Innovative low-grade sorption desalination technology for application on board of vessels

A. Frazzica[a,*], Y. Zhang[a], A. Bonanno[a], V. Palomba[a], V. Brancato[a], W. Mittelbach[b]

[a] Istituto di Tecnologie Avanzate per l'Energia "Nicola Giordano", CNR ITAE, Messina, Italy.
andrea.frazzica@itae.cnr.it
[b] Sorption Technologies GmbH, Freiburg, Germany

Abstract:

This study aims to develop a high-water-yield adsorption desalination system by sorbents screening and lab-scale prototype testing, for future application on board of vessels. For sorbents optimization, silica gel-30%LiCl and vermiculite-45%LiCl composites were developed. The sorption isobars and sorption kinetics were measured and the results contributed to further calculations of SDWP (Specific Daily Water Production). Silica gel-30%LiCl composite was chosen as the optimized one with the highest SDWP. Afterwards, the ad/desorption dynamics of the adsorber made of finned flat-tubes heat exchanger and silica gel-30% LiCl composites were tested in a T-LTJ (thermal large temperature jump) adsorption apparatus. The obtained results were used to calculate the SDWP and optimized cycle time and to evaluate the performances of three system designs (2-reactors, 3-reactors and 4-reactors). The design of 3-reactors was selected, which can reach an SDWP as high as 69 m^3/tonne/day under the condition of $T_{eva/cond}$=20 °C and T_{de}=80 °C.

Keywords:

Adsorption desalination; Silica gel; LiCl; Water uptake; Sorption dynamics.

1. Introduction

Water scarcity was listed as the top 5 global risks in terms of potential impact by the World Economic Forum since 2012 [1]. Desalination has served as the governing technology to provide potable water since the 1980s [2]. Although commercial desalination plants like the multi-stage flash (MSF) are developing rapidly, their drawbacks of high energy consumption and negative environmental impacts [3] lead to the requirement of developing new desalination technologies. Adsorption desalination technology is proposed as a novel desalination method, where the sorbents extract water vapour from the saline water in the sorption process, and such adsorbed water will be released and condensed into potable water in the desorption process. Its dominant advantages are the utilization of renewable and waste heat energy and high-quality produced water [4].

The adsorption desalination technology is still in the early research stage, and the previous research interest lies in verifying the validity of freshwater production [5,6] and proposing advanced system configurations like the 2-evaporator cycle and multistage reactors [7,8]. Despite a large number of sorbents have been fully studied in other adsorption-based systems (adsorption cooling, thermal energy storage, etc.), only limited types of sorbents have been studied. Silica gel and zeolite are the most utilized sorbents for adsorption desalination systems by now, they have good hydrothermal stability, but their cyclic water uptake is lower than chemical sorbents and composite sorbents and the obtained SDWP in the system is generally lower than 15 m^3/tonne/day [9]. Composite sorbents [10] are regarded as the most promising sorbents for their high water uptake amount and tailored sorption properties. However, composite sorbents have not been widely studied for desalination applications. Besides the sorbents, the investigation of the performances in practical systems is also significant. Ad/desorption dynamics are critical to evaluate the operation performance, which is also not so extensively studied in previous publications. Thus, this study developed two types of LiCl-based composite to select the optimized one, whose ad/desorption dynamics in practical desalination systems were experimentally studied, resulting in the development of a high-water-yield system. The optimization of a composite sorbent for desalination purposes is here reported in details from the material development up to the lab-scale testing.

2. Materials synthesis and characterizations
2.1. Materials synthesis

The dry impregnation method was used to develop the silica gel-30%LiCl and vermiculite-45%LiCl composites. Briefly, the dry silica gel (pore size 8.377 nm, particle size 0.5-0.8 mm) or expanded vermiculite (pore size >20 nm, particle size 1.7-2.4 mm) was mixed with LiCl aqueous solution (its volume equals the total pore volume of the matrix and the contained salt mass equals the objective required amount) drop by drop, then composites were obtained after drying in an oven.

2.2. Sorption isobars and sorption kinetics

The sorption isobars of the sorbents were measured by the dynamic vapor sorption (DVS) instrument. The adsorption isobars under 17.21, 23.60 and 42.83 mbar were tested, the results are shown in Figure. 1. It shows that both composites experience multistage sorption process, including physisorption, hydration reaction + deliquescence and solution absorption. A hysteresis loop appears for silica gel-30%LiCl in the full range except for the solution absorption, possibly caused by the capillary phenomenon. No hysteresis loop appears for vermiculite-45%LiCl since its macropores have negligible impacts on the sorption behavior of the LiCl. Generally, the sorption amount increases with the increased vapor pressure or the decreased temperature. Vermiculite-45%LiCl can obtain higher sorption capacity than silica gel-30%LiCl under the same operation condition, owning to its higher salt concentration. The D-A (Dubinin–Astakhov) equation derived from the Polanyi theory was utilized to better describe the equilibrium sorption capacity under various operation conditions:

$$w = w_0 \, e^{-(k \, \Delta F^n)} \qquad \text{[g/g]} \tag{1}$$

where w_0 [g/g] is the maximum sorption capacity, both k [s^{-1}] and n are fitting parameters. ΔF is the free sorption potential and can be calculated by:

$$\Delta F = R \, T \ln\left(\frac{p_{sat}}{p}\right) \qquad \text{[kJ/kg]} \tag{2}$$

The parameters of Eqn.(1) and (2) were summaried in our previous publication [11].
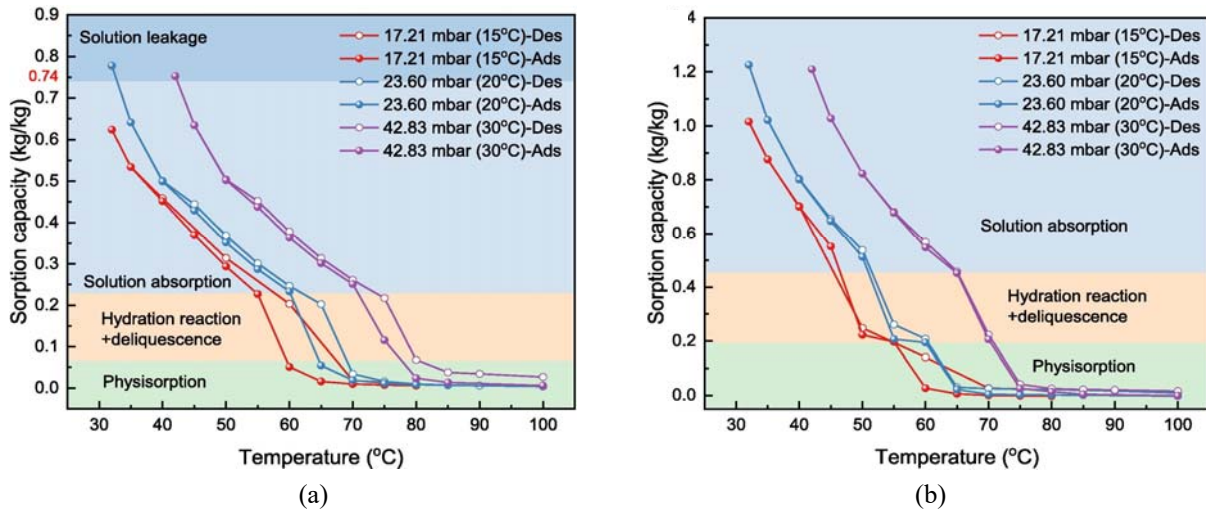

Figure. 1. The sorption isobar curves of (a) silica gel-30%LiCl and (b) vermiculite-45%LiCl composite [11].

Besides sorption equilibrium, sorption kinetic represents another important aspect to evaluate the achievable sorption properties, and it can be used to calculate the SDWP altogether with sorption equilibrium data. The ad/desorption kinetics at different temperature jump at 8.79, 17.21 and 31.98 mbar were measured by the DVS instrument. Partial results are depicted by Figure. 3. The commonly utilized linear driving force (LDF) model [12] is used to obtain the kinetics coefficient (k) for the evaluation of the sorption/desorption rate:

$$\frac{dw}{dt} = k \, (w_\infty - w) \qquad \text{[g/(g·s)]} \tag{3}$$

In general, the sorption rates of silica gel-30%LiCl and vermiculite-45%LiCl composites are much slower than the ones achieved by pure physical adsorbents commonly used in adsorption machines, such as silica gel and zeolites. This is due to the slower reaction rate of the salt-water hydration reaction as well as to the higher sorption capacity of the composites. Nevertheless, looking at the results reported in Figure. 2, a clear difference can be identified also between composites. Indeed, thanks to the mesoporous structure of the silica gel, the crystal size of the embedded salt is much smaller than the one inside the macropores of the vermiculite. This causes a much faster reaction in silica gel-based composite.

Accordingly, for a lab-scale comparison, the composite embedding LiCl into silica gel was selected to be compared against the reference microporous silica gel, usually applied in adsorption chillers.
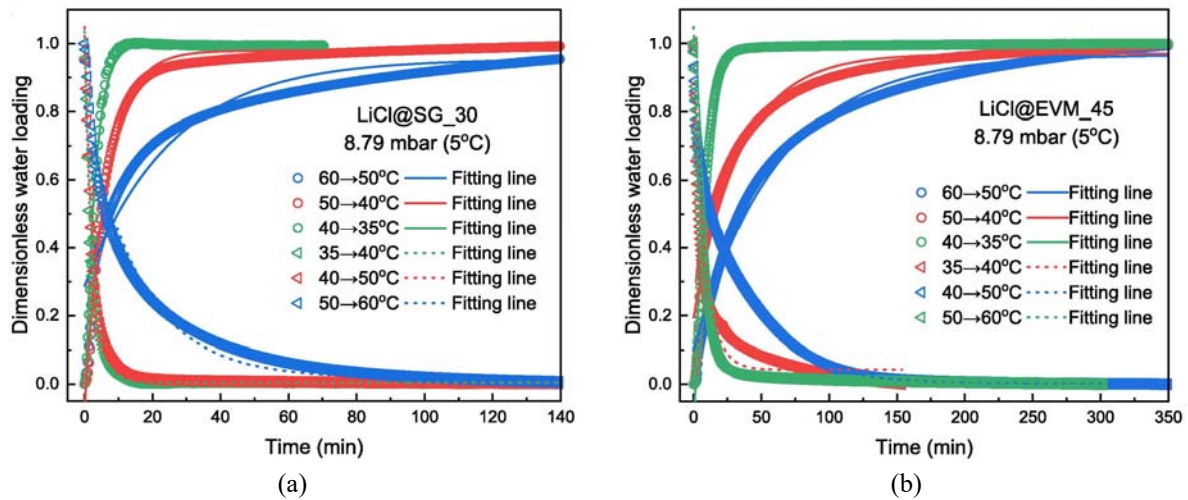

(a)   (b)

Figure. 3. The ad/desorption kinetics curves of (a) silica gel-30%LiCl and (b) vermiculite-45%LiCl composite [11].

3. Lab-scale adsorption desalination system

3.1. Experimental apparatus and methods

The lab-scale testing was performed aiming at investigating the adsorption kinetic performance of a small-scale adsorber, thus deriving the achievable performance in terms of cooling and desalination capacity.

The applied testing apparatus is reported in the literature as thermal large temperature jump (T-LTJ) (see Figure. 4a). It consists of a vacuum chamber, an evaporator/condenser, four thermostats and a vacuum pump. A finned flat-tubes aluminum heat exchanger (see Figure. 4b) serves as the ad/desorber, and 74.4 g sorbent particles were packed between the fins. Fast temperature jumps/drops are operated by quickly switching the valves after reaching desorption/adsorption equilibrium, aiming to simulate practical adsorption and desorption process.
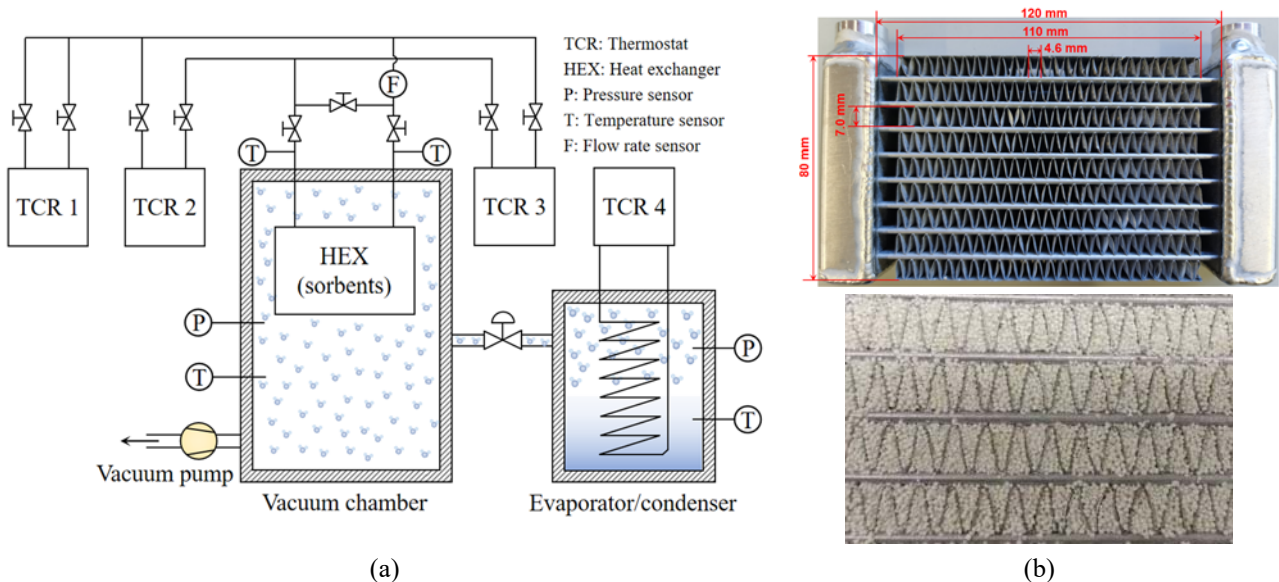

(a)   (b)

Figure. 4. (a) Schematic diagram of the T-LTJ testing system and (b) pictures of the blank heat exchanger and the heat exchanger packed with silica gel-30% LiCl [13].

The testing approach is based on the evaluation of the temperature difference measured at the inlet and the outlet of the adsorber during reference adsorption cycles. Due to the exothermic reaction of the adsorption process, the heat transfer fluid shows a temperature increase at the beginning of the test, due to the high sorption rate, followed by a continuous decreasing caused by the reduction of the sorption rate due to the saturation of the material occurring.

The sorption kinetic rate is then evaluated by analysing the decay (often exponential) of the ΔT measured and deriving typical parameters, such as the characteristic times and the average power, that can be employed to compare different materials and heat exchanger configurations. An uncertainty analysis of the method showed an accuracy in the range between 5% and 8% depending on the operating conditions.

3.2. Experimental results

Following the above introduced description of the methodology, the $\Delta T_{ad/de}$ contributed by the ad/desorption process is calculated by:

$$\Delta T_{ad/de}(t) = \Delta T_{ov}(t) - \Delta T_{bl}(t) \tag{4}$$

where ΔT_{ov} identifies the temperature differences of the inlet and outlet heat transfer fluid of the adsorber under ad/desorption mode, and ΔT_{bl} is this temperature difference of the related blank test, which is needed to depurate the test by the sensible heating and cooling effect of the inert masses (such as the metal of the heat exchanger and the sorbent material thermal capacity).

As demonstrated in previous publications [13], the $\Delta T_{ad/de}$ curves can be well fitted using the exponential function under most operation conditions:

$$\Delta T_{ad/de}(t) = \Delta T_{\infty} + \Delta T_0 \cdot \exp(-\frac{t}{\tau_{ad/de}}) \tag{5}$$

Both adsorption and desorption tests were carried out over the adsorber filled with the composite and the microporous silica gel. For the sake of brevity, only some of the results obtained on the composite sorbent are reported below.

Figure. 5a reports a comparison among different adsorption kinetic curves obtained while testing the composite sorbent, varying the reference desorption temperature. As expected at high temperature the adsorption capacity and thus the measured ΔT is higher, but, overall, the adsorption kinetic is comparable when the reference desorption temperature is varied.
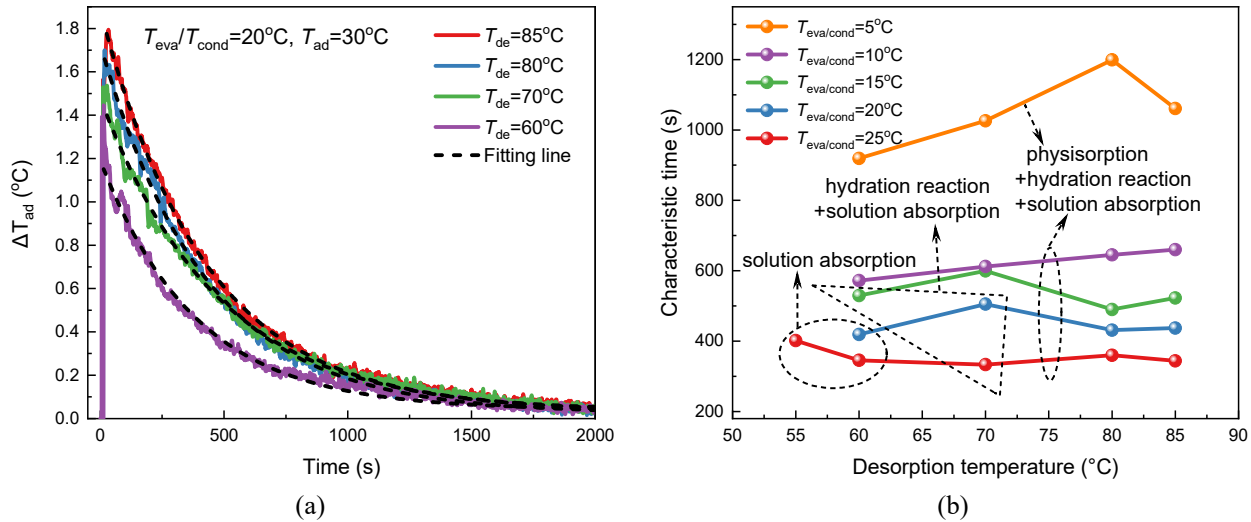

(a)   (b)

Figure. 6. (a) Comparison of different adsorption runs measured over the composite sorbent and (b) comparison of the achieved characteristic times for all the tests performed [14].

To investigate the effect of the boundary conditions over the kinetic performance, a large set of tests varying different boundaries were performed, and the characteristic times were calculated. Figure. 7b compares the different characteristic times as a function of the reference desorption temperature and evaporation/condensation temperature. As highlighted, the desorption temperature does not play a critical role, while the main difference is obtained by varying the evaporation/condensation temperature. Indeed, the kinetic performance increase by increasing the evaporation/condensation temperature. This can be justified by the higher absolute water vapor pressure inside the testing chamber at higher evaporation/condensation temperature. This reduces the mass transfer resistance across the material packed between the fins of the heat exchanger, thus minimizing the time to reach the equilibrium (i.e. maximizing the kinetics).

Figure. 8a compares the achievable desorption kinetic for two different desorption temperatures, namely, 60 °C and 80 °C, at the same evaporation/condensation temperature, 20 °C. As expected, there is a clear increase in the measured temperature difference passing from 60 °C to 80 °C, due to the higher degree of reaction between water vapor and embedded salt. Similarly, a comparable effect can be highlighted when the evaporation/condensation temperature increases, as reported in Figure. 9b.

Overall, from a direct comparison of adsorption and desorption kinetic performance under similar conditions, usually the desorption run is between 2 and 3 times faster than the adsorption run. This can be ascribed to the

higher pressure gradient occurring between the adsorber and the condenser during the desorption phase, compared to the same existing during the adsorption between evaporator and adsorber, that reduces the mass transfer resistance, thus allowing the vapor leaving the adsorber quickly.
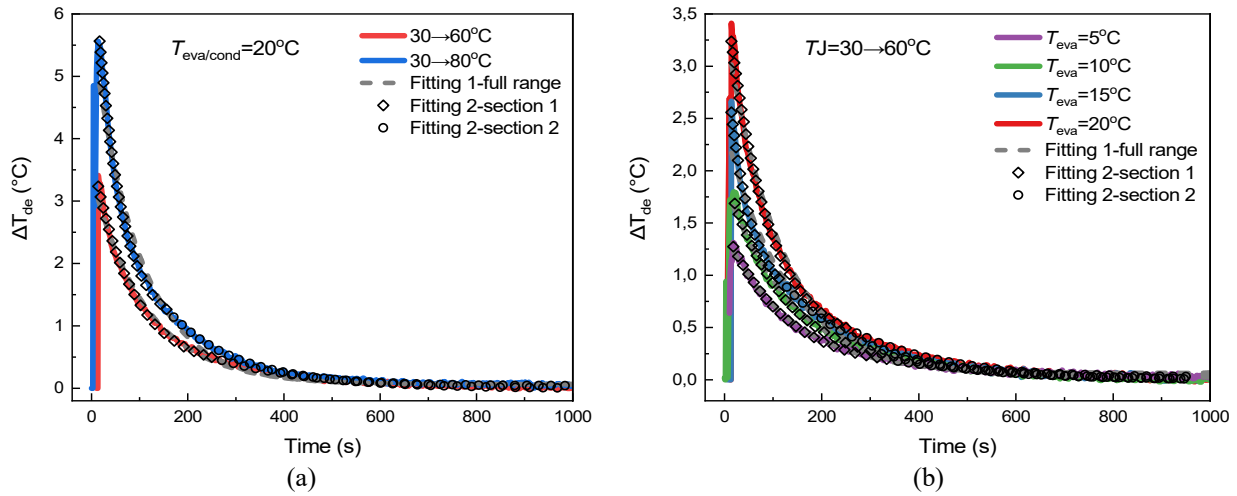

Figure. 10. (a) Effect of the desorption temperature on the sorption kinetic for the composite sorbent and (b) effect of the condensation temperature for the same configuration [14].

3.3. SDWP calculation and preliminary design for a large-scale desalination unit

As already mentioned, one of the most relevant performance indicators to be considered for an adsorption desalination unit is the specific daily water production (SDWP), namely, the volume of desalinated water produced daily per mass of adsorbent material employed, as reported below.

$$SDWP = \frac{86400 \left[\frac{s}{day}\right]}{t_{cycle}} (w_{ad} - w_{de}) \left[\frac{\frac{m^3}{tonne}}{day}\right] \tag{6}$$

This performance is strongly depending on the adsorption equilibrium difference processed during the cycle (w_{ad}-w_{de}) as well as on the sorption kinetic which is influencing the operating cycle time. Increasing the sorption difference and decreasing the cycle time lead to an overall SDWP enhancement.

Starting from the small-scale testing in the lab, the SDWP for the composite silica-gel/LiCl was calculated for all the conditions tested, as summarized in Table. 1. As it can be highlighted, the SDWP is quite limited at low evaporation/condensation temperatures and it is also almost unaffected under these conditions by the desorption temperature. Differently, as soon as the evaporation/condensation temperature overcomes a certain threshold, i.e. 15 °C, the SDWP increases and shows a relevant difference when the desorption temperature raises from 60 °C and 80 °C. This is justified by the higher amount of water vapor exchanged which does not affect negatively the sorption kinetic.

In general, the composite sorbent can guarantee a SDWP increase in a range from 25% to 50% compared against the standard microporous silica gel, thus confirming the potentiality of reducing the size of adsorption desalination units, which is of utmost importance in mobile applications such as the naval one.

Table. 1. SDWP calculated for all the testing conditions measured at lab scale.

Rererence cycle	$T_{eva/cond}$ 5 °C	$T_{eva/cond}$ 10 °C	$T_{eva/cond}$ 15 °C	$T_{eva/cond}$ 20 °C
$T_{ads/des}$ 30-60 °C	14	25	25	40
$T_{ads/des}$ 30-80 °C	11	24	40	57

The reported calculations were carried out considering a standard 2-adsorbers desalination unit design. Nevertheless, looking at the kinetic testing results, it is clear that, since the desorption process is much faster, it could be reasonable to increase the number of adsorbers, thus being able to re-allocate the adsorption/desorption phases, optimizing the overall performance and exploiting the sorption properties of the material at their maximum level. Preliminary calculations showed that having a 3-adsorbers design can help in further increasing the SDWP in a range from 10% to 15% compared to the 2-adsorbers design.

On this basis, the first large scale setup for testing in the lab is under design, for further investigation before being realized in larger scale for validation on board of a demo vessel.

4. Conclusions

The development of innovative, high efficiency and compact adsorption-based desalination machines requires investigation at materials and components levels. In this paper new innovative composite sorbents were developed and tested both from the equilibrium and kinetic point of view. The most efficient one, based on LiCl embedded inside mesoporous silica gel, was manufactured in large scale and tested in a lab-scale device developed for characterizing sorption kinetic properties under real operating conditions for desalination and cooling applications. A small-scale finned-flat tubes aluminium heat exchanger was used to embed the grains of the composite as well as a reference material (i.e. microporous silica gel). The results demonstrated that the water vapor mass transfer across the adsorber is limiting the kinetic performance, thus affecting the achievable SDWP. Moreover, the desorption kinetic resulted being 2 to 3 times faster than the corresponding adsorption process.

Starting from the obtained results, the estimation of the SDWP of this configuration against the one employing microporous silica gel was carried out, showing a performance increase ranging from 25% up to 50%. Moreover, the possibility of using a 3-adsorbers based adsorption machine resulted the most appropriate one, to manage the difference kinetic performance of adsorption and desorption phases.

This investigation will represent the basis of the design of a lab-scale adsorption desalination machine to be tested in the lab and subsequently on board of a demo vessel.

References

[1] World Economic Forum. The Global Risks Report 2020. 2020.

[2] Shahzad MW, Burhan M, Ybyraiymkul D, Ng KC. Desalination Processes' Efficiency and Future Roadmap. Entropy 2019;21:84. https://doi.org/10.3390/e21010084.

[3] Ihsanullah I, Atieh MA, Sajid M, Nazal MK. Science of the Total Environment Desalination and environment : A critical analysis of impacts , mitigation strategies , and greener desalination technologies. Sci Total Environ 2021;780:146585. https://doi.org/10.1016/j.scitotenv.2021.146585.

[4] Riaz N, Sultan M, Miyazaki T, Shahzad MW, Farooq M, Sajjad U, et al. A review of recent advances in adsorption desalination technologies. Int Commun Heat Mass Transf 2021;128:105594. https://doi.org/10.1016/j.icheatmasstransfer.2021.105594.

[5] Wu JW, Hu EJ, Biggs MJ. Thermodynamic cycles of adsorption desalination system. Appl Energy 2012;90:316–22. https://doi.org/10.1016/j.apenergy.2011.04.049.

[6] Zhang H, Ma H, Liu S, Wang H, Sun Y, Qi D. Investigation on the operating characteristics of a pilot-scale adsorption desalination system. Desalination 2020;473:114196. https://doi.org/10.1016/j.desal.2019.114196.

[7] Riaz N, Sultan M. Investigation of Adsorption and Desorption Characteristics of Metal-Organic Frameworks for The Development of Desalination Systems. Proc Int Exch Innov Conf Eng Sci 2021;7:261–7. https://doi.org/10.5109/4739231.

[8] Mitra S, Kumar P, Srinivasan K, Dutta P. Simulation study of a two-stage adsorber system. Appl Therm Eng 2014;72:283–8. https://doi.org/10.1016/j.applthermaleng.2014.04.023.

[9] Zhang Y, Palomba V, Frazzica A. Understanding the effect of materials , design criteria and operational parameters on the adsorption desalination performance – A review. Energy Convers Manag 2022;269:116072. https://doi.org/10.1016/j.enconman.2022.116072.

[10] Aristov YI, Restuccia G, Cacciola G, Parmon VN. A family of new working materials for solid sorption air conditioning systems 2002;22:191–204. https://doi.org/10.1016/S1359-4311(01)00072-2.

[11] Zhang Y, Palomba V, Frazzica A. Development and characterization of LiCl supported composite sorbents for adsorption desalination. Appl Therm Eng 2022;203:117953. https://doi.org/10.1016/j.applthermaleng.2021.117953.

[12] Glueckauf E, Coates JI. 241. Theory of chromatography. Part IV. The influence of incomplete equilibrium on the front boundary of chromatograms and on the effectiveness of separation. J Chem Soc 1947:1315–21. https://doi.org/10.1039/JR9470001315.

[13] Palamara D, Palomba V, Calabrese L, Frazzica A. Evaluation of ad/desorption dynamics of S-PEEK/Zeolite composite coatings by T-LTJ method. Appl Therm Eng 2022;208:118262. https://doi.org/10.1016/j.applthermaleng.2022.118262.

[14]   Zhang Y, Palamara D, Palomba V, Calabrese L, Frazzica A. Performance analysis of a lab-scale adsorption desalination system using silica gel/LiCl composite. Desal 2023;548:116278. https://doi.org/10.1016/j.desal.2022.116278