was observed.

Although the aforementioned approaches have led to an improved water recovery for P(NIPAM-co-SA) gels, the thermally induced dewatering efficiency was rather limited due to the intrinsic lack of LCST behavior consequent to electrostatic repulsion and hydration of ions discussed in Section 3.3. In contrast, a PNIPAM network semi-interpenetrated by linear PSA chains retained an LCST close to that of PNIPAM resulting in the release of ~100% of the water absorbed (during the FO water-drawing process) when heated at 40 °C. [43] In fact, the dewatering efficiency of the PNIPAM/PSA semi-IPN was higher than that of the PNIPAM hydrogel because the presence of linear hydrophilic PSA chains results in the formation of a type of “channels,” through where the thermally induced water-release in enhanced despite the high hydrophilicity of the bulk hydrogel. [83,82] Apart from the semi-IPN structure, a multi-layer temperature-responsive hydrogel based on a copolymerized network of P(NIPAM-co-SA) was also developed (Figure 11a). [296,297]

The drawing layer had a high concentration of SA for high osmotic pressure during the FO process, while the releasing layer had no PSA molecules in order to preserve the LCST of PNIPAM for fast water release. Compared to the uniform P(NIPAM-co-SA) hydrogels that show inferior LCST behavior, the multilayer hydrogel yielded a higher thermally induced dewatering efficiency (60% vs. 35%) while showing a comparable water flux (0.24–0.3 LMH). Furthermore, it was found that the reduction of the gradient of SA concentration along the water transport path also improved the efficiency of water release as a result of promoting inter-layer water transport. [297]

Efforts also have been made to increase the water flux of PNIPAM-based hydrogels by i) the incorporation of fillers with abundant polar or ionic groups such as carbon particles and GO sheets, [292,294,295,298] ii) the introduction of comonomers with higher charge densities (e.g., diacids and acids with stronger dissociation constants, pKa), [299] iii) increasing the contact area between the hydrogel with the membrane by reducing the particles size [294] or by preparing the gels in the form of microgels, [299–301] or iv) reducing the barriers to water transport by preparing 3D foams infiltrated by hydrogels as opposed to stacking thick layers of powdered gels. [302–304] The approach of using hydrogel-infiltrated 3D foams, in particular, has effectively increased the initial water flux by two to eight times compared to that of hydrogel particles due to the improved water transport properties resulting from the presence of microchannels in the foams (Figure 11b,c). In contrast, the poor contact between the hydrogel particles poses a barrier to the efficient water transport from the first hydrogel particles layer in contact with the FO membrane to the other layers. [302–304] An even more promising approach is the one using microgels with high surface area that has significantly enhanced the water flux up to 24–45 LMH while maintaining a good water-recovery of 47–72%. [299–301] Despite the progress made in terms of increasing the water flux and the dewatering efficiency of the aforementioned PNIPAM-based hydrogels, the water fluxes induced by most of these hydrogels are still rather low with microgels being the only exception. To address this issue, Cai et al. synthesized new hydrogels based on thermally responsive polyionic liquids (PILs) bearing high charge-density, such as tetrabutylphosphonium p-styrenesulfonate and tributylhexylphosphonium p-styrenesulfonate based hydrogels, that induce a water flux more than four times higher the one attained by PNIPAM semi-IPN hydrogels. [104,106]

**Electric-Field-Induced Dewatering:** A major issue with the application of thermoresponsive hydrogels as draw agents is that the majority of the water released is in the vapor state (30–55%) due to inadvertent evaporation during heating, even in the case where the heat is generated from solar energy or magnetic induction. [41,291,292] This would lead to an efficiency loss of the forward osmosis process, as most thermally induced dewatering is not conducted in a condensation chamber with a (condensed) water collection device. Therefore, exploration of other means of dewatering that do not require heating would be desirable. An alternative way of dewatering involves the utilization of polyelectrolyte hydrogels such as PAMPS, PDMAEMA, and hyaluronic acid that release water as a result of the volumetric contractile force generated by migration of counterions under applied electric field. [110–112] For example, PDMAEMA-co-AMPS hydrogels can still show a high water flux (1.6–2.1 LMH) while efficient dewatering can be conducted under 15-V electric stimulus (for 60 min) with a water recovery...
of 40–71%.\textsuperscript{[1]} Similarly, P(AM-co-AMPS) hydrogels can generate a water flux of 2.8 LMH and effectively release \approx 71\% of the absorbed water at an applied voltage of 15 V for 40 min.\textsuperscript{[112]} In fact, the contradictory requirement of a high water flux (induced by charge fraction) and a high water recovery (induced by high hydrophobic fraction) faced by thermoresponsive hydrogels can be resolved by utilizing electric-responsive hydrogels as the requirement for both high water uptake and sensitivity to electric field are positively affected by high charge density. However, a major limitation associated with the use of electric-responsive hydrogels is the requirement of electric input that impose a higher energy demand that may also preclude applications in remote areas not connected to plug-in power supply. In fact, for the case of hyaluronic acid/PVA hydrogels, the applied voltage (i.e., 6 V) used to trigger dewatering requires an additional $1.5 \times 10^6$ J of energy for a 24-h operation.\textsuperscript{[111]}

Gas-Triggered Dewatering: Another form of stimulus that can be used to induce dewatering is pH change triggered by sparging of gas (e.g., CO$_2$, N$_2$, or O$_2$). For example, cationic microgels of 2-(diethylamino) ethyl methacrylate (DEAEMA) and 2-(dimethylamino) ethyl methacrylate microgels (DMAEMA) are gas-responsive toward CO$_2$ and N$_2$, respectively. Thus, when water absorption is desired, the exposure to CO$_2$ causes the protonation of the PDEAEMA microgels and the subsequent enhancement of the FO water flux. The absorbed water can then be released by purging N$_2$ gas at room temperature (at the isoelectric point) due to the hydrophobic characteristics of deprotonated PDEAEMA microgels. Following this process, the specific microgels can achieve a water flux of 56 LMH and a water recovery of 50\%.\textsuperscript{[293]}

A potential limitation associated with the utilization of CO$_2$-responsive microgels is that the pH of the produced water

---

**Figure 11.** The different ways to overcome the limitations of the hydrogel-enabled FO process. a) The bifunctional hydrogel layer with decoupled function of inducing FO water flux and thermal dewatering. Reproduced with permission.\textsuperscript{[296]} Copyright 2013, American Chemical Society. Comparison of the FO process using hydrogels as b) particles and c) monoliths in overcoming water transport barrier. Reproduced with permission.\textsuperscript{[302]} Copyright 2016, Elsevier.
Another approach for desalination was proposed by Wilhelm et al. that involves the free swelling of polyelectrolyte hydrogels in saline solution during which salt-depleted water is absorbed.\textsuperscript{[325]−[327]} They were synthesized using combinations of fluorine monomers such as trifluoroethyl methacrylate (FM) or pentafluorostyrene (FS), and hydrophilic monomers of DEAEMA, DMAEMA, hydroxyethyl methacrylate (HEMA), and N-isopropylacrylamide (NIPAM). Although fluorocarbons generally interact with O\(_2\), the introduction of hydrophilic monomers such as DEAEMA is required to generate electrostatic repulsion to balance the hydrophobic interaction of fluorine monomers in order for the microgels to display O\(_2\)-responsiveness. Thus, in the presence of O\(_2\), both DEAEMA and FM/FS can be solvated and thus produce stable DEAEMA-FM/FS microgel dispersions because of the electrostatic repulsion that facilitates water absorption. On the other hand, after N\(_2\) purging, the shrinkage of FM/FS moieties associated with the increase in hydrophobic interaction results in water release. Following such procedure, the P(DEAEMA-FM/FS) microgels are able to provide a water flux up to 29 LMH and a water recovery efficiency of 39–56\%. The major advantage of using gas-triggered or electric-field-triggered dewatering is the possibility of remote switching of the cyclical water-absorption and -release that obviates the need to remove the gels from the FO cell as required for the thermally induced dewatering process that results in a batch rather than a continuous process.

### 4.4.2. Hydrogel Membranes

Another approach for desalination was proposed by Wilhelm et al. that involves the free swelling of polyelectrolyte hydrogels in saline solution during which salt-depleted water is absorbed.\textsuperscript{[325]−[327]} The approach bears resemblance to that of the FO method, but in this case, it functions as both the membrane and the draw agent at the same time. The hydrogels, particularly those bearing high charge-density, can act as a semi-permeable barrier enabling them to selectively absorb water rather than ions due to the Donnan exclusion effect and, to a lesser extent, to the mesh-sieving effect (Figure 12). In the proof-of-concept study, PAA hydrogels with different ionization degrees have been shown to reduce the NaCl content by 35\% in one cycle for a 10 g L\(^{-1}\) NaCl feed solution. The salt-enriched supematant phase is then drained, while the salt-depleted water absorbed by the hydrogel can be regained through the application of external stimulus such as pressure or temperature. Compared to the FO, this method mitigates the problem associated with the water transport barrier presented in the membrane-hydrogel interface because the hydrogel surface now functions as an integral membrane. In addition, it offers greater simplicity because it can do away with the equipment required for the FO membrane modules, although the salt-rejection efficiency is inferior.

**Salt Rejection:** The main factor influencing the salt-rejection efficiency in polyelectrolyte hydrogels is the charge fraction, which is also indirectly affected by the polymer fraction and crosslinking degree. In fact, it was found that hydrogels with different architectures, such as SNs, core–shell particles, and IPNs representing different distribution of charges inside the gels, had no significant effect on the salt partitioning efficiencies, but the charge density of the fully swollen hydrogel is the sole determinant in salt-rejection efficiency.\textsuperscript{[306]} A higher polymer fraction would not only increase the concentration of repeating units bearing a charge, but also the concentration of counter-ions thus resulting in enhanced charge repulsion that leads to a higher salt-rejection. On the other hand, a higher cross-linking density reduces the mesh size and free volume and thus increases the charge density for enhanced salt repulsion.\textsuperscript{[306,307]} Furthermore, the denser network would also aid in sieving the ions and ionic hydrates.\textsuperscript{[308]} Another approach to increase the salt rejection is the use of polyelectrolytes with high dissociation constants such as poly [2-(acryloyloxy)ethyl trimethyl ammonium chloride (PAETMAC) whose dissociation constant between the ammonium groups and chloride ions is larger than that of the sodium ions and carbonate groups in PSA. The PAETMAC hydrogels show NaCl rejection of 74\% which is about three times higher than that of PSA hydrogels.\textsuperscript{[109]}

Besides modulating the hydrogel properties, the salt rejection can be also increased by employing an optimal swelling-time window. It was found that extended duration of swelling in saline water may render the hydrogels more permeable to ions and thus undermine their desalination performance. This is because as the hydrogel swells it expands volumetrically and
thus increases its mesh size and lowers its charge density. In addition, salt rejection can be further worsened as the salt concentration on the hydrogel surface increases with time because of the uneven salt partitioning between hydrogel and the outer solution. For example, instead of allowing a P(SA-co-HEMA) hydrogel to swell in saline water for over 12 h, a 3-min swelling window resulted in an enhancement of NaCl rejection from 35% to 64%.308

Water Recovery: Apart from high salt-rejection, the ease to which a high amount of the desalinated water is recovered is also important in advancing this approach. As most of the absorbed water has strong affinity to the hydrogels, a large amount of pressure is required to desorb the water molecules. This result not only in a high consumption of energy, but also poses operational challenges associated with high-pressure operations. As such, polymers with switchable wettability such as PNIPAM have also been explored in conjunction with polyelectrolyte hydrogels for this approach.41,44 A major challenge associated with fabricating thermoresponsive hydrogels with high salt-rejection (and swelling capacity) is the conflicting requirement for high fractions of charge and hydrophobic components at the same time. Increasing the hydrophilic volume fraction, that is, the ability to reject salt, counteracts the water recovery that is triggered by the hydrophobic volume fraction of the hydrogel. As discussed in Section 3.3, an increase in the charge fraction increases the LCST that results in a lack of thermally induced dewatering behavior, particularly when the ionic and hydrophobic segments are present in the form of thermally induced dewatering behavior, particularly when the charge fraction increases the LCST that results in a lack of the hydrogel. As discussed in Section 3.3, an increase in the charge fraction increases the LCST that results in a lack of thermally induced dewatering behavior, particularly when the ionic and hydrophobic segments are present in the form of thermally induced dewatering, it is important for PNIPAM to be the main network while PSA to be present as (interpenetrating or graft) chains, or as a loosely cross-linked network. For example, the water recovery efficiency of a PSA-g-PNIPAM hydrogel was only 10% compared to a PNIPAM-g-PSA that shows up to 60% while both hydrogels had similar NaCl rejection rates of 15–20%.

4.4.3. Interfacial Solar-Driven Evaporation

Both the FO and the hydrogel membranes require two separate steps of water absorption and recovery that could only lead to a semi-continuous desalination process at best. Interfacial solar-driven evaporation enables not only the utilization of sustainable energy for desalination, but also allows for continuous operation. Furthermore, it solves the conflicting demand presented by the aforementioned desalination methods in which the hydrogels are expected to have not only a high water-uptake and salt-rejection, but also a high water-recovery. Specifically, this technique involves the absorption and conversion of solar energy into heat to drive the evaporation of water from non-volatile contaminated solutions followed by the collection of the purified water via vapor condensation. Compared to traditional solar-driven evaporation that involves bulk heating of water, the interfacial solar evaporation process selectively heats up the evaporative portion of water via the heat localization effect presented by well-designed photothermal materials.14,98,310 Unlike the aforementioned membrane-based methods, this technique can be used to desalinate hypersaline water (up to 100 g dissolved salt per kg seawater, i.e., equivalent to the water of Dead Sea).21,99,101 Furthermore, the water quality of the distillate is superior compared to other membrane- and thermal-based desalination technologies.99 Besides seawater desalination, solar-driven evaporation has been shown suitable to purify water contaminated with strong acids and bases, industrial wastewaters contaminated with heavy metals, radioactive wastes, and non-volatile organics (dyes and detergents).53,87,99,311–313

As shown in Figure 14, interfacial solar evaporation is a coupled process of solar absorption, solar-to-heat (photothermal) conversion, heat transfer, water transport, and utilization of the converted heat through various mechanisms (conduction, radiation, convection). Ideally, the heat converted is maximally utilized for vaporization without heating the bulk water underneath, while a continuous supply of water is drawn up to replenish the evaporated water. Solar evaporation rate, in particular, is an important parameter because it influences the final yield of purified water. In fact, the yield is influenced by the efficiency of solar absorption, solar-to-heat conversion, and...
Figure 14. Schematic of the processes involved in the solar–thermal conversion process for the interfacial solar-driven evaporation. Reproduced under the terms of the CC-BY license.© 2021 The Authors. Advanced Materials Interfaces published by Wiley-VCH GmbH

Remarkable progress has been made in terms of developing photothermal materials that absorb and convert solar energy into heat with efficiencies near 100% using various broadband solar absorbers such as plasmonic nanoparticles,[315–317] semiconductors,[318] metal–organic frameworks,[319] graphene/graphite,[320,321] carbon nanotubes (CNTs),[322–324] graphene[325] and graphdiyne,[326] biochar,[327–328] and conjugated polymers.[329] The presence of rough porous structures in photothermal materials can also facilitate light-trapping via multiple internal reflections and scattering effects that improve their light absorption and thus photothermal heating abilities. Highly porous materials, especially those with hierarchical pores[330,331] or directionally arrayed pores[332–334] have also been shown to have enhanced solar evaporation rate due to augmented water transport and vapor escape properties.

Despite the progress made in advances in the performance of the solar evaporators, the solar evaporation rates of these materials are limited to 1.47 kg m⁻² h⁻¹ (KMH) under a solar flux of 1-Sun due to the relatively high intrinsic energy demand for water evaporation (>40 kJ mol⁻¹).[23,333] Hydrogel-based solar evaporators have been developed using a range of synthetic polymers (e.g., PAM, PSA, poly(sodium p-styrenesulfonate), polyhydroxypropyl acrylate, PVA, PILs)[341] and natural polymers (e.g., agarose, cellulose, konjac glucomannan, carboxymethylcellulose, alginate, chitosan)[311,312,336–339] incorporated with solar absorbers such as CNTs,[334,338] graphene/graphite,[340] plasmonic nanoparticles,[318] metal organic frameworks,[317] poly(3,4-ethylenedioxythiophene),[334] PANI[341] and carbon black particles[313] among others. As will be discussed in detail below, compared to conventional solar evaporators, hydrogels generally show better solar evaporation efficiency due to their: i) hydrophilicity, ii) tailorable pore structures, ii) presence of bound water, and iii) presence of abundant functionalities that engender improved water transport, efficient utilization of heat generated, mitigation of salt scaling, and impartment of multifunctionalities (Figure 15). Apart from their superior performance, hydrogels fabricated using stimuli-responsive polymers also enable the application of innovative and intelligent solar evaporation systems.[333,341]

Hydrophilicity: Hydrogel-based solar evaporators show superior water transport properties due to the presence of numerous polar functional groups with strong water affinity, especially those with high osmotic potential (Figure 15). Polyelectrolyte hydrogels such as PSA (14 wt%), for example, has an osmotic pressure of ≈90 atm, which is about two orders of magnitude higher than the capillary pressure in micropores. As a result of the high osmotic potential of hydrogels, their water transport properties are superior compared to other materials whose mechanism of water transport is solely dependent on the surface tension via capillary pumping.[312] The water transport rate induced by hydrogels has been measured to range from 250 to 650 KMH,[342,343,344] more than two orders of magnitude higher than that of solar evaporation, which ensures a sufficient water supply to the evaporation interface. This can contribute to high vaporization efficiency by sustaining high heat-transfer rate through the rapid water replenishment to “hot zones” for continuous evaporation and through the prevention of the formation of insulating vapor films.[39,40] It should be noted, however, that a higher water content in a hydrogel does not necessarily lead to a more efficient vapor generation rate due to the increased potential for convective heat loss to the bulk water owing to the relatively high thermal conductivity of water.[41,42]

Presence of Bound Water: Notably, a breakthrough performance was reported by Zhao et al.[21] using a hierarchically nanostructured PVA hydrogel interpenetrated with PPy chains as solar evaporator that has significantly enhanced the solar vaporization rate well beyond the assumed upper limit of the water production rate to 3.2 KMH. In fact, apart from the excellent photothermal conversion and water transport efficiency of the hydrogel, the significant advancement in solar evaporation rate was attributed to the presence of the unique water states in hydrogel networks, specifically the bound water comprising polymer-bound water and intermediate water that was discussed in Section 3.2 (Figure 15). The smaller thermal mass of polymer-bound water surrounding the solar absorber further enhance heat concentration that enables efficient in situ utilization of the converted heat.[97,101,337,343,344] Moreover, the polymeric chains wrapped around the light absorber can also act as the energy-insulating media to reduce the convective heat loss of water, achieving the confinement of thermal energy to the water clusters filled in the molecular meshes.[14,21] The presence of intermediate water, on the other hand, results in the reduction in the energy demand for the evaporation of water trapped in the hydrogels compared to that of bulk water.[21] This is because when water molecules are confined in the molecular mesh, they are more likely to escape the polymer network as small clusters rather than individual molecules. As such, the water in hydrogels is evaporated through a lower enthalpy change than the conventional latent heat of bulk water. In fact, it was determined that the reduction of the enthalpy of vaporization of the water trapped in hydrogels can reach up to 52% to that of the bulk water.[21,39] The extent of the reduction in
the vaporization enthalpy increases with the amount of intermediate water present in a fully swollen gel. In addition, by tuning the amount of intermediate water, through the control of the hydrogels swelling by combining two polymeric components, for example, the solar evaporation rate can be further increased to 3.6 KMH as a result of further reduction in the energy demand for evaporation of the water in the hydrogels. Overall, the reduction in the vaporization enthalpy of water in hydrogel significantly improves the performance of the hydrogel based solar evaporators, obviating the need for concentration of the solar irradiation through optics, and opening up the possibility for steam generation under low solar-flux conditions.

Tailorable Pore Structures: Generally, the inner pore architecture in hydrogels can be easily modulated, giving them a competitive advantage compared to other conventional solar evaporators. Pores of various structures, such as i) large and well-interconnected macropores, ii) small and oriented channels, or iii) gradient pores with tapering size, can be formed due to the multitude of porogenation methods that can be employed during the hydrogels fabrication (e.g., yeast and sugar fermentation, ice-templating, induction, etc). The tailorable pore structures of hydrogels enable them to achieve high effective surface area for evaporation, efficient water transport via increased capillary effect, and reduced convective heat loss through direction-limited water transport in gradient-structured hydrogels.

It has been found that the solar evaporation rate can be significantly enhanced by the additional non-photothermal contribution from the exposed area on the side walls of a...
hydrogel-based solar evaporator. In particular, an 8-cm tall PVA/Ti$_3$C$_2$ hydrogel with exposed side wall shows an impressive apparent solar evaporation rate of 6.35 KMH, but when the evaporation from the side wall is suppressed by wrapping with Al foil, the solar evaporation rate drops significantly to 1.1–1.6 KMH. Note that the term apparent is used here because the solar evaporation rate is calculated by considering the illuminated area (which is the conventional method) while excluding the exposed surface area on the side wall as this is not directly exposed to the solar illumination. It is worth noting that simply increasing the side surface area of a solar evaporator is not sufficient—it needs to be coupled with strong capillary effects to ensure that water can be efficiently transported from the bottom to the top evaporative surface over long distances. Vertically aligned pores, in particular, has been found to significantly enhance the bottom-to-top water transport rate compared to that of random pores. To enhance the capillary effect for long-distance water transport, narrow channels have been found to outperform large macropores showing ≈18% enhancement in the solar evaporation rate. In particular, unlike PVA/Ti$_3$C$_2$ hydrogel with narrow microchannels, those with large macropores could not generate sufficient capillary force to maintain water transport throughout its height, thereby causing a drying out of the top evaporative surface.

Apart from narrow microchannels, “positive” gradient pore structures, whereby the bottom layer has larger pores while smaller pores are concentrated at the top layer, has also been found to be effective in promoting a unidirectional flow of water from bottom to top (Figure 16b,c). To do so, PAM and carbon powder (C) hydrogels with gradient pore structures were created by inducing a gradient distribution of hydrophobic microgels (poly(2,2,3,4,4,4-hexafluorobutyl methacrylate-co-allylamine)) by placing them between two plates of opposing wettability, that is, polytetrafluoroethylene and glass, during the polymerization of the PAM hydrogel. Due to the presence of amino groups on the microgels, they can also act as the initiator and cross-linker, thereby locking-in the gradient distribution of cross-link density and network size in the final gel. Besides the enhancement of bottom-to-top water transport, such a pore structure also endow the PAM/C hydrogel with excellent heat localization and an inhibited convective heat loss from top to bottom, which is in stark contrast to its inverse configuration, that is, “negative” gradient (Figure 16b,d). The reduced convective heat loss can be explained by the smaller pores at the evaporative surface that restricts the movement of the highly thermal-conductive water which would cause heat loss from top to the bulk water at the bottom.

Abundant Functional Groups: Apart from salts, there are various types of contaminants that may concurrently be present
in water (e.g., non-volatile and volatile organics, suspended solids, heavy metals, dyes, microbes, etc.). As such, solar evaporators with multifunctionality (e.g., bacterial inactivation, contaminant degradation and adsorption) is highly sought after.[350] The discussion thus far has demonstrated that hydrogels show superior photothermal evaporation performance while at the same time they possess various functional groups (e.g., \(-\text{NH}_2\), \(-\text{OH}\), \(-\text{COOH}\), \(-\text{CONH}_2\), \(-\text{SO}_3\text{H}\)) which can impart additional functions to the final system such as i) adsorption of contaminant species and ii) antiscaling properties (Figure 15). Indeed, the hydrogels have been shown to effectively remove a range of heavy metals via the adsorption process as we have discussed in Section 4.2.1. However, the main significance of this functionality with regard to the solar evaporation process is the removal of volatile species that if not removed prior to evaporation would escape together with the vapor and subsequently contaminate the condensed distillate. One example is the Hg\(^{2+}\) that is well-known for its evaporative property. Distillation of Hg\(^{2+}\) contaminated water through photothermal evaporation using conventional materials has been found ineffective in reducing its concentration. However, the utilization of hydrogels as photothermal evaporators has been shown to result in a lowering of the Hg\(^{2+}\) concentration by seven orders of magnitude, and this is attributed to the presence of functional groups in their structure that are able to sorb Hg\(^{2+}\) during the evaporation process.[53,337] Interestingly, solar irradiation was also found to accelerate or promote rapid ion uptake leading to enhanced ion adsorption rate by six times because the solar-induced evaporation drives the uptake of water-soluble ions into the gel.[53]

Another significant advantage of the hydrogel-based solar evaporators is the fact that in most of the cases they do not experience any significant salt clogging, which can deteriorate the efficiency of the solar evaporation process due to the reduction of the solar absorption over time and the pores clogging, and the need for periodic cleaning.[333] Besides the presence of porous channels in hydrogels that facilitated the dilution of salt solutions at the evaporating interface via back diffusion to the bulk solution,[101,324,312] the anti-scaling property of hydrogels can also be attributed to the hydrated layers which prevent supersaturation of salts and to the salt rejection via coulombic repulsion. In fact, the presence of numerous hydrophilic groups provides adequate hydration and thus sufficient water supply that ensures the salt solution at the evaporation interface would not cause supersaturation due to excessive concentration.[334] Also, as discussed in Section 3.4, salt-rejection at the brine/foam interface can be realized on hydrogels with high charge density such as PSA. Even if some ions (<20%) might penetrate into the PSA hydrogel, they are trapped by the charged group in the PSA network (i.e., the carboxylate groups on the network and mobile Na\(^+\) counter ions) during the water transport in the micropores, thus resulting in little salt sediment on surface ensuring their long-term stability.[132]

**Intelligent Solar Evaporation Systems:** Another advancement brought forth by the use of hydrogel-based solar evaporators is the innovation of intelligent solar evaporation systems enabled by smart polymers such as PNIPAM that leads to new configurations for water collection. One such example is a plant leaves-inspired design which employs the cooperative transpiration and guttation process to increase the water collection rate to 4.2 KMH under 1-Sun irradiation (Figure 17a).[333] Guttation is brought forth by the thermally induced dewatering of the PNIPAM enabling rapid water collection as the absorbed water oozed out of the gel which measures ≈3.1 KMH under 1-Sun irradiation. On the other hand, transpiration is similar to a conventional solar steam generator, and produces a rate of ≈1.1 KMH under 1-Sun irradiation. Another example is a thermoresponsive and microstructured graphene/poly(N-isopropylacrylamide) (mG/PNIPAM) membrane reminiscent of the stomatal opening/closing of natural leaves as it switches itself on and off depending on the intensity of the sunlight irradiation (Figure 17b).[341] Below the LCST, which is under weak solar irradiation (<1 Sun), the mG/PNIPAM micro pores open and thus fast water evaporation with a rate of 1.66 KMH occurs. Under intense solar irradiation (between 1 and 2 Sun), the temperature is higher than the LCST of the mG/PNIPAM. The shrinking of the PNIPAM chains pulls the graphene sheets together, and the mG/PNIPAM microstructures are contracted or even blocked, resulting in a reduced water evaporation of 0.24 KMH. This is in contrast to the conventional solar evaporators that show increasing solar evaporation rate with solar flux intensity. As such, this configuration may find niche application in cases where high solar flux intensity is not available.

**4.5. Atmospheric-Water Harvesting**

Atmospheric moisture is another potential source of water supply that contains about 13,000 km\(^3\) of freshwater, 98% of which is vapor and 2% is in the condensed phase (i.e., clouds and fog).[351]
In water-scarce environments, fog and dew represent potentially exploitable ancillary water resources that, if efficiently harvested, could ameliorate the water-scarce situation particularly for communities in landlocked and arid regions where even seawater may be inaccessible.[33] There are several ways of harvesting water from the atmosphere, for example, fog harvesting, active refrigeration (or dew-point water collection), and sorption in conjunction with easily accessible low-grade energy.[333–335] Fog harvesting directly collects air-borne water droplets via impaction of fog droplets on collection surfaces, which are usually vertically placed nets or meshes.[336,337] However, the main limitation of this approach is the global unavailability of the necessary meteorological conditions (high RH and wind speed) that support frequent fog occurrences making them even less accessible than seawater as an alternative freshwater source.

The refrigeration method, on the other hand, involves the utilization of an engineered cold surface to cool the adjacent air mass below the dew point to produce water droplets via condensation. Generally, large volumes of air and low temperatures at the condenser are required, especially in regions of low RH, to reach a satisfactory level of water productivity. However, the cooling of the heat sink for the condensation can be energy consumptive, since a difference in temperature between the condensation unit and the ambient has to be maintained. Additionally, the heat of condensation of the collected water has to be discharged. Thus, refrigeration is not feasible for regions with consistently low RH (<40%) or those lacking electricity.[334] Therefore, both the dew-point water and fog collection methods rely on the availability of high RH (usually above 50%) and these conditions are usually found in regions that offer other possibilities for fresh water production such as water extraction from lakes, rivers or oceans. For cases of RH below 30%, only a few applications have been presented that are able to harvest water from air. These conditions are especially interesting because regions where the RH is so low (e.g., arid regions such as deserts) usually offer no efficient ways for fresh water production.[335,334,338]

The sorption-based method, in contrast to the aforementioned methods, is based on capturing moisture from the atmosphere passively using moisture sorbents, and then desorbing it actively (as aided by external heat sources powered by electricity or solar energy) in a closed environment.[338] The most attractive advantage of this sorption-based method is its capability of producing water from dry air, where the RH level may reach values even lower than 20%. Thus, the water vapor sorption method enables significant moisture capture capacity and water storage capability due to their network swelling.[334,336,337] i) direct recovery of liquid water via incorporation of stimuli-responsive polymers,[332,333] and ii) low enthalpy of vaporization which facilitates desorption of sorbed water molecules via solar evaporation.[321,324] Furthermore, the presence of a large amount of pores within the hydrogels can also increase the water vapor sorption rate via i) their high affinity to water,[339] ii) the unhindered vapor transport via interconnected pathways,[339] and iii) the capillary condensation effect.[360,361] In such porous hydrogels, water vapor initially attaches to the outer surface of the hydrogel followed by their transfer to the inner pores space, and finally they diffuse to the internal porous structure of the hydrogel through capillary channels.

Hydrogels can also be applied in the form of additives or coatings on sorbents of desiccants to enhance their water vapor sorption capacity,[359] or as coatings on support materials such as cotton and cellulose acetate nanofibers for moisture harvesting.[362–366] Furthermore, stimuli-responsive polymers or compounds such as the PNIPAM and spiropyran were combined with hydrogels in order to demonstrate their ability to reversibly switch from a state of high moisture-capture ability to another that repels the sorbed water by either a temperature change and/or light irradiation.[362–366] However, the direct conversion of the water vapor in the air to collectible liquid water (or liquefaction) was not demonstrated in those studies.

The first to demonstrate the conversion of the sorbed water vapor into collectible liquid water using a PNIPAM/calcium alginate semi-IPN hydrogel sorbent system was Matsumoto et al.[23] The developed hydrogel was composed of a PNIPAM (acting as a thermoresponsive component) and of a calcium alginate network (acting as the hydrophilic component) to enhance the moisture-absorption capacity (Figure 18). Below the LCST, the dried gel absorbs moisture up to 0.6 g g⁻¹ (at 80% RH, 27 °C), and during this process, the water molecules are sorbed on both alginate and PNIPAM chains. Subsequently, a portion of the water molecules sorbed as vapor from the air oozed out as liquid water from the dried gel when heated to 50 °C, due to the hydrophobic transition of the PNIPAM chains above the LCST.

4.5.2. Hydrogels as the Molecular Water Reservoir

Despite the successful proof-of-concept, the aforementioned study revealed that in order for the moisture sorption to be significant, the application of hydrogels for atmospheric-water harvesting should be limited to cases where the RH is above 60%.[23] To broaden the working range of hydrogels, hygroscopic or deliquescent materials that can capture a large amount of moisture over a larger window of RHs and release it in the form of water at a relatively low temperature (70–90 °C) such as clays (Laponite),[360] glycerin,[367] PPy-Cl,[22] LiCl,[368] CaCl₂,[358,369–370] or a binary mixture of LiCl and CaCl₂[372] have been incorporated into hydrogel matrices. For example, calcium alginate hydrogel beads doped with functionalized CNTs, when combined with the binary mixture of LiCl and CaCl₂ can reach a remarkable moisture absorption of 5.6 g g⁻¹.[372]
In this case, the moisture-capturing and liquefaction functions are predominantly attributed to the hygroscopic or deliquescent material, while the hydrogel functions as a molecular water reservoir which absorbs and stores the liquefied water. In the absence of a hydrogel support, the deliquescent salt in the presence of moisture becomes liquid and its reuse is not possible due to difficulty in separating the salt from the water. In fact, the deliquescent salts have been shown to function better when they are encapsulated in support materials (e.g., silica) because the surface area of the sorbent accessible to water vapor is increased, leading to much faster sorption kinetics. Such an increase can also be expected when hydrogels are used as the support material. Compared to rigid hosts, the flexible hydrogel networks provide an excellent support platform with minimal constraints on the water absorption performance by the salt, and an excellent liquid-withholding capacity. This strategy does not only broaden the RH working window of the hydrogel composites, but it also significantly enhances their moisture sorption capacities. For example, photothermal PAM/CNT hydrogels loaded with CaCl₂ can absorb an amount of water of 4.5 to 6.3 times their initial dry weight, mainly due to the addition of the CaCl₂ as only 32% of the water vapor absorption was attributed to the PAM hydrogel (Figure 19a).

On the other hand, to significantly enhance the recovery of the liquid water, stimuli-responsive polymers can be introduced into the hydrogel to enable a rapid stimulus-induced dewatering of the liquefied water vapor. One example is a PNIPAM network semi-interpenetrated by chloride-doped polypyrrole (PPy-Cl), which has a high hygroscopicity and solar absorption, allowing high moisture absorption capacity and solar-induced thermal dewatering of the absorbed liquefied vapor (Figure 19b). The gel can rapidly release ~50% of the absorbed moisture within 20 min once slightly heated to 40 °C (which is above its LCST) and thus enhancing the efficiency of water production. In fact, although the activation energy for thermally induced dewatering above LCST is significantly lower than that of the bulk water evaporation (3.8 vs. 64.9 kJ mol⁻¹), not all the water released is in the liquid form and thus the residual water was collected via solar-induced evaporation followed by condensation. The PNIPAM/PPy-Cl semi-IPN also shows exceptional moisture absorption capacities of 6.7, 3.4, and 0.7 g g⁻¹ at environmental RHs of 90%, 60%, and 30%, respectively, and this process lasts only 100, 120, and 180 min, respectively. This can be attributed to the molecular level interaction between PPy-Cl and hydrophilic-switchable PNIPAM that allows internal water rearrangement when several layers of water molecules are captured from air through physisorption, reactivating the sorption points to harvest more water molecules. The application PNIPAM/PPy-Cl semi-IPN in an atmospheric-water irrigation system has also been recently demonstrated to show improved water retention that is supportive for plant growth.

### 4.5.3. Purity of Liquefied Water Vapor

However, the thermally induced dewatering method serves only as a means for liquefaction of water vapor with no improvement of the collected water quality. On the other hand, solar-induced evaporation is essentially a distillation process, which significantly improves the quality of the water collected. This is proven by a photothermal PSA/rGO composite gel, capable of broadband light absorption and conversion of the absorbed light into heat, that shows excellent moisture sorption of 5.20 g g⁻¹ (at 100% RH) and 0.14 g g⁻¹ (at 15% RH) and rapidly releases the absorbed water into vapor within 7 min under 1-Sun irradiation achieving a solar evaporation rate of water up to 2.64 KMH (Figure 20). Despite being exposed to smoggy environment (contaminated with fine particles and harmful SO₂), the distillate collected is neutral in pH, free from bacterial-forming colonies and show an over 97% reduction of dissolved solutes due to specific desorption of pure water vapor during the solar evaporation process. This is of particular significance if the harvested water is to be made drinkable because, in view of global air pollution, direct water harvesting from moisture tends to be contaminated by impurities, such as microorganisms, fine particulate matter, and toxic gases like sulfur oxides as the water vapor tend to act as atmospheric scrubbers.
5. Conclusions and Perspectives

Polymeric hydrogels have contributed to the technological advancement in the field of water efficiency due to their outstanding performance, and to the simple, innovate and energy-efficient approaches in water remediation and recovery. To understand how hydrogels can lead to such impressive performances and technological innovation, we have identified the unique properties of hydrogels and discussed how these properties are correlated to the underlying mechanisms that lead to their remarkable performance. The insights gained from such a mechanistic understanding is not limited to advancing the design, synthesis, and application of hydrogels for water treatment, but it can also be extended to the development of other materials, particularly natural materials present in abundance, that can be engineered to display properties similar to that of hydrogels as identified in this review. Furthermore, we have presented a summary of the different approaches from

Figure 19. Hydrogels hybrids incorporated with deliquescent materials for atmospheric-water harvesting. a) PAM-CNT-CaCl₂ moisture harvester and its moisture sorption curves at different RHs. Reproduced with permission.[369] Copyright 2018, American Chemical Society. b) Recovery of collectible liquid water from harvested moisture using thermoresponsive PNIPAM/PPy-Cl semi-IPN. Reproduced with permission.[22] Copyright 2020, Wiley.

Figure 20. The microporous PSA/rGO composite gel harvests moisture from contaminated air and then desorbs the vapor, as induced by absorption of solar energy, to produce water free from contaminants. Reproduced with permission.[24] Copyright 2019, Wiley.
which hydrogels with tailored morphologies, structures and functions can be prepared. This can provide a guideline to the rational design of hydrogels tailored to the specific requirements of their applications. Despite the remarkable progress made in hydrogel research for water treatment applications, there are some challenges that remain to be solved. Table 1 summarizes how the unique properties of hydrogels enable the performance requirements of the different WTs to be met with high effectiveness as well as our proposed solutions and some recommendations for prospective research directions to address the remaining challenges specific to each hydrogel-enabled WT.

In particular, the following research directions are proposed. First, most of the hydrogels that have been applied for water treatment are typically prepared using the traditional cross-linking methods which result in permanent linkages limiting dynamic behavior such as moldability, on-demand reversible gelation behavior, self-healing (i.e., the ability to repair damage and restore to its original properties), and stimuli-responsive-ness among others. These limitations can be addressed by employing dynamic and reversible noncovalent interactions in supramolecular chemistry such as hydrogen-bond, metal-to-ligand coordination, electrostatic, or host–guest interactions.[32] The high association and dissociation rates of these reversible interactions endow supramolecular hydrogels with the capacity to actively reconfigure themselves by remodeling, reshaping, and adapting to environmental conditions. This allows the hydrogels to become responsive, dynamic and smart systems going beyond their merely resistant nature towards environmental damage. For example, the on-demand reversible gelation behavior of supramolecular hydrogels may facilitate enhanced water uptake during the FO draw due to its enhanced osmotic pressure in its dissociated state, while the dewatering step and recovery of the draw solute can be achieved by triggering the gelation process.

Second, although most of the hydrogel-enabled WTs have explored the use of stimuli-responsive polymers, the entrapment of biomass in biological water treatment systems (discussed in Section 4.2.5.) is mainly performed using more traditional hydrogels. Thus, it would be interesting to see future research on this field based on the exploration of the use of stimuli-responsive polymers. PNIPAM may be a promising system for such application as it has shown its potentiality to entrap biomass for biomedical applications.[210]

Finally, although PNIPAM is a particularly popular thermo-responsive polymer as evidenced by its broad application in the WTs reviewed herein, it should be mentioned that there is still a vast repertoire of unexplored thermo-responsive polymers for WTs. Specifically, poly(N-substituted (meth)acrylamides), poloxamers (i.e., block co-polymers of poly(ethylene oxide) and poly(propylene-oxide)), poly(N-vinylcaprolactam) and some natural polymers (e.g., methylcellulose, hydroxypropyl methylcellulose, elastin-like polypeptides, etc) may be evaluated for applications in water treatment in the future.[45,375–377] In addition to thermo-responsive polymers, there is a multitude of polymers responsive to external stimuli that can be explored for development of intelligent water treatment systems. In fact, it would be interesting to develop hybrid systems capable of responding to multiple external stimuli in a predictable manner. When combined with supramolecular chemistry, materials with extraordinary adaptive and dynamic features capable of high performance, dynamism and resilience through autonomous self-healing can be designed and synthesized.

While it may seem appealing to fabricate hydrogels with highly complex chemistries and architecture for the sake of performance enhancement, it is also important that the hydrogel fabrication method is facile and cost-effective on a large-scale basis to facilitate practical implementation of hydrogel-enabled WTs. Overall, to advance hydrogels forward for water treatment applications, issues that need to be considered include: i) the feasibility of large-scale fabrication of hydrogels using the methods researched, ii) sustainability, iii) developing a mechanical understanding for how the material works in the specific application, iv) material robustness and the possible requirement of a device, v) the feasibility for real-world applications, and vi) multifunctionality for value-added material/application/performance.

Apart from the performance of the resultant hydrogels, the choice of hydrogel fabrication and modification methods should take into account whether the method can be easily scaled up for mass production and the overall production cost (i.e., capital investment, materials, and non-replenishable chemical/energy consumption during fabrication). Although the actual process for selection requires a detailed techno-economic analysis that is, however, beyond the scope of the current review, some considerations may be still provided herein. For example, among the different methods to create porosity in hydrogels, emulsion templating may be easier to scale up and offers better morphological control. However, as also other chemical-based templating methods (i.e., direct templating and self-assembly), it can be cost-intensive and less environmentally friendly due to the enhanced chemical consumption and generation of wastes (i.e., internal phase with high organic contents, sacrificial templates and surfactants. On the other hand, the ice-templating method (e.g., cryogelation) may present challenges in scaling up due to its sensitivity to heat transfer and difficulty in controlling the pore structure. The freezing step during cryogelation and the freeze drying of samples may also impose an additional energy demand that may raise the production cost. However, it may be a more environmentally benign approach and the performance increase may offset the production cost.

The choice of materials used should also consider sustainability factors such as cost, long-term availability and its end-of-life handling if the materials chosen are not biodegradable. It is noted that most studies have overlooked the issue of the biodegradability of the materials developed. It would be interesting to see future studies on combining natural and synthetic polymers to prepare hydrogels with enhanced biodegradability while maintaining a high performance. These issues are critical in ensuring translational success of the hydrogels developed in the lab into sustainable and practical technologies. Another critical issue to be considered during the research phase is developing an in-depth understanding of the underlying mechanisms through which the hydrogels function and the factors influencing its performance. This can be done either through the use of more advanced characterization tools or through designing a detailed and comprehensive study. Such a deep and comprehensive mechanistic understanding would lead
Table 1. Summary of challenges and prospective solution for each hydrogel-enabled WT.

| Water technology | Requirements | Hydrogel-enabling properties | Remaining challenges and prospective directions |
|------------------|--------------|------------------------------|--------------------------------------------------|
| Disinfection     | • No leaching of harmful reagents (DBPs, toxic agents); • Reduced sensitivity of performance toward different water sources, e.g., organic-rich water; • Long-term disinfection enabled by the controlled action of the bactericides anchored and self-cleaning of active sites (e.g., thermally induced kill-and-release switchability). | • Abundant groups to control the release of bactericides; • Support for fine nanosized bactericides for enhanced reactivity; • High hydrophilicity enables efficient (i) dissolution and rapid delivery of biocides, and (ii) antiadhesive surfaces to avoid the formation of conditioning films when used in highly contaminated waters; • May have compatible surface energy with bacterial cell walls that facilitates contact-killing—further enhanced by pore-size matching with bacteria; • High elasticity enables an innovative squeeze-release approach that significantly increases the efficacy and rate of disinfection, and the rapid recovery of disinfected water. | • Applications may be limited for small-scale water production for cryogels that produce disinfected water via a squeeze-release approach. This can be mitigated by the development of well-designed and engineered devices for high-throughput applications; • Research into different materials design and chemistry (e.g., self-cleaning, antifouling, smart surfaces, etc) to enable excellent disinfection efficacy and rate even when used for treatment of water containing large amounts of organic matter ubiquitous in natural water; • Development of bactericidal composite materials that disinfect via multiple mechanisms (e.g., photogenerated radicals, release of toxic agents, and physical disruption via contact killing, etc) to effectively disinfect water from traditional and emerging pathogens, and minimize risks of developing antimicrobial resistance; • Because the potential leaching of harmful agents into water bodies may pose health risks, greater research efforts in developing non-leaching biocidal polymers is needed especially targeting application in water treatment—most relevant reports focus on biomedical applications; • Development of new hydrogel-based bactericidal composites needs to be coupled with investigations into the underlying mechanisms to provide insights for future design of materials with improved performance. |
| Decontamination  | • Rapid and high sorption capacity; • Improved contact between sorbent and sorbate or target pollutant with active sites; • Offer environmentally benign alternative approaches to regenerate sorption sites after saturation; • Resilient toward enzymatic activities, photocatalytic oxidation, and fouling; • Ease of modification to facilitate impartment of multifunctionality that may either enhance the capacity/selectivity or the regeneration for subsequent use. | • Presence of abundant functional groups increase sorption sites and facilitates chelation of pollutants; • High water permeability facilitates rapid sorption; • Flexible but sturdy 3D frameworks enable repeated use—no collapse that obstruct subsequent sorption cycles; • A porous network further enhances the accessibility of the sorption sites; • Good support matrices (due to high water content and presence of abundant groups and porosity) for various filler materials such as catalysts, ion receptors, biomolecules, and microbes to impart multifunctionality, increased selectivity, and removal efficiency; • Functional groups formed from weak acids/bases can form a buffer system enabling a large operational window of pH; • Switchable wettability enables the recovery of active sites via changes in external stimulus such as temperature change without the continual consumption of caustic chemicals. | • Development of hydrogel-based sorbents that can be regenerated using more environmentally friendly approaches such as stimulus-triggered capture-and-release of target pollutant, or via the incorporation of photocatalysts that can photodegrade the sorbate; • Greater focus on developing hydrogels prepared from low-cost and widely available biomass-derived materials as high-capacity sorbent materials to ensure sustainability; • Adsorptive separation of ions may be coupled with sensing or detection applications for added value; • The adsorption process is typically a batch process. Thus, innovation in new ways of conducting the adsorption process either through ingenious materials design or the operational design that can enhance the continuity of the process to either a quasi-continuous or ideally a continuous process would be desirable; • Exploration of stimuli-responsive polymers that are biocompatible such as PNIPAM as the entrapment agent with smart properties. |
Table 1. Continued.

| Water technology          | Requirements                                                                 | Hydrogel-enabling properties                                                                 | Remaining challenges and prospective directions                                                                 |
|---------------------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| Oil–water separation      | • High separation efficiency and selectivity;                                | • High hydrophilicity coupled with its nano-hierarchically structured surface that can become underwater superoleophobic and permits rapid water flow and high separation efficiency; | • Although the pressure applied to the hydrogel filters for the water-removing operation is rather low, long-term application may cause performance deterioration due to mechanical degradation or loosening of networks due to weakened crosslinking that may affect their selectivity. As such, development of durable and robust hydrogels that can resist prolonged exposure to moderate transmembrane pressures is recommended; |
|                           | • High absorption capacity for the component to be removed;                   | • The presence of a hydrated layer that has low oil-adhesion and thus anti-oil-fouling;     | • Most of the previous works have focused on the separation of oil–water mixtures, while limited work has been performed on the emulsion separation. Since it is more challenging to achieve high separation efficiency for emulsions, development of innovative materials and approaches in this area are needed; |
|                           | • Simple and fast separation/absorption ability                              | • Highly tunable pore structures to meet specific demands, e.g., large pores for reduced flow resistance of permeating species, while small pores for enhanced selectivity in retaining small oil droplets in emulsions; | • As very small pores are desired for enhanced emulsions separation, hydrogels may be coupled with a FO membrane to enhance the rejection efficiency via size-sieving effect, while it induces the osmotic flow of water from the emulsions—such a configuration would probably work well for a water-rich emulsion. |
|                           | • Robust and high reusability;                                               | • The presence of abundant functional groups that can facilitate demulsification of oil droplets; | • Apart from size-sieving, the demulsification approach should also be explored further by exploiting the functional groups already present in hydrogels or via further functionalization. Also, the stimuli-responsive behavior (e.g., toward pH, ions, electric field, magnetic field, solar energy, etc) of smart hydrogels can be explored as a means to control and facilitate the demulsification process. |
|                           | • High durability and stability under harsh conditions;                       | • Smart controllable separation materials can perform a water-removing or oil-removing separation process on-demand in response to environmental stimuli; | • Future studies can also explore the development of multifunctional capabilities (such as antibacterial, dye adsorption/degradation, desalination) into the oil–water separators; |
|                           | • Low-energy separation;                                                     | • The highly porous network of hydrogels makes them suitable platforms for subsequent functionalization such as hydrophobization to transform them into oil-removing materials; | • The tunable wettability of hydrogel-based oil–water separator is also an interesting area and there is an ample opportunity of innovation in terms of exploring different types of stimuli to induce the wettability switching or incorporating multiple stimulus-responsive functionalities into a single material. |
|                           | • Environmentally friendly;                                                  | • The ease of hydrogel fabrication enables to be used as a coating on diverse porous substrates or as a self-standing porous matrix by various fabrication methods; | • Smart hydrogels with dual photothermal and thermoresponsive properties could be an interesting solution for in situ absorption and recovery of oil spilled in oceans with good exposure to the sun. |
|                           |                                                                               | • Because hydrogel monomers or oligomers are water-soluble, the hydrophilization of substrates can be done in aqueous solutions avoiding toxic organic solvents; | • The tunable wettability of hydrogel-based oil–water separator is also an interesting area and there is an ample opportunity of innovation in terms of exploring different types of stimuli to induce the wettability switching or incorporating multiple stimulus-responsive functionalities into a single material. |
|                           |                                                                               | • Controllable crosslinking process that endows them with high stability in harsh environments | • Smart hydrogels with dual photothermal and thermoresponsive properties could be an interesting solution for in situ absorption and recovery of oil spilled in oceans with good exposure to the sun. |
|                           |                                                                               | • Natural-based hydrogels are mostly used which represent a sustainable alternative to replace petroleum-based polymers. | • Future studies can also explore the development of multifunctional capabilities (such as antibacterial, dye adsorption/degradation, desalination) into the oil–water separators; |
Table 1. Continued.

| Water technology                  | Requirements                                                                 | Hydrogel-enabling properties                                                                 | Remaining challenges and prospective directions |
|-----------------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|--------------------------------------------------|
| FO draw agent                     | • Have a high osmotic swelling effect to induce high FO water flux;         | • High hydrophilicity of hydrogels facilitates high FO water flux;                            | • The application may be limited to low-salinity solutions unless the concentration polarization issues are mitigated. Furthermore, the inherent cyclical switching of hydrogel wettability from water absorption to water release can only result in a quasi-continuous process at best. Engineering designs coupled with judicious design of hydrogels may be explored to mitigate these issues, e.g., using layered hydrogels with decoupled functions of water-drawing and water-releasing functions; |  |
|                                   | • Low solute reverse flux;                                                  | • Can be easily regenerated using external stimuli. In addition, external stimuli cause the release of the purified water for the next FO cycle; | • While the hydrogels may induce a high initial water flux, this decreases drastically over time resulting in a rather low overall water flux—further optimization and engineering may be required, e.g., using a shorter time frame for FO drawing; |  |
|                                   | • Antifouling and antiscaling properties;                                  | • Zero reverse solute diffusion due to the semi-solid nature of well-crosslinked hydrogels;    | • Most of the works reported were based on thermosensitive PNIPAM-based hydrogels, which pose the dichotomy between osmotic swelling and thermosensitive dewatering efficiency. As such, greater focus should instead be directed to other means for dewatering such as electric-responsive hydrogels where both the water uptake and release behavior are supported by the presence of high charge-fraction in the gels; |  |
|                                   | • Easy and rapid regeneration without significant loss of the draw agent.   | • Can be fabricated into very small sizes—e.g., microgels—with large surface area that enhances the water flux; | • Exploration of other stimuli-responsive polymers, especially non-PNIPAM-based systems; |  |
| Hydrogel membranes for desalination| • High charge fraction to yield a high salt rejection;                     | • Suitable support matrix to anchor various filler materials that can enhance the dewatering efficiency and FO water flux. | • Explore supramolecular hydrogels with reversible on-demand gelation properties—this allows the switching from a solution state (with higher osmotic pressure) during the FO draw to an agglomerated gel state during the dewatering step that facilitates separation of the draw agent from the purified water. |  |
|                                   | • Antifouling and antiscaling;                                              | • Can be fabricated by a variety of polymers showing responsive behaviors to different external stimuli enabling thus water recovery using various means. | • Due to the large volumetric expansion and contractions during the FO water-drawing and water recovery processes, it may be coupled to energy-harvesting device to extract the work done during the reversible swelling–deswelling of the hydrogels. |  |
|                                   | • Rapid and high water-absorption and release.                             | • Can be fabricated by polymers with high charge fraction that improves salt rejection ability; | • Low salt-rejection compared to RO membranes—materials design coupled with operational engineering can be explored to enhance the rejection rate, e.g., using a shorter swelling window, and designing and synthesizing hydrogels using monomers with high charge fraction; |  |
|                                   |                                                                          | • High water absorption capacity due to the presence of high water-affinity functional groups in hydrogels; | • The process predominantly proceeds in a batch fashion due to the inherent cyclical switching of hydrogel wettability from water absorption to water release. Furthermore, if not careful, recontamination of desalinated water may happen as it is being expelled from the surface that has previously contacted with brine. So, a rational design and engineering of the operation of a device may facilitate its application to at least a semi-batch process to prevent recontamination of treated water. |  |
|                                   |                                                                          | • The absorbed salt-depleted water can be recovered using simple means such as by inducing a change in the external environment (e.g., application of pressure or heat). | • The pressure used to recover the desalinated water can be very high while the use of thermosensitive PNIPAM-based hydrogels presents the tradeoff between high water uptake and salt rejection, or high thermosensitive dewatering efficiency. More research needs to be conducted to improve the water recovery efficiency. For example, other stimuli-response polymers, e.g., photochromic hydrogels using BMAAB cross-linker, could be explored.[102,103] In particular, a more appropriate means to recover water from such hydrogel desalination membranes would be to employ electric-responsive hydrogels since the efficiencies for water uptake, salt rejection, and water recovery are all coherently supported by the presence of high charge fraction. Another possible method to indirectly recover the desalinated water would be to use the hydrogels hydrated with absorbed water (depleted with salt) to facilitate irrigation/horticultural/agricultural activities. |  |
|                                   |                                                                          | • The absorption capacity of hydrogels is high; due to the high water-affinity functional groups in hydrogels; | • Other questions related to the mechanism of desalination using polyelectrolyte hydrogels remain to be explored: how does the pore structure and the charges (i.e., whether it is positive, negative or zwitterionic and its strength of dissociation) on hydrogels affect the desalination efficiency? |  |
|                                   |                                                                          | • The absorbed salt-depleted water can be recovered using simple means such as by inducing a change in the external environment (e.g., application of pressure or heat). | • Due to the large volumetric expansion and contractions during the desalination and water recovery process, it may be coupled to energy-harvesting device to extract the work done during the reversible swelling–deswelling of the hydrogels. |
Table 1. Continued.

| Water technology                  | Requirements                                                                 | Hydrogel-enabling properties                                                                 | Remaining challenges and prospective directions                                                                 |
|-----------------------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| **Interfacial solar evaporation** | • High solar-to-vapor conversion rate and efficiency;                         • The high hydrophilicity of hydrogels improves the water transport efficiency;             • High water content in hydrogels may render the evaporators prone to conductive heat loss. So, the performance of hydrogels as solar evaporators may be further enhanced by reducing such heat loss either through intrinsic material design (e.g., hydrophilic/hydrophobic balance and pore structure control to regulate water content, insulation properties and distribution of water states) or through extrinsically coupling with a thermal barrier and reducing the contact area with water; |
|                                   | • Rapid water transport to replenish evaporated water;                        • The water trapped in hydrogels has a significantly lower vaporization enthalpy which requires a smaller energy demand making solar evaporation a feasible solution even under low solar flux conditions; | • Antifouling and antiscalant to facilitate long-term operation;                                 • Volatile compounds may escape together with the evaporated water and end up in the distillate. So, future studies may also explore multifunctional materials with the ability to remove such volatile compounds either through adsorption or degradation in the water prior to evaporation. |
|                                   | • Excellent solar absorption;                                                 • Improved heat concentration and localization effect which in turn result in high solar-to-vapor conversion efficiency; | • Able to generate vapor even under low solar flux conditions.                                  • Another important aspect in harvesting water through the solar evaporation process is the condensation of the generated vapor. The effect of the materials and structure of the condensation chamber on the efficiency of collecting the condensed vapor is less intensely studied. This requires more studies to be done in this area to ensure that the water production rate is not capped by the condensation rate as significant progress is being made in terms of the solar evaporation rate; |
|                                   | • Excellent photothermal conversion;                                         • The presence of abundant functional groups can be used to remove other compounds (e.g., volatile species) via adsorption or through anchoring active materials to degrade these species; | • Anti-salt-clogging due to the presence of high charge and high water-content;                   • Development of transparent antifogging hydrogels as part of the condensation chamber or water-collection device would be an interesting area for research. |
|                                   | • Minimal heat loss;                                                         • Intelligent systems with innovative water recovery strategies enabled by hydrogels fabricated using stimuli-responsive polymers. | • Anti-salt-clogging due to the presence of high charge and high water-content;                   • Development of transparent antifogging hydrogels as part of the condensation chamber or water-collection device would be an interesting area for research. |
|                                   | • Antifouling and antiscalant to facilitate long-term operation;             • The presence of abundant functional groups can be used to remove other compounds (e.g., volatile species) via adsorption or through anchoring active materials to degrade these species; | • Antifouling and antiscalant to facilitate long-term operation;                                 • Another important aspect in harvesting water through the solar evaporation process is the condensation of the generated vapor. The effect of the materials and structure of the condensation chamber on the efficiency of collecting the condensed vapor is less intensely studied. This requires more studies to be done in this area to ensure that the water production rate is not capped by the condensation rate as significant progress is being made in terms of the solar evaporation rate; |
|                                   | • Able to generate vapor even under low solar flux conditions.               • The presence of abundant functional groups can be used to remove other compounds (e.g., volatile species) via adsorption or through anchoring active materials to degrade these species; | • Antifouling and antiscalant to facilitate long-term operation;                                 • Another important aspect in harvesting water through the solar evaporation process is the condensation of the generated vapor. The effect of the materials and structure of the condensation chamber on the efficiency of collecting the condensed vapor is less intensely studied. This requires more studies to be done in this area to ensure that the water production rate is not capped by the condensation rate as significant progress is being made in terms of the solar evaporation rate; |
| **Atmospheric-water harvesting**   | • Absorb a large amount of water vapor with respect to weight and/or volume;    • The presence of functional groups having a high water-affinity in hydrogels facilitates high water vapor sorption capacity and broadens the RH working window; | • Most hydrogels (except for PSA) without the incorporation of hygroscopic or deliquescent materials may not have a substantial moisture uptake capacity, especially under low RH conditions. As such, the development of hydrogel-based composites utilizing different moisture sorbers may be explored to further enhance the moisture sorption capacities. Furthermore, fabrication of different types of ordered porous structure in these composites and evaluating its effect on further enhancement in the moisture sorption capacity would provide valuable insights. |
|                                   | • Able to harvest water even at low RHs;                                    • The chelating ability of the functional groups in hydrogels can also be used to trap contaminants present in the water vapor and thus improve the water quality of the liquefied water vapor; | • In view of the vast repertoire of smart polymers, the release of the absorbed water can also be explored using different means apart from thermal-based methods (e.g., thermostensitive dewatering and solar evaporation). |
|                                   | • The water can be collected with minimal energy input;                      • Low vaporization enthalpy of water trapped in hydrogels facilitates water recovery via solar evaporation even under low solar flux; | • Most studies neglected the water quality aspect of the water harvested from the atmosphere. As such, greater attention should be directed to this aspect in view of the increasing air pollution. |
|                                   | • Fast sorption/desorption kinetics and highly reusable.                     • When fabricated using smart polymers, the absorbed liquefied vapor can be recovered via changes in the external stimuli such as solar energy and temperature; | • The AWH system, which is generally composed of moisture-harvesting materials, materials substrate, and collection devices, can be optimized for efficient moisture concentration and water delivery; |
|                                   |                                                                             • Flexible network provides minimal constraints on water vapor sorption of the embedded hygroscopic material; | • Development of transparent antifogging hydrogels as part of the AWH device would be an interesting area for research. |
As hydrogels tend to be rather soft materials, their mechanical robustness may need to be improved through i) material reinforcement such as functionalization with high-aspect ratio filler materials, ii) blending or incorporating materials with higher toughness, and iii) formation of DN hydrogel comprising a soft and ductile network for stretchability and a rigid network for toughness. Self-healing hydrogels capable of reversing damage without external input are also desirable. Examples of hydrogels capable of such intrinsic repairs are usually designed by introducing dynamic covalent bonds or reversible noncovalent bonds, including imines, disulfide bonds, acylhydrazone, boronate esters, hydrogen bonds, coordination bonds, host–guest interactions, and hydrophobic interactions.[178] Apart from mechanical robustness, durability of the hydrogel in terms of chemical stability, for example, resilience to hydrolysis, corrosion, enzymatic degradation, photolysis, oxidation, etc., should also be considered to ensure practical applications of the hydrogels.

Apart from these material-based strategies, the development of appropriate devices to house the hydrogels would not only provide a safe and efficient way to handle the hydrogels, but they would also contribute to the maximization of the efficiency for high-throughput as well as for point-of-use applications. Examples of applications that would highly benefit from a well-designed device include the squeeze–release cryogels for disinfection that requires cyclical water absorption followed by application of pressure to recover the disinfected water, or condensation chambers for the collection of the distillation in interfacial solar desalination and atmospheric-water harvesting which requires cyclical exposure of the hydrogels to the atmosphere for moisture capture followed by recovery of liquefied water. Feasibility testing for real-world applications should also be addressed by conducting performance testing using either natural water samples or by employing testing conditions that simulate that of real-world applications. This is because some WTs are highly sensitive to the constituents present in the water that can deactivate their reactivity; for example, disinfection efficacy may be reduced in the presence of natural organic matters while the adsorption efficiency may be affected by other interfering ions or blocked by a layer of conditioning film. In some new and emerging applications such as atmospheric-water harvesting, the water quality aspect of the water harvested is neglected in most studies, thus greater attention should be directed to this aspect in view of the increasing air pollution and the fact that the harvesting process does not, by itself, necessarily purify the water.

Another prospective area of research is the development of multifunctional hydrogels to add further value to their current applications. For example, in the case of interfacial solar desalination, volatile compounds may escape together with the evaporated water and end up in the distillate. So, future studies may also need to explore multifunctional materials with the ability to remove such volatile compounds either through adsorption or degradation in the water prior to evaporation. The hydrogel membranes used for desalination can also be applied as a molecular water reservoir that supplies desalinated water for uptake by plants—the salt-depleted water absorbed by a polyelectrolyte hydrogel (showing no stimuli-responsive behavior) may be indirectly recovered. This strategy can resolve the dichotomous requirement of high charge-density and high hydrophobic-fraction within the same hydrogel. Also, considering the substantial volumetric changes experienced by the hydrogels during the water absorption and release, considerable amounts of energy may be extracted simultaneous to the water treatment process. For example, it has been recently shown that it is possible to harness energy from a salinity gradient based on extracting the work done during the swelling and shrinking of a superabsorbent hydrogel through alternating exposure to solutions of high and low salinity. The concomitant volumetric expansion as the hydrogel upon water absorption can be used to do work against an external load that is less than the swelling pressure of the hydrogel. Subsequent exposure of the swollen hydrogel in high salinity solution such as seawater induces release of the absorbed water due to a change in the osmotic pressure allowing them to be reused in numerous cycles. Although the reported energy recovery is rather low (about 124 mJ in 1 h), it will still be desirable when the hydrogels are used in remote locations not connected to the centralized power sources.[179,180]

In conclusion, hydrogel is a promising platform in enhancing water security for a sustainable future. Apart from its enhanced performance and technological innovation brought forth by its unique properties, hydrogels open the possibility to harvest water from sources beyond the conventional norm. This is critical in ensuring the ability of the future generations in meeting the rising global water demand in spite of the challenges presented by climate change, industrialization and population growth. More importantly, the simplicity and infrastructure-independent operations of the hydrogel-enabled WTs enable them to be resilient and adaptive solutions for decentralized applications catered for populations most afflicted by water scarcity such as those in developing nations and in disaster-prone regions. When sustainability factors such as the costs, environmental impact, and lifecycle of the materials and methods used to fabricate hydrogels are well-considered, hydrogel-enabled WTs can be effective yet sustainable solutions in delivering safe and affordable water supply for all, particularly for those in difficult circumstances not currently served by the mainstream technologies.
A. Entezari, M. Ejeian, R. Wang, N. Thakur, A. S. Ranganath, H. Jarimi, R. Powell, S. Riffat, H. Mittal, A. Al Alili, S. M. Alhassan, D. Beysens, I. Milimouk, K.-C. Park, S. S. Chhatre, S. Srinivasan, R. E. Cohen, Milimouk, D. Beysens, Energy 2011, 36, 2257.

K.-C. Park, S. S. Chhatre, S. Srinivasan, R. E. Cohen, G. H. McKinley, Langmuir 2013, 29, 13269.

P. A. Kallenberger, M. Fröba, Commun. Chem. 2018, 1, 28.

A. Entezari, M. Ejeian, R. Wang, Appl. Therm. Eng. 2019, 161, 114109.

H. Mittal, A. Al Alli, S. M. Alhassan, Colloids Surf. A 2020, 599, 124813.

H. Mittal, A. Al Alli, S. M. Alhassan, Microporous Mesoporous Mater. 2020, 299, 110106.

H. Yang, H. Zhu, M. M. R. M. Hendrix, N. J. H. G. M. Lousberg, G. de With, Adv. Mater. 2013, 25, 1150.

J. ter Schiphorst, M. van den Broek, T. de Koning, J. N. Murphy, A. P. H. J. Schenning, Adv. Mater. 2016, 4, 8676.

N. Thakur, A. Baji, A. S. Ranganath, Appl. Surf. Sci. 2018, 433, 1018.

N. Thakur, A. S. Ranganath, K. Agarwal, A. Baji, Macromol. Mater. Eng. 2017, 302, 1700124.

N. Thakur, A. Sargur Ranganath, K. Sopha, A. Baji, ACS Appl. Mater. Interfaces 2017, 9, 29224.

F. Ni, N. Qiu, P. Xiao, C. Zhang, Y. Jian, Y. Liang, W. Xie, L. Yan, T. Chen, Angew. Chem., Int. Ed. 2020, 59, 19237.

Y. Yang, D. Rana, C. Q. Lan, RSC Adv. 2015, 5, 59583.

R. Li, Y. Shi, M. Alsaedi, M. Wu, L. Shi, P. Wang, Environ. Sci. Technol. 2018, 52, 11367.

X. Wang, X. Li, G. Liu, J. Li, X. Hu, N. Xu, W. Zhao, B. Zhu, J. Zhu, Angew. Chem. 2019, 131, 12182.

H. Qi, T. Wei, W. Zhao, B. Zhu, G. Liu, P. Wang, Z. Lin, X. Wang, X. Li, X. Zhang, J. Zhu, Adv. Mater. 2019, 31, 1903378.

A. Entezari, M. Ejeian, R. Wang, ACS Mater. Lett. 2020, 2, 471.

K. Yang, Y. Shi, M. Wu, W. Wang, Y. Jin, R. Li, M. Wakil Shahzad, K. Choon Ng, P. Wang, J. Mater. Chem. A 2020, 8, 1887.

X. Zhou, P. Zhang, F. Zhao, G. Yu, ACS Mater. Lett. 2020, 2, 1419.

J. Hoque, N. Sangaj, S. Varghese, Macromol. Biosci. 2019, 19, 1800259.

M. Wei, Y. Gao, X. Li, M. J. Serpe, Polym. Chem. 2016, 8, 127.

Y. Jiang, Y. Wang, Q. Li, C. Yu, W. Chu, CMC 2020, 27, 2631.

C. Chai, Y. Guo, Z. Huang, Z. Zhang, S. Yang, W. Li, Y. Zhao, J. Hao, Langmuir 2020, 36, 10448.

X. Zhu, W. Yang, M. C. Hatzell, B. E. Logan, Environ. Sci. Technol. 2014, 48, 7157.

L. Arens, F. Weißenfeld, C. O. Klein, K. Schlag, M. Wilhelm, Adv. Sci. 2017, 4, https://doi.org/10.1002/advs.201770044.
Athanassia Athanassiou is Principal Investigator at the Italian Institute of Technology. She has a degree in Physics from the University of Ioannina in Greece, an MSc from the University of Manchester and a Ph.D. in Physics from Salford University in UK. From 2000 to 2005, she worked at FORTH in Crete, and in 2006 she became Senior Researcher at NNL, CNR-Istituto di Nanoscienze, Lecce. In 2011, she joint IIT and nowadays her group of Smart Materials counts 50 people that work on sustainable materials and technologies for the benefit of environmental and human health. She has published more than 350 articles in scientific journals and 26 patents.

Despina Fragouli is a researcher in the Smart Materials group of the Italian Institute of Technology. She graduated in physics, and she received an M.Sc. in Applied Molecular Spectroscopy, and a Ph.D. in chemistry from the University of Crete, Greece, focusing on imaging systems and laser–matter interaction. Since 2009, she works at the Italian Institute of Technology and her main research interests are focused on the development of functional polymeric composites for water technologies such as water treatment and water harvesting and for smart packaging applications.