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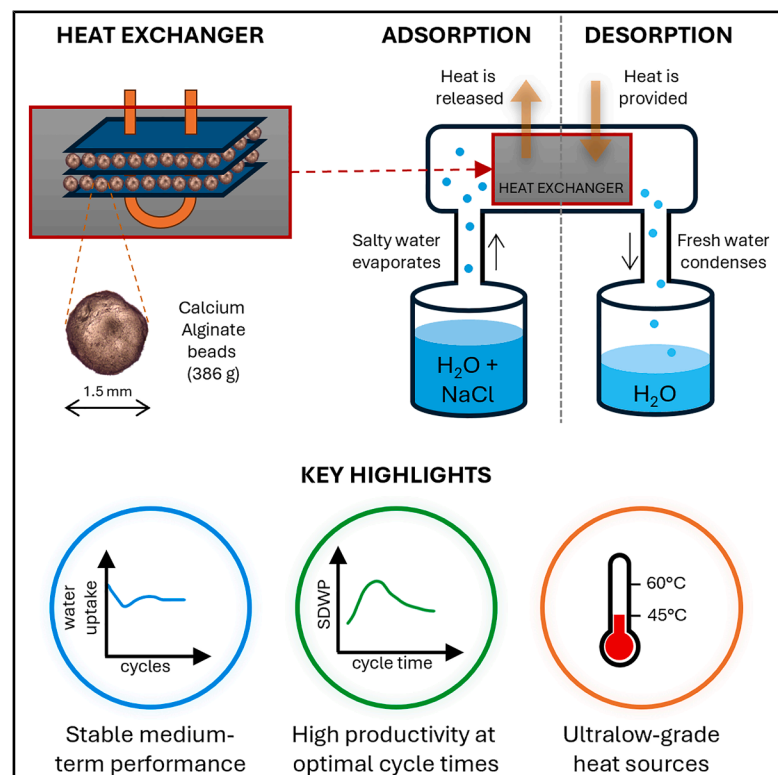
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Calcium alginate hydrogel for high-yield adsorption-based desalination driven by ultralow-grade heat

Graphical abstract



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In brief

Adsorption desalination stands out as a promising solution to produce freshwater, leveraging ultralow-grade heat. Calò et al. demonstrate that a bio-derived calcium alginate hydrogel can be used as an alternative to other common sorbents, with stable medium-term performance and water productivity even at temperatures below 60°C.

Highlights

- Calcium alginate hydrogel is tested for adsorption-based water desalination
- Stable material performance over 40 cycles of normal operation under vacuum
- An optimal specific daily water production of 6 m³/day/ton at 60°C is achieved
- Desalination driven by ultralow-grade heat sources at temperatures as low as 45°C

Article

Calcium alginate hydrogel for high-yield adsorption-based desalination driven by ultralow-grade heat

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SUMMARY

Adsorbent-based desalination stands out as a promising solution to produce fresh water leveraging on ultralow-grade heat. We investigate the use of a bio-derived calcium alginate (CaAlg) hydrogel, an alternative to other common sorbents. A batch of CaAlg is synthesized and characterized in a gravimetric sorption analyzer. The resulting type II isotherm at 30°C shows an exceptional water uptake equilibrium value of 1.28 g/g at a relative humidity of 70%, realizing nearly a 4-fold increase compared to standard silica gels under the same conditions. We test CaAlg under vacuum in a water desalination unit. Our material shows an excellent medium-term cyclability, with a stable uptake over 40 cycles of operation. We achieve water production even at a temperature as low as 45°C, with a specific daily water production (SDWP) of 6 m³/day/ton using a hot-source temperature of 60°C, realizing the most performant small-scale system in the context of ultralow-grade waste heat valorization.

INTRODUCTION

Freshwater scarcity is a global problem. The available reserves constitute only 3% of the total water on Earth; they are not uniformly distributed and they are often difficult to access or contaminated. As a result, billions of people in the world suffer from water shortage,^{1–4} making desalination a key technology to cope with this issue, especially when seawater is accessible. In this context, the research for new, effective, and sustainable desalination solutions is crucial.

The most common desalination technology is reverse osmosis (RO), a mature technology with elevated cost for installation but with optimized electricity consumption (1.8–5 kWh/m³) needed to reject over 99% of the solute. However, RO plants require high-exergy sources in order to apply the necessary work to overcome osmotic pressure, requiring additional investment costs in the case of integration with renewable energy.^{5,6} On the other hand, thermal desalination technologies have the advantage of requiring lower exergy sources, such as low-temperature heat. Multi-stage flash distillation (MSD) and multiple-effect distillation (MED) belong to this category, and their energy consumptions per cubic meter of water are 60–80 kWh of heat in addition to 1–5 kWh of electrical energy, needed to run auxiliaries of plants.^{7,8} Membrane distillation (MD) is an alternative low-cost distillation technique that can be driven with low-exergy heat, with energy consumption between 225 kWh/m³ and 500 kWh/m³ of condensed water.^{9–12} In adsorption desalination (AD), an emerging thermal technology, a sorbent material is used to drive water vapor from the

evaporator (EV) containing salty water to a condenser (CD) with fresh water.^{13,14} AD is scalable and, unlike membrane-based technologies, the distillation performance is not impacted by temperature, concentration polarization, and fouling.¹⁵ Furthermore, adsorbent-based solutions are generally environmentally friendly, highly integrable in renewable energy grids (e.g., they can be operated using renewable heat from thermal solar plants^{16,17}) and circular-economy viable solutions (they can be operated by using process waste heat¹⁸). The performances of an adsorption-desalination plant depend strongly on the choice of the adsorbent material: the latter should be sustainable, stable over time, and have large water uptakes and fast kinetics. In this context, the research for new materials is crucial. Conventional AD plants use sorbents such as silica gels, which are typically regenerated at temperatures of 65°C or above.¹³ This is a limitation when only lower-grade heat sources are available. In contrast, we propose calcium alginate (CaAlg) as alternative sorbent, a bio-derived adsorbent hydrogel. The material choice is based on the results of previous experimental campaigns,¹⁹ where CaAlg has proved high sorption rates and capacities even when regenerated at temperatures of 60°C or below. In particular, CaAlg has shown an equilibrium water uptake of up to 0.88 g/g (at temperature $T = 21^\circ\text{C}$ and relative humidity $\text{RH} = 47\%$), larger than ordinary silica gels in similar conditions (0.28 g/g at $T = 25^\circ\text{C}$ and $\text{RH} = 50\%$ ²⁰). Additionally, we decided to investigate CaAlg for AD because it is a bio-derived material and its disposal in case of material replacement comes with a low environmental impact.^{21–24} Nevertheless, until now, CaAlg has never been tested under vacuum in an AD unit.

In this research, we characterize experimentally CaAlg, both in a gravimetric analyzer (in comparison with reference microporous and mesoporous silica gels) and under vacuum in a prototype adsorption-based desalination unit, in particular comparing performances using mesoporous silica gel with the same unit. This allows us to prove that CaAlg has an excellent medium-term cyclability under vacuum, with a stable uptake over 40 cycles of operation. We achieve water desalination at a temperature as low as 45°C, with a specific daily water production (SDWP) of 2.2 m³/day/ton, higher than silica gel tested under the same conditions. Furthermore, we achieve an optimal SDWP of 6 m³/day/ton when using a hot-source temperature of 60°C.

RESULTS

Operating principle

In adsorption-based technologies, the separation of water from contaminated liquid solutions is obtained by operating a working cycle based on three consecutive phases: adsorption, desorption, and pre-cooling. First, a vacuum chamber (EV tank) containing the evaporating feedwater is put in communication with a second vacuum chamber (adsorber) containing the sorbent under test. During this phase (adsorption), water vapor evaporates and is physically bonded to material micropores. Then, the communication between the EV tank and adsorber is interrupted, and the desorption process starts. During this phase, increasing the sorbent temperature breaks the physical bonds between the water and the sorbent and the water vapor is released back. The latter condenses on the internal walls of the adsorber vessel, and it is collected from a third vacuum chamber placed at the bottom of the adsorber (CD pipe). Finally, all the chambers are isolated, and the machine is cooled down in preparation for the next cycle (pre-cooling phase).

The choice of a proper heat exchanger is crucial in order for the sorbent material to efficiently exchange both thermal energy and vapor mass with the environment. For this research, we packed the material in a finned coil heat exchanger (Figure 1A) and placed the latter in the adsorber chamber of the desalination unit (Figure 1B). In Figure 1C, we show the schematic of the setup, including the vacuum circuit (blue areas), the external hydraulic circuits exchanging heat with the machine (orange and magenta loops), temperature sensors, pressure sensor, flowmeter, and actuators (details are provided in the methods section).

Material characterization

The material studied in this research is a biopolymeric hydrogel referred to as CaAlg, obtained by crosslinking sodium alginate (NaAlg) (a salt contained in the cell membranes of brown algae²⁵) with calcium ions.^{26,27} More details on the hydrogel synthesis are reported in the methods section. Figures 1D, E, F, and G show increasingly larger details of CaAlg beads: first, when placed in the heat exchanger; second, under an optical microscope; and third and fourth, under scanning electron microscopy (SEM) imaging.

Figure 2A shows the adsorption and desorption isotherms at 30°C obtained on aged samples of CaAlg (details in the methods section). Vertical bars represent ± 3 standard deviations, modeling the uncertainty due to inhomogeneity in the pro-

duced samples (negligible in the case of silica gels). Isotherms carried out on silica gel samples (microporous silica gel with grain size 0.5–1.5 mm and mesoporous silica gel with grain size 1.5–3.15 mm) are also plotted for reference. At the RH of 70%, the CaAlg reaches an uptake of 1.28 g/g, while the microporous and mesoporous silica gel reach uptakes of 0.29 and 0.34 g/g (about 4 times smaller). Furthermore, the CaAlg isotherm shows higher linearity and less hysteresis. Given the reversed “S” shape, the CaAlg isotherm can be classified as “type II” according to the ISO classification.²⁸ Thus, the Guggenheim-Anderson-DeBoer model (GAB)—a variation of the Brunauer-Emmett-Teller (BET) model—can be used to best-fit the curve^{28,29}:

$$w = \frac{w_m \cdot c \cdot K \cdot RH}{(1 - K \cdot RH) \cdot [1 + K \cdot RH \cdot (c - 1)]}, \quad (\text{Equation 1})$$

where w_m is the monomolecular layer uptake, RH is relative humidity, K is a corrective coefficient extending BET validity, and c is the original BET coefficient. The latter can be written as a function of the enthalpy of the adsorption process H_{ads} , latent heat of evaporation of water H_{liq} (equal to 2430 kJ/kg at 30°C³⁰), universal gas constant $R = 8.315 \text{ J/(mol}\cdot\text{K)}$, and absolute temperature T , according to Equation (2):

$$c = e^{\frac{H_{ads} - H_{liq}}{RT}}. \quad (\text{Equation 2})$$

The resulting curve, best-fitted on the adsorption isotherm, is shown in Figure 2A (black dotted line). The values $w_m = 0.7317 \text{ g/g}$, $c = 3.4558$, and $K = 0.7704$, resulting from the best-fitting procedure, are physically consistent, being w_m below the maximum capacity, K between 0 and 1, and c greater than 2 (which is consistent with a type II isotherm).³¹ By inverting Equation (2), the enthalpy of adsorption can be estimated to be 2,600 kJ/kg. This value is approximately 7% larger than the latent heat of evaporation for water at 30°C. If compared with literature, this is close to the values for silica gels and slightly lower than metal organic frameworks (MOFs) (see also Tables S1 and S2 in Note S1). Figure 2B shows the adsorption equilibrium values of samples of CaAlg after 0, 20, 30, and 40 aging cycles in the desalination unit. The values after the first 20 cycles are, in the RH range between 40% and 70%, from 5% to 10% lower than the isotherm of the material “as produced.” This can be explained by the material not being perfectly dry after the production process (see also Figure S1 in Note S2). Using X-ray diffractions,³² authors have demonstrated that initial dehydration of the hydrogel (the first responsible for the loss of “composition water”) induces the formation of secondary junction zones among functional groups with un-crosslinked Ca cations. These junctions among parallel alginate chains are strong enough to be preserved also on successive rehydration of the hydrogel once it is exposed to moisture. However, the process of losing the composition water is not completed with one single dehydration and continues during the first thermal cycles. The progressive reduction in dry mass during the first cycles due to this aspect is visible in the initial drop of the equilibrium moisture uptake. After this initial drop, though, the equilibrium values stabilize. The convergence of the material’s behavior is coherent with what is observed for CaAlg samples in the literature.³³ Figure 2C compares the CaAlg adsorption isotherm at 30°C (vertical bars represent ± 3 standard deviations)

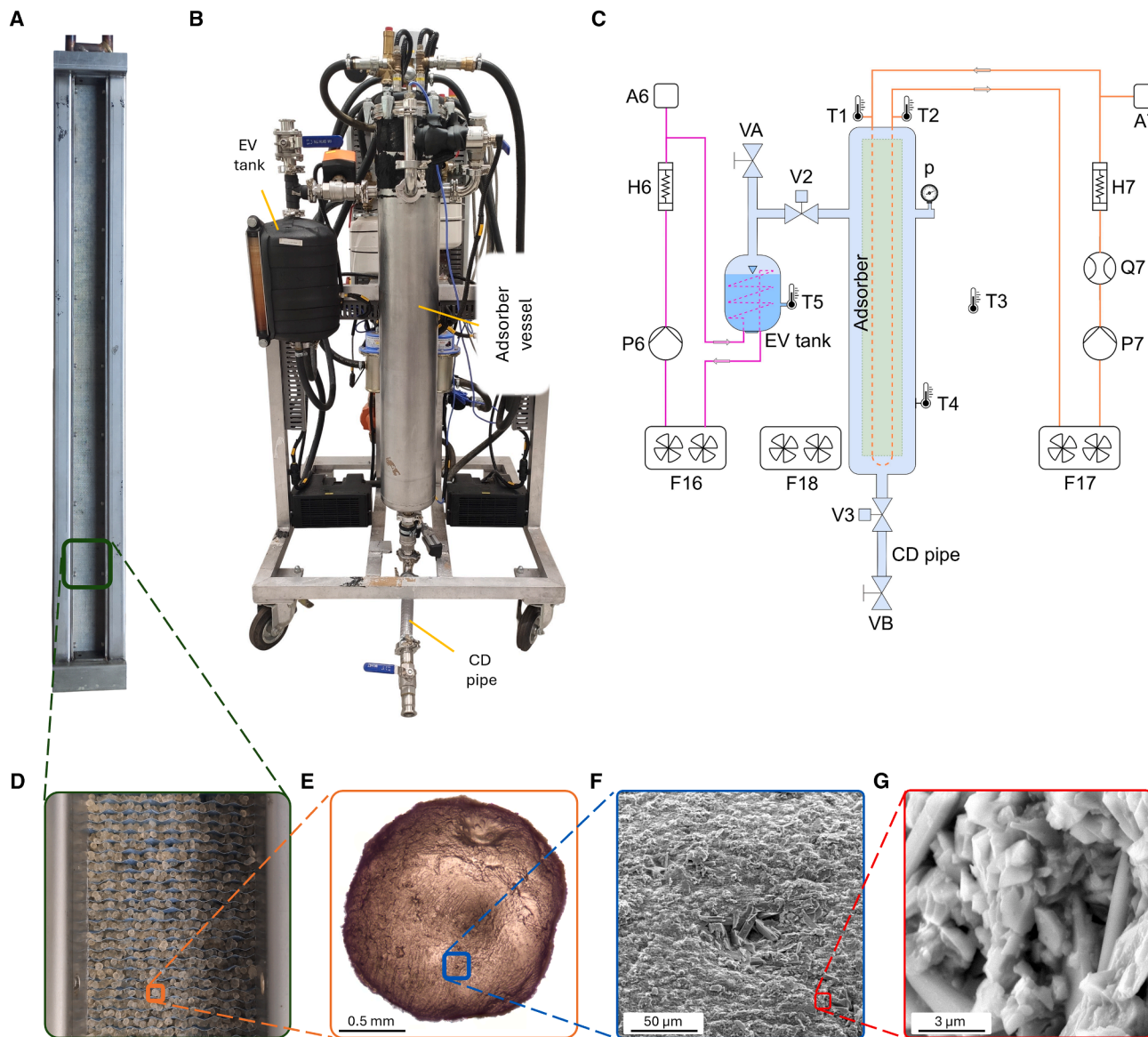


Figure 1. Single-bed adsorption desalination unit

(A) Heat exchanger containing the sorbent material under test.

(B) Desalination unit. The evaporator (EV) tank contains the feedwater; the adsorber vessel contains the heat exchanger filled with the sorbent material; and the condenser (CD) pipe collects the desalinated water.

(C) Schematics of the desalination unit, showing the vacuum circuit (blue areas), the external pressurized circuit exchanging heat with the adsorber (orange), and the external pressurized circuit exchanging heat with the EV tank (magenta). The unit is provided with temperature sensors (T1, T2, T3, T4, and T5), a pressure sensor (p), a flowmeter (Q7), four valves (V2, V3, VA, and VB), two pumps (P6 and P7), three dry-coolers (F16, F17, and F18), two electric heaters (H6 and H7), and safety accessories (A6 and A7).

(D) Detail of the heat exchanger, where the 3-mm-large spaces among the fins are filled with CaAlg beads.

(E) Zoom on a single bead of CaAlg under a 5 \times optical lens, with backlighting. Scale bars, 0.5 mm.

(F) A SEM image with magnification 1,000 \times of the surface of a bead of CaAlg. Scale bars, 50 μ m.

(G) A SEM image with magnification 20,000 \times of the surface of a bead of CaAlg. Scale bars, 3 μ m.

with results from the literature.^{34–39} For relative humidities higher than 20%, the aged CaAlg sample has the highest equilibrium water uptake, except in the range 45%–65% where it is outperformed by a modified MIL-101 MOF. The shape of the isotherm and high linearity are consistent with the results on the CaAlg sample from

the literature.³⁴ MOFs, such as MOF-801, are competitive at low RH values (below 20%). Figures 2D and 2E show pictures of the significant samples tested in this research, respectively: CaAlg “as produced” (no aging cycles), CaAlg after 40 aging cycles, microporous silica gel, and mesoporous silica gel.

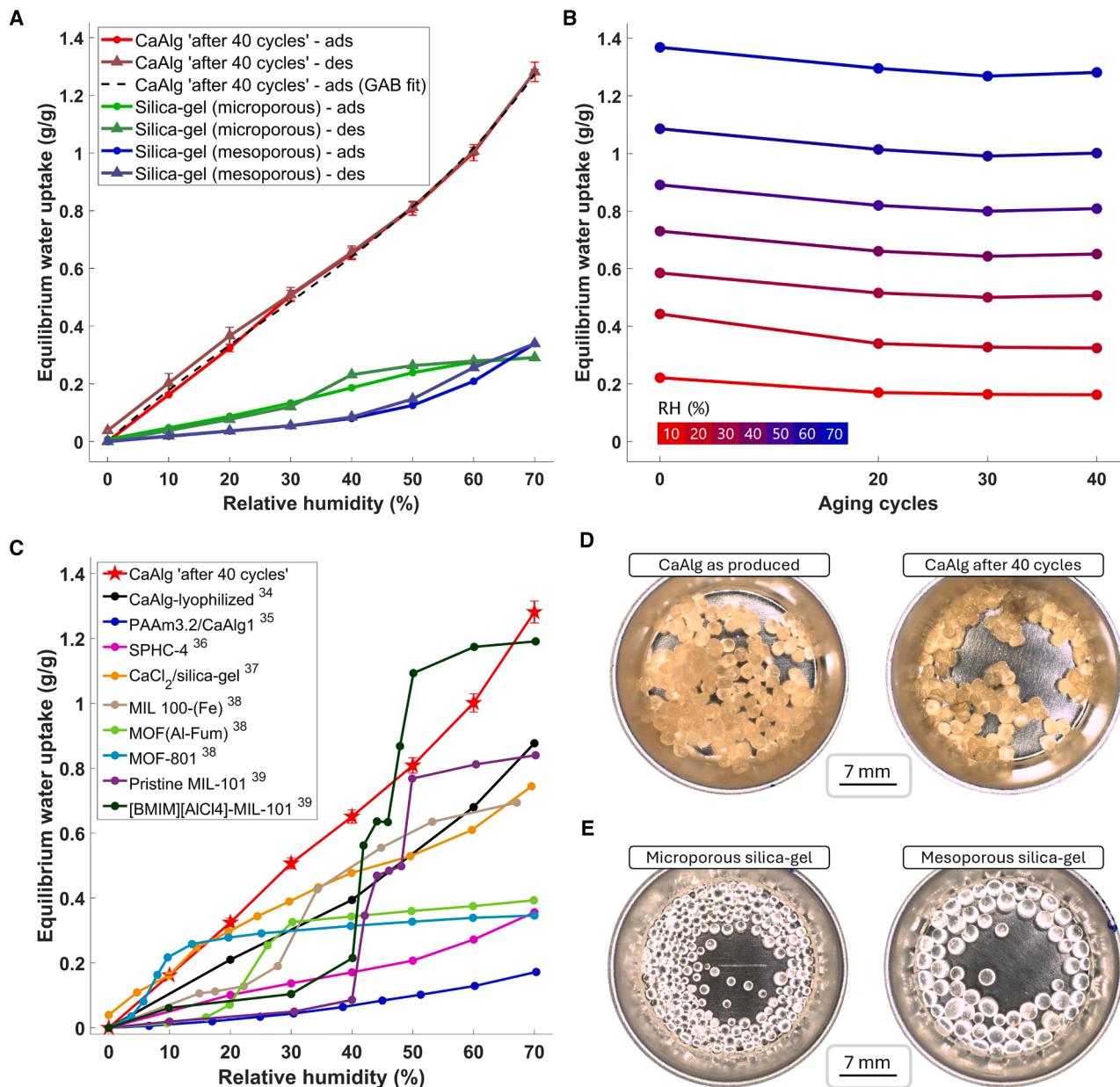


Figure 2. Material characterization: Isotherms and aging

(A) Isotherm at 30°C of CaAlg after 40 cycles of testing, compared with microporous and mesoporous reference silica gels. Both adsorption (ads) and desorption (des) ramps are shown. Vertical bars represent \pm three standard deviations. The Guggenheim-Anderson-DeBoer (GAB) best-fitting curve on the CaAlg adsorption ramp is plotted in comparison.

(B) Equilibrium values at different relative humidities for samples that underwent 0, 20, 30, and 40 cycles of testing.

(C) Adsorption isotherm at 30°C of CaAlg in comparison with materials from the literature. Vertical bars represent \pm three standard deviations.

(D) Samples of CaAlg as produced and after 40 cycles of testing, in equilibrium at temperature $T = 30^\circ\text{C}$ and relative humidity $\text{RH} = 40\%$. Scale bars, 7 mm.

(E) Samples of microporous and mesoporous silica gel, in equilibrium at $T = 30^\circ\text{C}$ and $\text{RH} = 40\%$. Scale bars, 7 mm.

Cycling CaAlg in the desalination unit

Figure 3A shows the resulting trends of the monitored thermodynamic variables when CaAlg is cycled in the desalination unit (details in the methods section). The test consists of 6 consecutive cycles, each composed of the adsorption phase ADS (30 min with the target adsorption temperature of 30°C),

the desorption phase DES (45 min with the target desorption temperature of 60°C, in this case), and the pre-cooling phase PC (15 min). The three phases are highlighted in the first cycle of Figure 3A and repeat identically for 9 h. At the beginning of the ADS phase, temperature T_2 (outlet of the adsorber) is greater than temperature T_1 (inlet of the adsorber), consistent with

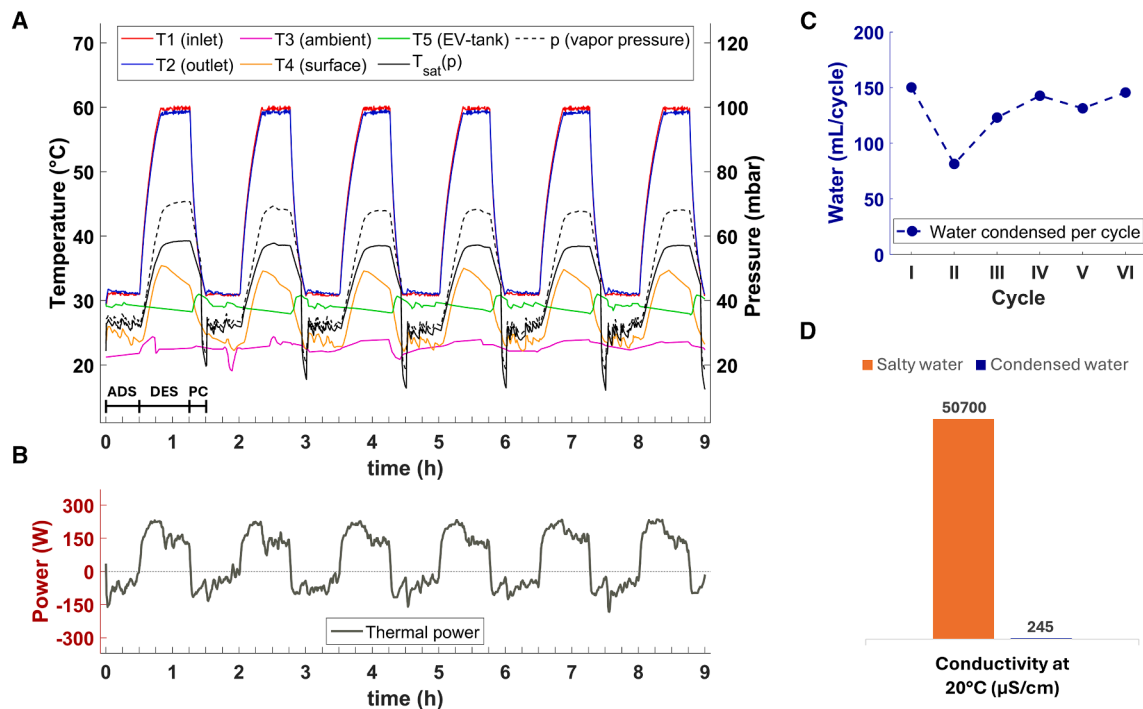


Figure 3. Cycling CaAlg in the desalination unit

(A) 1-day test using CaAlg in the desalination unit. The test consists of 6 consecutive cycles, each of which is composed of adsorption phase ADS, desorption phase DES, and pre-cooling phase PC, as highlighted in the first cycle. Temperatures T1 (inlet of the adsorber), T2 (outlet of the adsorber), T3 (ambient), T4 (vessel surface), T5 (evaporating water), and T_{sat} (saturation temperature at the vapor pressure in the adsorber) are shown on the left axis as a function of test time; vapor pressure p is shown on the right axis.

(B) Thermal power (positive when absorbed by the adsorber) is shown as a function of test time. It is evaluated as the product of the external circuit's water density ρ , flow rate Q, specific heat c_p , and the temperature difference (T1–T2).

(C) Water collected in the CD pipe at the end of each of the six cycles.

(D) Conductivity of water at 20°C before and after the desalination process.

adsorption being an exothermic process. The opposite is true during desorption, the latter being an endothermic process.

The heating transient in the first 20 min of the desorption phase is necessary to overcome the thermal inertia of the system and bring the adsorber to the target desorption temperature. The pressure p during desorption increases during the heating process and decreases slightly during the rest of the phase, while condensation happens in the adsorber. The saturation temperature T_{sat} is evaluated at pressure p using the Antoine equation.⁴⁰ From Figure 3A, T_{sat} follows qualitatively the temperature T4 (external surface of the adsorber vessel), which is consistent with the condensation process.

Figure 3B shows the thermal power exchanged with the adsorber (uncertainty propagation is discussed in Note S3). This is positive during desorption and negative during adsorption and pre-cooling, which is consistent with the nature of the processes. Figure 3C shows the water production at the end of each of the 6 cycles; after initial oscillations in the first 2 cycles, the production stabilizes. This occurs because the chosen adsorption and desorption times initially prevent the material from returning to its starting uptake values. Keeping on cycling, the cycle converges toward a range of uptakes that is compatible with the chosen parameters. This behavior is consistent across various conditions and supported by the literature.⁴¹

The results of the experimental campaign under all tested conditions are found in Note S4 (Table S3; Figures S2–S10).

In Figure 3D, we show the results of a water analysis (see methods section) conducted on samples collected from the desalination unit. A desalination effect was indeed achieved: we started from feedwater with the salinity level comparable with seawater (conductivity of 50700 $\mu\text{S}/\text{cm}$) and produced water with a conductivity of 245 $\mu\text{S}/\text{cm}$ at 20°C. For reference, the World Health Organization⁴² suggests for drinkable water, a limit of total dissolved solids equal to 600 mg/L, corresponding to approximately 900 $\mu\text{S}/\text{cm}$ at 20°C.⁴³ Nevertheless, some salt is still present in the condensed water. This can be explained by aerosol migrating from the EV into the adsorber (see also Figure S11, in Note S5). The complete list of results of the analyses performed on the water samples is reported in Supplementary 6 (Table S4; Figures S1–S13).

Desalination plant performance

Figure 4A shows the specific water production (i.e., the amount of condensed water divided by the amount of dry sorbent) achieved with the desalination unit at different desorption temperatures (vertical bars represent ± 1 standard deviation). The curves obtained with CaAlg and mesoporous silica gel are shown for comparison, proving that CaAlg can reach specific

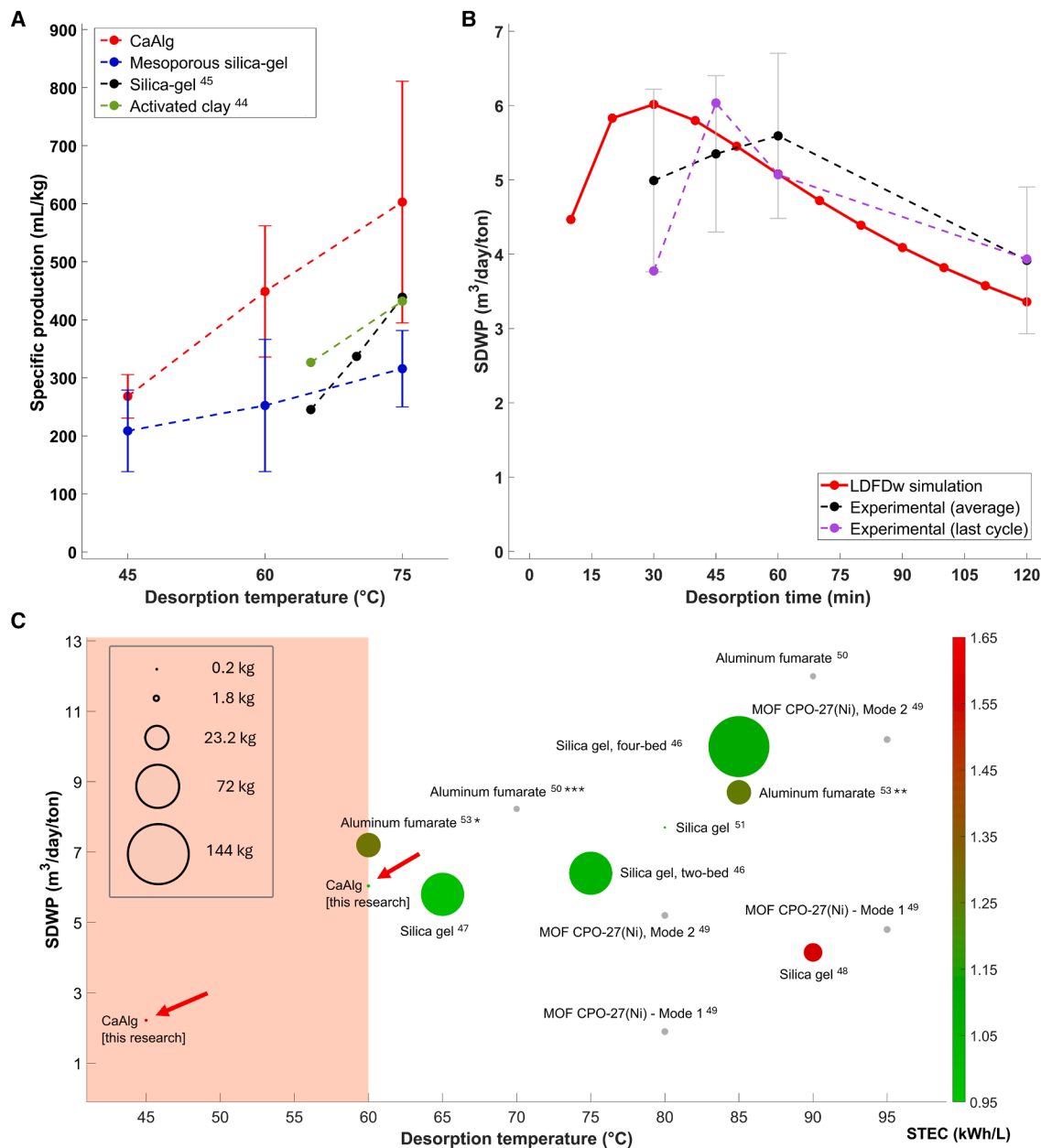


Figure 4. Performance of the desalination plant

(A) Specific water production as a function of test desorption temperature. Experimental results for CaAlg and mesoporous silica gel are shown, as achieved in the desalination unit with the adsorption time of 30 min, adsorption temperature of 30°C, and desorption time of 120 min. Vertical bars indicate \pm one standard deviation. Results achieved with different plants from the literature are shown in comparison.

(B) Specific daily water production (SDWP) as a function of test desorption time. Experimental results for CaAlg are shown, as achieved in the desalination unit with the adsorption time of 30 min, adsorption temperature of 30°C, and desorption temperature of 60°C. The graph contains the experimental SDWP evaluated considering the average production of the day (black, with vertical bars indicating \pm one standard deviation), the experimental SDWP evaluated considering the production from the last cycle of the day (purple), and the theoretical SDWP simulated through the model LDFDw.

(C) Map showing the performance of the desalination unit in comparison with adsorption-desalination plants from the literature. SDWP is shown as a function of desorption temperature. The dot's color shows the needed specific thermal energy consumption (STEC). The dot's area is proportional to the amount of sorbent in the plant. The ultralow-grade heat region for temperatures below 60°C is colored in orange. All reported plants use a CD temperature between 25°C and 30°C, except for * (20°C) and for our plant (23°C). All reported plants use an EV temperature between 27°C and 30°C, except for ** (24°C) and *** (20°C).

productions up to 90% larger than silica gel in the same test conditions. For these tests, we fixed adsorption time and temperature (30 min and 30°C, respectively) and desorption time (120 min). In the same picture, results from the literature are shown in comparison.^{44,45} The dependence of the SDWP (see [methods](#) section) on the cycle time is shown in [Figure 4B](#), where the black curve is experimentally derived considering the average production per cycle (vertical bars represent ± 1 standard deviation), while the purple curve refers to the production of the last cycle of the test. For this analysis, we fixed adsorption time and temperature (30 min and 30°C, respectively) and desorption temperature (60°C). We found that an optimal SDWP of 6.04 m³/day/ton can be achieved at an intermediate desorption time of 45 min.

We used the analytical model “LDFDw”, a variation of the linear driving force model “LDF” (where “D” and “w” stand for “Diffusivity” and “water uptake”, respectively)¹⁹ to best-fit the charging and discharging transient of the CaAlg (see [Figure S14](#) in [Note S7](#)) and found that the diffusivity at 30°C can be estimated as a function of water uptake w as: $D_{30^\circ\text{C}} = a + b \cdot w$, with $a = 4.4399 \cdot 10^{-12} \text{m}^2/\text{s}$ and $b = -2.2985 \cdot 10^{-12} \text{m}^2/\text{s}$. The estimated diffusivities for all samples are provided in [Note S7](#), [Table S5](#). Starting from this result, we simulated adsorption-desorption transient processes and derived the red curve in [Figure 4B](#) (see [methods](#) section for details). The result is close to the experimental outcome, except that the latter is right-shifted. This can be explained by the fact that approximately 20 min are needed at the beginning of each desorption phase to bring the adsorber to the target temperature, due to the large thermal inertia of the prototype, meaning that the effective desorption time is shorter than the nominal one.

In [Figure 4C](#), we compare the SDWP and the specific thermal energy consumption (STEC, see [methods](#) section) of this research with other adsorption-desalination plants from the literature.^{46–53} Most of the plants use high-temperature sources (70°C–95°C), with some of them reaching SDWP above 10 m³/day/ton; this research, on the other hand, is among the most performant at temperatures below 65°C. This is true especially for the test at 60°C, where desorption time was optimized and the SDWP was maximized ([Figure 4B](#)); also, the STEC (0.97 kWh/L) is the lowest, comparable with the ones of the most efficient plants. The temperature range below 60°C is here highlighted and referred to as “ultralow-grade heat” range, based on an expression proposed in Luberti et al.,⁵⁴ and it is of particular importance given that most of the waste heat coming from the energy sector (especially coal and nuclear plants) is rejected in such temperature interval and in particular between 40°C and 59°C.⁵⁴

DISCUSSION

We propose CaAlg hydrogel as a sorbent material for high-performance adsorption-based water desalination. We experimentally observed that the CaAlg shows an SDWP of up to 6.04 m³/day/ton under optimal cycle times (30 min adsorption at 30°C, 45 min desorption at 60°C) in a prototypal desalination unit. When compared with other existing plants, this value is among the largest in the temperature range below 65°C, being only sur-

passed by the best large-scale solutions using aluminum fumarate with the same hot-inlet temperature and a lower condensation temperature. The estimated STEC of 0.97 kWh/L is the lowest among the analyzed plants, indicating a high thermal efficiency despite the small scale of the unit (less than 1 kg of the sorbent).

Importantly, we achieved a sub-optimal water production even with a desorption temperature as low as 45°C (SDWP of 2.2 m³/day/ton): this makes the integration of adsorption-based solutions using CaAlg with the power sector an interesting option. Other applications of special interest include data center cooling, where CPU and GPU racks are becoming progressively denser and more energy consuming.⁵⁵ In this context, AD employing CaAlg allows combined data center cooling plus desalination. For example, assuming a 500 kW data center cooled via two-phase immersion (fluid temperature of up to 50°C⁵⁶), we can expect to drive an AD plant with the rejected heat and potentially produce up to 12 m³ of fresh water per day.

We derived experimentally the CaAlg isotherm at 30°C. When plotted in comparison to other sorbents from literature, such as silica gels, MOFs, and other hydrogels, the CaAlg shows larger uptake values (up to 1.28 g/g), higher linearity, and lower hysteresis. The type II resulting isotherm is well modeled by the GAB model, from which an adsorption enthalpy of 2600 kJ/kg was estimated for the hydrogel. The diffusion coefficient during the adsorption process at 30°C and RH = 50% was estimated to be approximately $3 \cdot 10^{-12} \text{m}^2/\text{s}$. This value is more than three times lower with respect to mesoporous silica gel ($1 \cdot 10^{-11} \text{m}^2/\text{s}$); this means that silica gel allows to perform more cycles in a given amount of time, and might still be a competitive alternative to CaAlg when short cycles can be performed. Future research should include comparing the SDWP achieved by CaAlg and silica gel undergoing short cycles.

We performed tests using a starting feedwater solution with a conductivity close to seawater. The water condensed by the machine in this case has been analyzed, and a desalination effect was indeed achieved, with a salt rejection rate of over 99.2%.

The material medium-term stability is particularly promising and it was assessed by comparing isotherms on CaAlg samples after they underwent 0, 20, 30, and 40 cycles under the real working conditions in the desalination unit. The demonstrated durability of CaAlg, combined with its biodegradability,²⁴ make the hydrogel a sustainable and environment-friendly alternative to traditional sorbents. Future research should include extending the analysis to more cycles, in order to check even longer-term stability.

METHODS

Materials preparation

For this research, a batch of 386 g of CaAlg was produced. The polymerization (ionotropic gelation^{33,57}) was obtained by dripping a solution of NaAlg (from supplier Carlo Erba Reagents) and water 1% w/w into a solution of CaCl₂ and water 8% w/w. The chemicals’ concentrations have been chosen based on previous research.¹⁹ The composition of the hydrogel induces variation of moisture capacity and diffusivity: lower levels of NaAlg and higher amounts of CaCl₂ enhance the equilibrium water

uptake. The introduction of additional elements can further push performances in a specific direction. For example, the addition of micronized graphite induces faster desorption kinetics while decreasing the moisture capacity. Further details on the effect of CaCl_2 on bead volume and porosity and on the production setup built to synthesize the material are provided in [Note S8 \(Figure S15\)](#). The resulting beads of CaAlg have a grain size of approximately 1.5 ± 0.1 mm and a density of approximately 2000 ± 400 kg/m³. For comparison, we purchased and tested microporous and mesoporous silica gels from supplier Oker-Chemie. The mesoporous silica gel has a grain size of 1.5–3.15 mm, and a total of 530 g was placed in the exchanger. The amounts of CaAlg and silica gel were measured after drying in a ventilated oven at 75°C for 12 h. The picture in [Figure 1E](#) was obtained using an OPTIKA B-383MET optical microscope. The images in [Figures 1F](#) and [1G](#) were obtained using a Quanta 200 FEG environmental SEM.

Desalination unit description

The prototype used to test CaAlg and silica gel for desalination is a single-bed desalination unit from the German company Sorption Technologies GmbH ([Figures 1B](#) and [1C](#)). The main vacuum circuit of the machine (blue areas in [Figure 1C](#)) consists of the EV tank and a stainless steel and vacuum-proof container of around 5 L, containing the water to be treated; the adsorber vessel (adsorber), a stainless steel, and vacuum-proof cylinder (approximately 20 cm diameter and 100 cm length) contains the heat exchanger filled ([Figure 1A](#)) with the adsorbent material under test; the CD pipe, a vacuum-proof reinforced plastic pipe (approx. 400 mL) positioned at the bottom of the machine. A temperature sensor T5 is placed in the vacuum circuit, submerged in the feedwater in the EV tank. In the adsorber, a pressure sensor is placed: this measures the absolute total pressure p around the sorbent, which, when no air or other gases are trapped in the machine, corresponds to the vapor pressure and can be used for later considerations (the machine was checked for leakages and no significant ones were found). The vacuum pressure during a test ranges between 10 and 80 mbar, depending on the test conditions and on the cycle phase. A second circuit in the machine (orange loop on the right in [Figure 1C](#)), consisting of an external pressurized hydraulic closed loop moving water at 1.5 bar, is used to transfer thermal energy to the sorbent during the desorption phase and extract energy from the sorbent during the adsorption phase. The copper pipes exchange heat with the material through the exchanger fins. Two temperature sensors T1 and T2 are placed in this circuit, respectively, at the inlet and outlet of the exchanger. A flowmeter Q7 is placed in the circuit: the flow rate was found to be constant during the tests and equal to 3.4 L/min (with an uncertainty of ± 0.2 L/min). A pump P7 provides the necessary flow rate. An electric heater H7 and a small dry cooler F17 are used to control the temperature of the water in the loop, in the range 25°C–80°C, according to the needs. The electric heater H7 plays an important role since it simulates the thermal load that, in a real application, is provided by a low-exergy thermal source (e.g., solar panels, low-temperature process waste heat, and so on). The implemented control logic activates the heater whenever the T1 temperature is more than 1°C below the set adsorber temperature. The dry

cooler F17 is used for heat dissipation into the environment; it runs whenever the T1 temperature is more than 1°C above the set adsorber temperature. Since there is no buffer tank, but only heater and dry-cooler to act on the water temperature, 15–20 min are necessary for the machine to work against the thermal inertia of the system (the adsorber vessel and exchanger together weight 23 kg in total, most of which is stainless steel AISI-316) and bring the adsorber temperature up to the desired value at the beginning of each working phase. A third circuit (the magenta hydraulic loop in [Figure 1C](#)) is used to control the temperature of the feedwater in the EV tank. This loop circulates pressurized water at 1.5 bar and contains similar components as the previous circuit: a pump P6, an electric heater H6, a dry cooler F16, and the necessary safety accessories A6. Unlike the previous circuit, it is not provided with any temperature sensors or any flowmeter; nevertheless, the flow can be reasonably estimated to be the same as in the other circuit (3.4 L/min), given the similar geometry and since the pumps and all the other components are identical. The temperature T5 is used as a feedback value for the temperature control: H6 will heat up the circuit water until T5 is more than 1°C below the set value for the adsorption temperature and F16 will start when T5 is more than 1°C above the same value. Finally, since the condensation process on the adsorber vessel's walls is exothermic and such heat must be dissipated, a further dry cooler F18 has been positioned next to the vessel: by blowing air at 1.42 ± 0.24 m/s (average and standard deviation on 6 measurements at the vessel surface, taken with an anemometer Testo 410i 729), it helps in cooling the vessel walls. In order to monitor such temperature, a sensor T4 has been installed in contact with the vessel's external surface, on the opposite side with respect to F18. A further temperature sensor T3 is positioned at the center of the machine frame, distant from pipes, heaters, and fans, and used to measure the room air temperature. The complete list and description of components, including sensors' accuracies, is provided in [Note S9 \(Table S6\)](#).

Material characterization with a gravimetric sorption analyzer

The sorption materials have been characterized using a gravimetric vapor sorption analyzer from supplier ProUmid, model SPSx-1 μm High Load, with a weighting resolution of 1 μg and reproducibility of ± 5 μg . The analyzer allows parallel testing of 23 different samples under a temperature between 20°C and 40°C and a RH between 10% and 70%. Note that the ProUmid analyzer performs the tests under positive pressure (nitrogen is injected in the chamber to control the relative humidity), while the desalination unit works under vacuum; thus, the resulting charging and discharging transients might be characterized by a different diffusivity or equilibrium values. We used the ProUmid analyzer to measure the adsorption and desorption isotherms of the samples at a temperature of 30°C and in the RH range 10%–70%. During this test, the material is kept at 30°C; the RH is gradually increased from 10% to 70% with 10%-step ramps, then decreased back from 70% to 10% with 10%-step ramps. Each RH ramp lasted until the equilibrium condition was satisfied for all samples: according to the settings on the ProUmid analyzer software, a sample is considered in

equilibrium when its mass variation with respect to its initial mass in the last 40 min has been below 0.05%. During this test, the machine takes a mass measurement once every 15 min and takes a picture of the sample once in each equilibrium condition. Samples of CaAlg and the reference microporous and mesoporous silica gel have been tested. All the samples are preconditioned in a ventilated oven at 75°C for 12 h before starting the procedure. More details on the experiments and the samples are reported in [Note S10 \(Figure S16; Table S7\)](#). The ProUmid analyzer measures the change in a sample's absolute net mass (m) over time, enabling the calculation of water uptake (w), a key indicator of the material's adsorption performance, defined as follows:

$$w(t) = \frac{m(t) - m_0}{m_0}, \quad (\text{Equation 3})$$

where m_0 is here the lowest value of mass of the material during the test. Given that the ProUmid analyzer has never been used below RH = 10%, the m_0 value is the net mass of the sample in equilibrium in such conditions. In order to compare the collected isotherm with curves from literature and theoretical models, we added an offset to the curves: the isotherms were indeed evaluated assuming the sample mass at RH = 10% as “dry-mass,” which means that the uptake is null by definition at RH = 10% for all the curves. In the literature, available models and experimental isotherms assume $w = 0$ g/g when RH = 0%, which is a condition not achieved in this experimental campaign. For this reason, the CaAlg isotherms were linearly extrapolated outside of the experimental range (the implications of this choice are discussed in [Note S11, Figure S17](#)), and the resulting “adjusted” adsorption isotherm is discussed in [Figures 2A, B, and C](#). The GAB model has been used to best-fit the CaAlg isotherm. The GAB model is a generalization of the common BET model, where a third parameter K is added to extend the best-fitting validity to a larger RH range (the BET is usually a valid best-fitting model for RH below 30%).^{28,29} The parameter K is defined in such a way that for $K = 1$ the GAB model coincides with the original BET model. The expression used for the GAB model is given in Equation (1).

Two theoretical expressions have been used to model the material change in water uptake over time. The first one is the LDF model^{58,59}:

$$w(t) = w_0 + (w_{eq} - w_0) \cdot \left(1 - e^{-\frac{F_0 D}{R_p^2} t} \right), \quad (\text{Equation 4})$$

where t is time, w_0 is the water uptake at $t = 0$ s, w_{eq} is the equilibrium uptake in the test conditions, R_p is the particle radius (assumed to be half of the grain size, under the approximation of spherical beads), F_0 is a shape factor equal to 15 in the case of spheres, and D is the diffusivity. The second one is modified LDF (LDFDw)¹⁹:

$$\frac{w(t) - w_0}{w_{eq} - w_0} = \frac{e^{\frac{F_0(a+bw_{eq})t}{R_p^2}} - 1}{e^{\frac{F_0(a+bw_{eq})t}{R_p^2}} + b \cdot \left(\frac{w_{eq} - w_0}{a + b \cdot w_0} \right)}, \quad (\text{Equation 5})$$

where t , w_0 , w_{eq} , R_p , F_0 have the same meaning as in Equation (4). The constant diffusivity D is replaced by a linear function of water uptake: $D(w) = a + b \cdot w$, with a and b being the model's main parameters. The LDFDw model is a generalization of the LDF model (when $b = 0$, the two models coincide), and takes into account that, when a large range of uptake is considered, the diffusivity cannot be assumed constant. The two models have been used to estimate the vapor transport diffusivity through a least squares fitting procedure,⁶⁰ starting from the experimental data available on the material. Starting from the diffusivity and the equilibrium values known from the isotherms, we simulated repetitive cycles of adsorption followed by desorption (details in [Note S12, Figure S18](#)). This allowed us to estimate the theoretical SDWP expected under various test conditions and trace the red curve in [Figure 4B](#).

Experimental campaign in the desalination unit

Each experimental test consists of a repetition of 3–6 consecutive cycles at fixed conditions. Each cycle consists of three sequential phases.

- Adsorption phase: valve V2 is opened and valve V3 is closed, so that the feedwater in the EV tank evaporates, fills the EV tank and adsorber chamber, and it is adsorbed by the sorbent material; the exchanger is cooled down by the external circuit and the EV tank water is heated up by the other external circuit.
- Desorption phase: valve V2 is closed and valve V3 is opened; the material is heated up by the external circuit, using the heater H7, and water condenses on the adsorber internal walls and falls by gravity into the CD pipe.
- Pre-cooling phase: valves V2 and V3 are closed; the material is cooled down again in preparation for the adsorption phase of the successive cycle, for 15–17 min, depending on the desorption temperature; during this time interval, the CD pipe is emptied of the condensed water, and vacuum is made again in this portion of the circuit.

The parameters that can be controlled during a test are: T_{EV} (EV tank temperature during adsorption, with control feedback sensor T5), T_{Ads} (adsorber temperature during adsorption, with control feedback sensor T1), T_{Des} (adsorber temperature during desorption, with control feedback sensor T1), t_{Ads} (adsorption time, i.e., the duration of the adsorption phase), t_{Des} (desorption time, i.e., the duration of the desorption phase), and t_{Cool} (pre-cooling time, i.e., the duration of the pre-cooling phase).

Before starting the actual experimental campaign, the material had been subjected to 50 cycles under vacuum within the machine, adsorbing and desorbing vapor in conditions analogous to those of the subsequent experimental campaign. This allowed the material to stabilize and lose any residual water from production, as well as to characterize the material aging over the cycles; after 20, 30, and 40 cycles, the machine was opened and a small sample of material was removed and stored for successive testing ([Figure 2B](#)) to check how the material performance changed.

After the preliminary cycles, a full experimental campaign (tests 1 – 9 in [Table 1](#)) has been performed. In the campaign,

Table 1. Tests conducted in the desalination unit

Test	1	2	3	4	5	6	7	8	9
Material	CA	CA	CA	CA	CA	CA	SG	SG	SG
T_{Des} (°C)	60	45	75	60	60	60	60	45	75
t_{Des} (min)	120	120	120	60	45	30	120	120	120

Material, desorption temperature, and desorption time are specified. CA, calcium alginate and SG, mesoporous silica gel.

T_{Ads} and T_{EV} were kept constant, both equal to 30°C; the adsorption time t_{Ads} was kept constant and equal to 30 min; t_{Cool} was chosen always equal to 15 min (17 min for the tests at 75°C). On the other hand, the desorption temperature T_{Des} and time t_{Des} as well as the sorbent material were changed in a one-factor-at-a-time approach. This does not allow a complete characterization of the machine, but it helps in understanding the influence of the parameters taken separately.

A preliminary start-up procedure is carried out every time the material is replaced (more details in Note S13, Figure S19). Then, for each test, the normal experimental procedure is described here.

- (1) The water level in the EV tank is restored (approximately 4.5 L at the beginning of all tests).
- (2) The vacuum pump is powered 10 min to remove any residual air in the EV tank before starting the test.
- (3) The testing parameters are adjusted according to Table 1.
- (4) The external circuits are powered and the temperatures of both the EV tank and adsorber are brought to 30°C, in preparation for the adsorption phase of the first cycle.
- (5) The first cycle starts and phases 1 to 3 run in sequence.
- (6) During phase 3, the condensed water is collected from the CD pipe and weighed on a KERN PCB scale (accuracy of 0.1 g).
- (7) The vacuum pump is connected to the CD pipe (valve VB) and it is powered for 1 min to remove the air entering the CD pipe during the water collection and 1 further min with V3 open to remove any residual vapor in the chamber (see also Note S14).
- (8) Points 5 to 7 repeat for the successive cycles of the day.

All the tests started in the morning around 9:00 a.m. central European time and have taken place during the month of March 2025, trying to minimize the influence of seasonal variations in the room temperature.

The main aim of this research was to compare the thermal cycles and the mass transport of water, rather than the desalination performance (i.e., the solute rejection rate); thus, in most of the tests run in the machine, we used distilled water in the EV tank. Replacing distilled water with salty water might change the water fugacity; therefore, a detailed and comprehensive investigation using salty water is left to future campaigns. For the limited scope of this work, in order to preliminarily test the ability of hydrogel to work with a salty solution, few cycles using salty water were performed after the main experimental campaign and a preliminary analysis has been conducted on the water samples, including estimations of conductivity, solid content, pH, total organic carbon (TOC), and copper (Cu) content (see also Note S6).

Starting from the test results, we evaluated two key performance indicators (KPIs). The first one is SDWP, a KPI indicating the amount of condensed water achievable in 24 h of continuous operation and defined as follows:

$$SDWP = \frac{V_w}{m_{dry}} \cdot \frac{1}{t_{cycle}}, \quad (\text{Equation 6})$$

where V_w is the volume of condensed water produced in a cycle, m_{dry} is the amount of dry sorbent material, t_{cycle} is the duration of the cycle (including adsorption, desorption, and pre-cooling). The used units are $[V_w] = m^3$, $[m_{dry}] = ton$, $[t_{cycle}] = day$, from which: $[SDWP] = m^3/day/ton$.

The second indicator is STEC, a KPI indicating the amount of positive thermal energy used to condensate one liter of water and defined as follows:

$$STEC = \frac{E_{hot}}{V_w}, \quad (\text{Equation 7})$$

where E_{hot} is the thermal energy used during desorption in a test and V_w is the volume of water condensed in the same test. If V_w is evaluated in L and E_{hot} in kWh, then $[STEC] = kWh/L$. The KPIs defined above are then compared with results from the literature.

Further details on the choice of the best-fitting equilibrium model are provided in Note S15 (Figure S20). The experimental dependence of CaAlg beads' volume on RH is discussed in Note S16 (Figure S21). A theoretical discussion on the dependence of SDWP on the CaAlg beads' diameter is provided in Note S17 (Figure S22).

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to the lead contact, Dr. Eliodoro Chiavazzo (eliodoro.chiavazzo@polito.it).

Materials availability

This study did not generate new, unique reagents.

Data and code availability

- Material data on water vapor-calcium alginate equilibrium adsorption isotherms have been deposited at Zenodo and are publicly available as of the date of publication at <https://doi.org/10.5281/zenodo.18219709>.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

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AUTHOR CONTRIBUTIONS

M.C. and E.C. conceived the experiments and supervised the work. M.C. performed the experiments. M.C., E.C., V.G., and M.F. analyzed the data, interpreted the results, and wrote and reviewed the paper. E.C., V.G., and M.F. contributed materials and analysis tools.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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