



Article Advanced Adsorbent Materials for Waste Energy Recovery

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Abstract: Nowadays, waste thermal energy represents a huge quantity of energy that, in most cases, is unfortunately dispersed rather than recovered. Although it is well known that its recovery could result in a considerable impact reduction of human activities on the environment, it is still a challenging issue. In view of this, absorption chillers and heat pumps, based on the use of porous materials capable of reversibly adsorbing and desorbing water vapor, can be considered among the preferred systems to recover waste thermal energy, especially at medium–low temperatures. This study deals with the preparation and performance of a new generation of advanced adsorbent materials specifically produced as coatings for water adsorption systems driven by low temperature heat sources (around 150 °C). The proposed coating consists of hybrid SAPO-34/polyacrilonitrile microfibers directly deposited on the surface to be coated by means of the electrospinning technique. Their zeolite morphology and concentrations, as well as their distribution over the polymeric microfibers, were key variables in achieving the best combination of adsorption properties and hydrothermal stability of the coating.

Keywords: microfibers; electrospinning; water adsorption; SAPO-34

1. Introduction

Microfibers made by electrospinning have been studied and proposed for many applications in different fields, from tissue engineering to the production of carbon microfibers or microfiltration systems [1–4]. Our previous studies on electrospun microfibers focused on the production and characterization of an adsorbent coating made of hybrid (organic/inorganic) microfibers for an innovative adsorber for adsorption heat pumps [5–8]. Adsorption and absorption heat pumps are alternative technologies competing with standard (compression) heat pumps for heating or cooling buildings [9]; they operate in a more energy efficient and ecofriendly way, as they are based on different phenomena than the electrical compression of vapors. Although less economically competitive compared to compression heat pumps for their lower COP (coefficient of performance), these systems are particularly attractive, because they are "thermally" driven, which means that their main energy source is thermal energy, which could be recovered from waste heat from industrial or civil activities. Moreover, adsorption pumps use water as the working fluid, making these systems particularly ecofriendly and safe. Wasted thermal energy constitutes a huge quantity of energy which is not used, but rather, is dispersed into the environment; it has enormous potential in terms of energy saving and impact reduction of human activities on the planet. According to recent studies [10–13], world energy production was estimated to be 474.171 PJ per year; more than 70% of this energy is lost after conversion. The waste heat potential of the industrial sector in the EU has been estimated to be about 300 TWh/year; more than 30% of this waste heat is low-temperature, which means <200 °C. The remaining 70% is divided as follows: 25% at medium-temperature (200–500 °C) and 45% at high-temperature (>500 °C). Adsorption heat pumps are the preferred candidate to recover thermal energy at low temperatures, i.e., the most difficult setting due to the low thermal-jump available. Adsorption chillers can be driven by heat sources at temperatures as low as 70–90 °C, while absorption chillers and heat pumps generally require waste heat at $T > 90 \degree C$ [14–16]. Some potential applications of adsorption chillers are low-temperature heat recovery from High-Performance Computing (HPC) data centers, industrial production of compressed air, the food industry (pasteurization and cooking), bio-waste incineration and gasification [17,18]. The economical convenience of adsorption chillers is, however, strictly dependent on their price per kW compared to compression systems and the industrial price for electricity. At the moment, an improvement in terms of COP of adsorption pumps would facilitate their marketing growth. For these reasons, research on these systems has put a lot of emphasis on developing more efficient components and improving the adsorbing materials. An important issue that has a direct influence on the performance of adsorption systems is the efficiency of heat and mass transfers between the adsorbent (the porous material) and the adsorber (the module). Traditionally, adsorbent materials are granules or beads of inorganic, porous compounds with good hydrophilicity, like zeolites or silica gel. Kinetic studies on the adsorption/desorption of water vapor on granular materials have demonstrated that heat and mass transfers are dependent on the particles size of the adsorbent [19–22]. A typical adsorption heat pump has a cycle time in the range of 5–15 min, so that all heat and mass transfer phenomena have to be considered to be in an unsteady state. Improvement of the heat and mass transfer coefficients is obtained when the adsorbent is not used as loose granules but as a component of a coating directly covering the metallic surfaces of the adsorber [23–26]. Coatings made of the adsorbent particles glued by a binder improve contact with the adsorbent/metal interface and increase heat transfer, although they can have a negative effect on mass transfer due to their low porosity [22,24,27,28]. Different solutions have been proposed to maintain an adequate permeability of the adsorbent coatings, for example, the use of metal foams [29], or sintered metal fibers [30] or silicone-based foams [31,32]. Coatings made of electrospun hybrid microfibers have the advantage of tying the zeolite crystals in polymeric microfibers to the surface of the adsorber while maintaining a high porosity and permeability through the coating layers.

In this work, we discuss the preparation and performance of a new generation of hybrid SAPO-34 microfibers for water adsorption based on PAN (polyacrylonitrile) as the polymeric component, and specifically produced as coatings for adsorption systems driven by low temperature heat sources. The operating conditions of an adsorption heat pump are particularly challenging for the adsorbing coatings, because they have to be stable to cyclic variations of pressure and temperature in the presence of water vapor. The polymeric component of microfibers, in particular, is the most critical element for the coating durability, because the zeolite crystals are generally much more stable in the operating conditions of the heat pump. For these reasons, research on more effective and compatible polymers for hybrid microfibers is continuing. PAN is a versatile polymer which is widely used to produce fibers for membranes, filters and textiles, showing chemical resistance to organic solvents and acid reagents, and being insoluble in water. PAN is classified as thermoplastic, although it degrades before melting (Tm = 300 °C); however, it shows good thermal stability up to T = 250 °C. Moreover, PAN fibers have good mechanical properties and are easily spinnable, with good compatibility with ceramic fillers [33–35]. Finally, polyacrylonitrile electrospun microfibers are an ideal precursor for the synthesis of carbon nanofibers (CNF) [36,37].

PAN/SAPO-34 microfiber coatings were obtained by electrospinning mixtures of zeolite and a polymeric precursor, with the objective of maximizing the zeolite content to increase the adsorption

capacity of the coating while maintaining good morphological characteristics of the microfibers. The effect of the zeolite particle size on the properties of microfibers has been studied using three different specially synthesized SAPO-34 powders. The microfiber morphology was characterized by scanning electron microscopy (SEM), while thermogravimetric tests (TGA-DSC) were carried out to evaluate structural variations with temperature. The adsorption properties of the microfiber coatings were assessed by measuring the water uptake at the equilibrium in isothermal conditions and different water vapor pressures. Finally, an evaluation of the hydrothermal stability of the microfibers was made by aging the coatings in a saturated vapor environment in an autoclave.

The results showed that depending on the particle size of the zeolite, PAN/SAPO-34 microfibers with a zeolite content of up to 85% by weight could be easily deposited on a metallic surface by electrospinning. The water adsorption properties of the adsorbent in the hybrid microfibers were not negatively influenced by the polymeric matrix, and the coating could be operated in the typical conditions of adsorption chillers driven by waste heat at temperatures of up to 150 °C, with no evidence of thermal degradation of the PAN component.

2. Materials and Methods

2.1. Zeolite Synthesis

Pure SAPO-34 was synthesized by the hydrothermal route adopting the formulation $1Al_2O_3:1P_2O_5:0.6SiO_2:0.7TEA_2O:70H_2O$, as already used to produce hybrid microfibers. Details of the synthesis procedure are reported elsewhere [5]. The SAPO-34 powder obtained from this procedure (labeled SAPO-34M from now) had the same morphological characteristics as commercial zeolite. A SAPO-34 with smaller particle size (SAPO-34S) was synthesized with the formulation $1Al_2O_3:2P_2O_5:0.6SiO_2:2TEA_2O:140H_2O$, according to the procedure described in [38], while to increase the particle dimensions of the zeolite (SAPO-34L), the formulation $1Al_2O_3:1P_2O_5:0.6SiO_2:1TEA_2O:60H_2O$ was used, where the template (TEA_2O) quantity was increased and the water content lowered.

All zeolites were prepared starting from the same raw materials, i.e.: aluminum isopropoxide (98 wt.% Al(OC_3H_7)₃, Sigma Aldrich, St. Louis, MO, USA), tetraethylammonium hydroxide (35 wt.% TEAOH, Sigma Aldrich) and an aqueous solution of colloidal silica (40 wt.% SiO₂, Sigma Aldrich).

2.2. Electrospinning SAPO-34/PAN Microfibers

Solutions of different concentrations were prepared by stirring the SAPO-34 powders obtained as previously described in N,N-dimethylformamide (DMF) for 1 h at room temperature. The polyacrylonitrile precursor (PAN, Mw = 150,000, Sigma Aldrich) was then added to the mixture, stirred for 1 h at 50 °C and, finally, stirred for 1 h at room temperature. The composition of the precursor mixtures, polymer/solvent (PAN/DMF) and zeolite/polymeric solution (SAPO-34/PAN solution) ratios are shown in Table 1 in terms of weight percentage (w/w%).

Sample	PAN/DMF (Polymer/Solvent Ratio, w/w%)	SAPO-34/Solution (Zeolite/Solution Ratio, w/w%)	SAPO-34
PAN-45	5.5/94.5	45/55	М
PAN-60	5.5/94.5	60/40	М
PAN-75	5.0/95.0	75/25	Μ
PAN-80	5.0/95.0	80/20	S-M-L
PAN-85	4.5/95.5	85/15	S-M-L

 Table 1. Composition of precursor solutions before electrospinning.

S = small, M = medium, L = large.

The electrospinning parameters were kept constant for all mixtures. Each solution was loaded into a 10 cc syringe fitted with a 0.7 mm steel needle and driven by a syringe pump at a flow rate of

1.1 mL/h. The applied voltage was 13 kV and the distance between the needle tip and the collector was 15 cm. Aluminum foils previously cleaned and degreased with acetone were used as collectors.

2.3. Samples Characterization

The synthesized SAPO-34 powders were analyzed by X-Ray diffractometry (Bruker D2 Phaser, Karlsruhe, Germany) in the 20 range 5–40° (Cu K α 1 = 1.54056 Å) to verify their crystallographic structure and the possible presence of amorphous or extraneous phases. The morphological characterization of zeolites and electrospun microfibers was carried out by scanning electron microscopy (SEM Phenom ProX, Deben, Suffolk, UK). The microfiber diameters were measured by digital image analysis using the software ImageJ and the plugin DiameterJ [39], specifically developed for the characterization of nanofibers.

TGA/DSC analysis (STA 409 PC Netzsch, Selb, Germany) was carried out on zeolites and hybrid microfibers by increasing the temperature from 25 °C to 500 °C at a rate of 10 °C/min in nitrogen flow.

The adsorption properties of the SAPO-34 microfibers were assessed measuring adsorption isotherms in water vapor pressure by a volumetric apparatus made in house for testing samples of microfiber coatings. The volumetric equipment consisted of two communicating sections separated by vacuum valves, i.e., the sample chamber and a water vapor reservoir. The two sections were connected to a distilled water tank immersed in a thermostatic bath maintained at a constant temperature $(\pm 0.1 \,^{\circ}\text{C})$. The vacuum in the volumetric equipment was obtained by a turbomolecular pumping station (Edwards, T-Station). The vacuum in the two sections of the apparatus was measured by two capacitance gauges (Barocel 7025, Edwards, pressure range = 1000-0.1 mbar, accuracy = 0.2%). The sample temperature was measured by a thermocouple inserted directly into the sample holder (±0.1 °C) and connected to a thermoregulator which changed the sample temperature by a ring heater placed outside the sample chamber. Before each adsorption measurement, the microfiber sample was degassed at 150 °C in a high vacuum (P = 10^{-4} mbar) for 12 h. Then, the sample was allowed to cool in a high vacuum to the temperature of the adsorption isotherm. When the sample temperature was stable, the water vapor (at known pressure) in the reservoir was allowed to flow into the sample chamber and to be adsorbed by the microfibers. Knowing the volume, temperature and the pressure differences before and after opening the valve to the sample chamber, the amount of the adsorbed water was determined [40,41].

3. Results and Discussion

3.1. SAPO-34 Zeolite Characterization

The x-ray diffractograms of SAPO-34 powders in Figure 1 show the overlap of the X-ray peaks of the synthesized zeolites with diffraction data of SAPO-34 reported in PDF 00-047-0429, PDF 00-047-0617 and PDF 00-055-0829. There is no evidence of extraneous phases in the diffractograms in Figure 1; the observed differences in peaks intensity are related to the different particle sizes among the three zeolites, i.e., SAPO-34M, SAPO-34L and SAPO-34S. The XRD of SAPO-34S shows diffraction peaks with the lowest intensity and greatest width because it is the powder with the smallest crystals.

The SEM images of the three SAPOs in Figure 2 confirm that the differences observed in X-ray diffractograms are due to the dimensions of the powder granules. The typical cubic shape of SAPO-34 zeolite is evident in all samples. SAPO-34M shows the most diffuse particle sizes, i.e., between 5 and 10 μ m, while in SAPO-34L, the granules reach dimensions of between 10 and 30 μ m; finally, in SAPO-34S, the smallest size powder, the zeolite crystals show sizes of between 1 to 3 μ m.



Figure 1. XR-diffractograms of the synthesized SAPO-34. Reference peaks are reported for comparison [42].



Figure 2. SEM images of the synthesized zeolites: SAPO-34L, SAPO-34M and SAPO-34S (from left).

3.2. Morphological Characterization of Hybrid Microfiber Coatings

The objective of the proposed coatings was to improve the performance of adsorption heat pumps driven by recovered waste heat in a "medium-low" temperature range, i.e., around 150 °C, aiming at further decreasing this value in the future to below 90 °C [43]. The active phase, i.e., the adsorbing material, is the zeolite SAPO-34, whose properties are known to be ideal for this specific application and temperature range [44]. The fibrous polymeric matrix has no absorption properties; however, it plays an important structural role because it facilitates the fixing of the powder granules to the metal surface of the adsorber. The goal is to reach the highest concentration of SAPO-34 in the coating while maintaining good structural and mechanical properties of the microfibers. For this reason, this part of the study was focused on increasing the quantity of zeolite in the precursor formulation, using the standard SAPO-34M, from a minimum concentration of 45 w% to 85 w% or more (Table 1). Figure 3 shows low magnification SEM images of the hybrid microfibers from samples PAN-M45 to PAN-M85. At a first glance, in all samples, the SAPO-34M granules appear to be completely entrapped in a net of PAN microfibers. Increasing the zeolite weight ratio in the precursor solution, the SAPO-34 powder quantity in the electrospun microfibers also increased (Figure 3). At concentrations of SAPO-34M higher than 85 w%, however, it was difficult to achieve a stable jet during electrospinning, and the result was unsatisfactory.



Figure 3. SEM images of PAN/SAPO-34M microfibers at increasing zeolite concentrations.

The effect on the microfiber structure of increasing the zeolite concentration is more evident at higher magnifications, as shown in Figure 4, where samples PAN-M45, PAN-M75 and PAN-M85 are compared. At the lowest concentration of SAPO-34, the mean diameter of the microfibers was 0.68 µm (measured by digital image analysis), similar to the diameter shown by microfibers of pure PAN electrospun under similar conditions. Increasing the concentration of SAPO-34, the microfiber mean diameter increased to 0.93 µm for PAN-M75 and to 1.27 µm for PAN-M85 (Figure 4). The low standard deviation values of the diameter distributions in Figure 4 evidence that the size variations of the electrospun microfibers were narrow, confirming that electrospinning mixtures of PAN and SAPO-34M is a stable and controlled process. To support the hypothesis that the microfiber diameters of the three samples were effectively different, an analysis of variance with a significance level of 0.05 was conducted, resulting in a probability of difference of >95%. It can be concluded that there is a direct correlation between the quantity of SAPO-34 added to the precursor and the diameter of the hybrid microfibers. This effect was be attributed to the modification of the physical properties of the precursor solution due to the addition of the zeolite powder, because the electrospinning conditions, i.e., flow rate, electric field, needle diameter and collector distance, were kept constant throughout the experiments. By increasing the weight ratio of SAPO-34 in the precursor, an equivalent increase of the solution electrospinnability was observed. This correlation between precursor electrospinnability and microfiber diameter is in good agreement with literature data [35,45,46].

To evaluate the effect of the zeolite particle size, microfiber coatings with the highest concentrations, i.e., 80 w% and 85 w%, were produced using SAPO-34S and SAPO-34L (Table 1). The SEM image of sample PAN-L85 in Figure 5 shows a microfiber morphology similar to samples with SAPO-34M, being the large crystals of SAPO-34L entrapped in a net of microfibers with mean diameter $\approx 1 \mu m$. Increasing the initial weight ratio of SAPO-34L, the number of entrapped crystals in the microfibers increased, although the final quantity of zeolite in the microfibers was always lower than in coatings filled with SAPO-34M. The particle size of SAPO-34L hindered the entrapment effect exerted by the PAN microfibers, and part of the zeolite powder was left in the syringe. A different morphology was observed when adopting SAPO-34S, as shown in sample PAN-S80 of Figure 5. The granules of this zeolite had dimensions that enabled their alignment along the microfibers, resulting in a

"necklace" morphology like that already observed in PEO/SAPO-34 and PVA/SAPO-34 microfibers [5]. This morphology (Figure 5) showed homogenous distribution of the adsorbing particles that indicated the presence of more zeolite in the deposited coating compared to samples with SAPO-34 powders with bigger particles sizes. The addition of SAPO-34S, however, had a significant impact on the electrospinnability of the precursor solution, and at the highest concentration, as in sample PAN-S85 (not shown here), the formation was observed of lumps of zeolite and a polymeric matrix that compromised the homogeneous distribution of the adsorbing particles. Comparing the mean diameters of the samples in Figure 5, the correlation between microfiber size and precursor electrospinnability discussed above was confirmed. The PAN-S80 microfibers had a mean diameter (1.17 μ m), bigger than PAN-L85 (1.12 μ m), although the amount of zeolite added to the precursor was lower, because the solution electrospinnability increased more rapidly with the powder with smaller particle size.



Figure 4. SEM images and related mean diameters evaluation of PAN/SAPO-34M samples at increasing zeolite concentrations (45, 75 and 85 wt%).



Figure 5. SEM images of coating PAN-L85 and coating PAN-S80.

3.3. Thermal and Adsorption Properties of the Microfibers

An important issue for microfiber coatings for water adsorption is to prove that there is no thermal degradation of the polymeric matrix under the operating conditions of an adsorption heat pump. The thermal analyses in Figure 6a,b show the behavior of the basic components, the zeolite SAPO-34M and the electrospun microfibers of the pure PAN, in a temperature range of 25–500 °C and N_2 flow. The gravimetric curve of the zeolite (Figure 6a) shows a maximum weight loss of 20%, which was reached at a temperature of 220 °C and a peak of endothermic heat in the DSC curve at T = 127 °C. In an adsorption heat pump driven by low temperature sources, the thermodynamic cycle varies within a pressure range of 10–40 mbar and a temperature range of 25–100 °C. The TGA curve of pure PAN microfibers (Figure 6b) shows that they are thermally stable up to 250 °C; above that temperature, an exothermic peak appears, which is associated with the greatest mass loss. The observed heat flow at ~300 °C was an indication that cyclization and dehydrogenation reactions had occurred in the PAN microfibers [46]. Dehydrogenation and cyclization of the polyacrylonitrile structure gives rise to the formation of double bonds and rings along the carbon chain that "stabilize" the PAN microfibers [36,37,47]. Microfiber coatings with the highest quantity of SAPO-34 are the most suitable for water adsorption, and in Figure 6c, the TGA-DSC curves of sample PAN-M85 compared to those of pure PAN microfibers are shown. The DSC curve of PAN-M85 shows two main peaks, i.e., an endothermic peak at T = 97 °C and an exothermic one at T = 315 °C, that can be attributed to two main events during the heating up of the microfibers: water evaporation from the zeolite particles at low temperature and the stabilization of the polymeric chains at a higher temperature. Compared to pure PAN microfibers, the shift to 315 °C of the exothermic peak (Figure 6c) is an indication that dehydration and cyclization reactions in PAN-M85 were delayed by the chemical interactions of the PAN microfibers with SAPO-34 crystals. At T = 250 $^{\circ}$ C, before the exothermic reactions, the mass decrease of PAN-M85 was \approx 18 w%, and considering that the mass loss of pure PAN microfibers at the same temperature is only few percent (Figure 6b), the weight loss of the sample can be attributed to simple water desorption, which is in agreement with the initial quantity of 85 w% of SAPO-34M in the precursor solution. In conclusion, the TGA-DSC results confirmed that PAN hybrid microfibers were thermally stable far beyond the maximum temperature reached during the heat pump cycling, and that the SAPO-34M adsorption/desorption properties were not compromised by the polymeric matrix because the porosity was not occluded. The thermodynamic cycle in the operating conditions, however, varied from 10 mbar to 40 mbar water vapor pressure, so the adsorption properties of the microfibers coatings had to be measured under similar conditions. For this reason, the adsorption isotherms of hybrid microfibers were measured using the volumetric apparatus described in the experimental section.



Figure 6. TGA-DSC curves of SAPO-34M (a), PAN microfibers (b) and sample PAN-M85 (c).

The adsorption isotherms at T = 25 °C of the synthesized SAPOs are shown in Figure 7a. From a comparison, it is evident that the particle sizes did not make a difference in the adsorption behavior of the zeolite, an expected result because the isotherms were measured at equilibrium. The maximum water uptake of 30% is typical for SAPO-34 [48,49], as is the trend of the water adsorption isotherm, which is classified as Type V according to the IUPAC classification [50]. This characteristic behavior is the main reason for preferring SAPO-34 in adsorption cycles driven by low temperature heat sources. By a narrow pressure swing, i.e., between 10% and 40% of P/P₀, the water uptake rose from a few percent to 90% of the total (Figure 7a). In Figure 7b,c the isotherms (at T = 25 °C) for sample PAN-M85 are presented in comparison with the related zeolite and PAN-S80 with the related zeolite. In both cases, the maximum amount of water adsorbed by the two hybrid microfiber samples was in agreement with the SAPO-34 content in the precursor formulations, i.e., the water uptake (g water/g sample) of PAN-M85 was almost 85 % of the maximum water capacity of SAPO-34M, while that of PAN-S80 was

close to 80% of the maximum capacity of SAPO-34S. This result confirms that even at low pressure, the polymeric microfiber matrix did not hinder the zeolite granules from adsorbing/desorbing the water vapor. Moreover, although the microfiber morphologies of the two samples were different (compare Figures 4c and 5a), in both cases, the isotherm pressure maintained the typical S-shape of SAPO34.



Figure 7. Isotherms of SAPO-34 zeolites (a), PAN-M85 (b) and PAN-S80 (c).

Finally, PAN-M85 microfibers showed the best combination of adsorption properties and morphological characteristics, so further tests were conducted on PAN-M85 coatings to evaluate the material's stability.

3.4. Hybrid Microfiber Hydrothermal Stability

The use of hybrid (organic/inorganic) coatings in adsorption system cycles, in which the adsorbent is mixed with a polymeric component—e.g., just a binder [51,52] or a foamed matrix [32], or in our case, fibrous—is useful for evaluating hydrothermal stability after multiple thermal cycles at low water pressure. The coating must not become detached from the metal surface, or show cracking or swelling over time, and there must be no solvent emission (which would increase the adsorber pressure) or loss of adsorption capacity.

To test the hydrothermal stability of hybrid PAN microfibers, samples of aluminum sheets $(3 \times 4 \text{ cm})$ were coated with PAN-M85 and exposed to a saturated water vapor atmosphere by putting the coated sheets on a stand over a layer of distilled water inside an autoclave and allowing them to age for 4 h at T = 150 °C and autogenous pressure. Figure 8 shows SEM images of the coating before (Figure 8a) and after (Figure 8b) the aging test. An estimation of the coating porosity and microfiber diameters obtained by digital image analysis is reported in Table 2.



Figure 8. Sample PAN-M85 coating before (a) and after the hydrothermal test (b).

Parameters	Sample PAN-M85	Sample PAN-M85 Aged
Mean diameter (µm)	1.27	2.06
SD	0.18	0.27
Porosity (%)	47	42
Mean pores area (µm ²)	8.42	5.26
N. pores	447	407

Table 2. Main morphological characteristics of the aging test for PAN-M85. All reported parameters are mean values of three measurements by digital image analysis of different samples.

The hybrid microfibers appeared to be more compacted after aging, with an evident increase of interlayer density (Figure 8). The coating did not show macroscopic shrinkage; this would have caused the appearance of detachments from the aluminum sheet (insets in Figure 8). According to the data in Table 2, the mean diameter of the aged microfibers increased slightly, while the mean pore area and the number of pores decreased after aging. As such, the porosity was reduced from 47% before aging to 42% after.

According to our TGA-DSC analysis, the temperature of the hydrothermal treatment was below the limit of possible cyclization and dehydrogenation reactions in PAN, so the thickening and densification observed were morphological effects of the coupled action of temperature and vapor pressure inside the autoclave, rather than being due to chemical modifications of the coating.

The stability of the microfiber coating after cycling was assessed by measuring the same adsorption isotherm (at T = 25 °C) ten times consecutively on the same sample. Figure 9 depicts the repeated isotherms for sample PAN-M85. The error bars refer to a percentage error of 5% on the values of the first isobar. The test showed that there was substantial repeatability of the curves in the repetitions, due to the variation of the water uptake for PAN-M85 being lower than 5% at all of the measured pressures. The adsorption properties of hybrid microfibers did not worsen after 10 consecutive isotherms; therefore, although more and longer aging tests are needed to definitively determine the stability of the coating in the operating conditions of an adsorption pump, these first indications are positive. Moreover, a SEM analysis of the microfiber coating after the cyclic test (not shown here for brevity) did not reveal significant variations in terms of the microfiber diameters or texture porosity, confirming the hydrothermal stability of the PAN/SAPO-34 microfibers.



Figure 9. Cyclic test of adsorption isotherms.

4. Conclusions

The motivation for proposing an adsorbent coating made of hybrid microfibers is based on the necessity to increase the efficiency of adsorption chillers and pumps driven by low temperature waste heat in order to make these systems economically viable. In this sense, the electrospinning of adsorbing microfibers directly on the metal surfaces is a feasible process, and PAN was shown to be an ideal polymeric component because it is easy to spin, thermally stable and has a good chemical affinity with the zeolite. An important factor in maximizing the SAPO-34 quantity while maintaining good microfiber morphology is particle size; our results showed that the ideal mixing was obtained with zeolite particles of few microns in size. The particular morphology of the microfibers and their interactions with the zeolite allowed us to produce coatings with high thickness while maintaining excellent porosity and permeability through the deposited layers.

A SAPO-34 content of 85 w% in PAN hybrid microfibers yielded the best combination of adsorption properties and hydrothermal stability, although more aging measurements are needed. These preliminary results are an incentive to scale up the coating process over an entire absorber to test the material in a real adsorption heat pump.

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References

- 1. Angammana, C.J.; Jayaram, S.H. Fundamentals of electrospinning and processing technologies. *Part. Sci. Technol.* **2016**, *34*, 72–82. [CrossRef]
- 2. Frontera, P.; Malara, A.; Stelitano, S.; Fazio, E.; Neri, F.; Scarpino, L.; Antonucci, P.L.; Santangelo, S. A new approach to the synthesis of titania nano-powders enriched with very high contents of carbon nanotubes by electro-spinning. *Mater. Chem. Phys.* **2015**, *153*, 338–345. [CrossRef]
- Kara, H.; Xiao, F.; Sarker, M.; Jin, T.Z.; Sousa, A.M.M.; Liu, C.; Tomasula, P.M.; Liu, L. Bio-based packaging. J. Appl. Polym. Sci. 2016, 133, 42475. [CrossRef]
- 4. Ke, P.; Jiao, X.N.; Ge, X.H.; Xiao, W.M.; Yu, B. From macro to micro: Structural biomimetic materials by electrospinning. *R. Soc. Chem. Adv.* **2014**, *4*, 39704–39724. [CrossRef]
- Malara, A.; Frontera, P.; Bonaccorsi, L.; Antonucci, P.L. Hybrid zeolite SAPO-34 fibres made by electrospinning. *Materials* 2018, 11, 2555. [CrossRef]
- 6. Freni, A.; Calabrese, L.; Malara, A.; Frontera, P.; Bonaccorsi, L. Silica gel microfibres by electrospinning for adsorption chillers. *Energy* **2019**, *187*, 115971. [CrossRef]
- 7. Frontera, P.; Kumita, M.; Malara, A.; Nishizawa, J.; Bonaccorsi, L. Manufacturing and Assessment of Electrospun PVP/TEOS Microfibres for Adsorptive Heat Transformers. *Coatings* **2019**, *9*, 443. [CrossRef]
- Frontera, P.; Malara, A.; Bonaccorsi, L.; Antonucci, P.L. Metodo per la Realizzazione Dello Scambiatore di Calore di una Macchina Termica ad Adsorbimento e Rispettiva Macchina Termica. Nr.102018000003884. EP19164536.5, 22 March 2018.
- 9. Ardente, F.; Beccali, M.; Cellura, M.; Mistretta, M. Energy and environmental benefits in public buildings as a result of retrofit actions. *Renew. Sustain. Energy Rev.* **2011**, *15*, 460–470. [CrossRef]
- 10. Forman, C.; Muritala, I.K.; Pardemann, R.; Meyer, B. Estimating the global waste heat potential. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1568–1579. [CrossRef]
- 11. Ziemele, J.; Kalnins, R.; Vigants, G.; Vigants, E.; Veidenbergs, I. Evaluation of the industrial waste heat potential for its recovery and integration into a fourth generation district heating system. *Energy Procedia* **2018**, *147*, 315–321. [CrossRef]
- 12. Papapetrou, M.; Kosmadakis, G.; Cipollina, A.; La Commare, U.; Micale, G. Industrial waste heat: Estimation of the technically available resource in the EU per industrial sector, temperature level and country. *Appl. Therm. Eng.* **2018**, *138*, 207–216. [CrossRef]

- 13. Agathokleous, R.; Bianchi, G.; Panayiotou, G.; Arestia, L.; Argyrou, M.C.; Georgiou, G.S.; Tassou, S.A.; Jouhara, H.; Kalogirou, S.A.; Florides, G.A.; et al. Waste heat recovery in the EU industry and proposed new technologies. *Energy Procedia* **2019**, *161*, 489–496. [CrossRef]
- 14. Jouhara, H.; Khordehgah, N.; Almahmoud, S.; Delpech, B.; Chauhan, A.; Tassou, S.A. Waste heat recovery technologies and applications. *Therm. Sci. Eng. Prog.* **2018**, *6*, 268–289. [CrossRef]
- 15. Bloess, A.; Schill, W.P.; Zerrahn, A. Power-to-heat for renewable energy integration: A review of technologies, modeling approaches, and flexibility potentials. *Appl. Energy* **2018**, *212*, 1611–1626. [CrossRef]
- 16. Cabeza, L.F.; Solé, A.; Barreneche, C. Review on sorption materials and technologies for heat pumps and thermal energy storage. *Renew. Energy* **2017**, *110*, 3–39. [CrossRef]
- Fasolini, A.; Cucciniello, R.; Paone, E.; Mauriello, F.; Tabanelli, T. A Short Overview on the Hydrogen Production Via Aqueous Phase Reforming (APR) of Cellulose, C6-C5 Sugars and Polyols. *Catalysts* 2019, *9*, 917. [CrossRef]
- Xu, C.; Paone, E.; Rodríguez-Padrón, D.; Luque, R.; Mauriello, F. Reductive catalytic routes towards sustainable production of hydrogen, fuels and chemicals from biomass derived polyols. *Renew. Sustain. Energy Rev.* 2020, 127, 109852. [CrossRef]
- 19. Freni, A.; Maggio, G.; Cipitì, F.; Aristov, Y.I. Simulation of water sorption dynamics in adsorption chillers: One, two and four layers of loose silica grains. *Appl. Therm. Eng.* **2012**, *44*, 69–77. [CrossRef]
- 20. Girnik, I.S.; Aristov, Y.I. Dynamics of water vapour adsorption by a monolayer of loose AQSOATM-FAM-Z02 grains: Indication of inseparably coupled heat and mass transfer. *Energy* **2016**, *114*, 767–773. [CrossRef]
- 21. Aristov, Y.I.; Tokarev, M.M.; Freni, A.; Glaznev, I.S.; Restuccia, G. Kinetics of water adsorption on silica Fuji Davison RD. *Microporous Mesoporous Mater.* **2006**, *96*, 65–71. [CrossRef]
- 22. N'Tsoukpoe, K.E.; Restuccia, G.; Schmidt, T.; Py, X. The size of sorbents in low pressure sorption or thermochemical energy storage processes. *Energy* **2014**, *77*, 983–998. [CrossRef]
- 23. Restuccia, G.; Freni, A.; Maggio, G. A zeolite-coated bed for air conditioning adsorption systems: Parametric study of heat and mass transfer by dynamic simulation. *Appl. Therm. Eng.* **2002**, *22*, 619–630. [CrossRef]
- 24. Wang, S.G.; Wang, R.Z.; Li, X.R. Research and development of consolidated adsorbent for adsorption systems. *Renew. Energy* **2005**, *30*, 1425–1441. [CrossRef]
- 25. Freni, A.; Dawoud, B.; Bonaccorsi, L.; Chmielewski, S.; Frazzica, A.; Calabrese, L.; Restuccia, G. *Characterization of Zeolite-Based Coatings for Adsorption Heat Pumps*; Springer: Berlin/Heidelberg, Germany, 2015; ISBN 978-3-319-09326-0.
- Sapienza, A.; Gullì, G.; Calabrese, L.; Palomba, V.; Frazzica, A.; Brancato, V.; La, D.; Vasta, S.; Freni, A.; Bonaccorsi, L.; et al. An innovative adsorptive chiller prototype based on 3 hybrid coated/granular adsorbers. *Appl. Energy* 2016, 179, 929–938. [CrossRef]
- 27. Girnik, I.S.; Grekova, A.D.; Gordeeva, L.G.; Aristov, Y.I. Dynamic optimization of adsorptive chillers: Compact layer vs. bed of loose grains. *Appl. Therm. Eng.* **2017**, 125, 823–829. [CrossRef]
- 28. Saha, B.B.; Uddin, K.; Pal, A.; Thu, K. Emerging sorption pairs for heat pump applications: An overview. *JMST Adv.* **2019**, *1*, 3. [CrossRef]
- 29. Bonaccorsi, L.; Freni, A.; Proverbio, E.; Restuccia, G.; Russo, F. Zeolite coated copper foams for heat pumping applications. *Microporous Mesoporous Mater.* **2006**, *91*, 7–14. [CrossRef]
- 30. Wittstadt, U.; Füldner, G.; Laurenz, E.; Warlo, A.; Große, A.; Herrmann, R.; Schnabel, L.; Mittelbach, W. A novel adsorption module with fiber heat exchangers: Performance analysis based on driving temperature differences. *Renew. Energy* **2017**, *110*, 154–161. [CrossRef]
- 31. Calabrese, L.; Bonaccorsi, L.; Freni, A.; Proverbio, E. Silicone composite foams for adsorption heat pump applications. *Sustain. Mater. Technol.* **2017**, *12*, 27–34. [CrossRef]
- Calabrese, L.; Bonaccorsi, L.; Bruzzaniti, P.; Frazzica, A.; Freni, A.; Proverbio, E. Adsorption performance and thermodynamic analysis of SAPO-34 silicone composite foams for adsorption heat pump applications. *Mater. Renew. Sustain. Energy* 2018, 7, 1–13. [CrossRef]
- Teo, W.E.; Inai, R.; Ramakrishna, S. Technological advances in electrospinning of nanofibers. *Sci. Technol. Adv. Mater.* 2011, 12, 013002. [CrossRef]
- 34. Kalashnik, A.T.; Smirnova, T.N.; Chernova, O.P.; Kozlov, V.V. Properties and structure of polyacrylonitrile fibers. *Polym. Sci. Ser. A* 2010, *52*, 1233–1238. [CrossRef]
- 35. Wang, T.; Kumar, S. Electrospinning of polyacrylonitrile nanofibers. *J. Appl. Polym. Sci.* **2006**, *102*, 1023–1029. [CrossRef]

- 36. Ismar, E.; Sarac, A.S. Synthesis and characterization of poly (acrylonitrile-co-acrylic acid) as precursor of carbon nanofibers. *Polym. Adv. Technol.* **2016**, *27*, 1383–1388. [CrossRef]
- 37. Ismar, E.; Sarac, A.S. Oxidation of polyacrylonitrile nanofiber webs as a precursor for carbon nanofiber: Aligned and non-aligned nanofibers. *Polym. Bull.* **2018**, *75*, 485–499. [CrossRef]
- Van Heyden, H.; Mintova, S.; Bein, T.; Van Heyden, H.; Mintova, S.; Bein, T.; Van Heyden, H.; Mintova, S.; Bein, T. Nanosized SAPO-34 synthesized from colloidal solutions. *Chem. Mater.* 2008, 20, 2956–2963. [CrossRef]
- Hotaling, N.A.; Bharti, K.; Kriel, H.; Simon, C.G. DiameterJ: A validated open source nanofiber diameter measurement tool. *Biomaterials* 2015, 61, 327–338. [CrossRef]
- 40. Gorbach, A.; Stegmaier, M.; Eigenberger, G. Measurement and Modeling of Water Vapor Adsorption on Zeolite 4A—Equilibria and Kinetics. *Adsorption* **2004**, *10*, 29–46. [CrossRef]
- 41. Zheng, X.; Wang, R.Z.; Ge, T.S.; Hu, L.M. Performance study of SAPO-34 and FAPO-34 desiccants for desiccant coated heat exchanger systems. *Energy* **2015**, *93*, 88–94. [CrossRef]
- 42. International Zeolite Association. Available online: http://www.iza-online (accessed on 20 May 2020).
- 43. Lenzen, D.; Zhao, J.; Ernst, S.J.; Wahiduzzaman, M.; Ken Inge, A.; Fröhlich, D.; Xu, H.; Bart, H.J.; Janiak, C.; Henninger, S.; et al. A metal–organic framework for efficient water-based ultra-low-temperature-driven cooling. *Nat. Commun.* **2019**, *10*, 3025. [CrossRef]
- 44. Kohler, T.; Hinze, M.; Müller, K.; Schwieger, W. Temperature independent description of water adsorption on zeotypes showing a type V adsorption isotherm. *Energy* **2017**, *135*, 227–236. [CrossRef]
- Tański, T.; Matysiak, W.; Hajduk, B. Manufacturing and investigation of physical properties of polyacrylonitrile nanofibre composites with SiO₂, TiO₂ and Bi₂O₃ nanoparticles. *Beilstein J. Nanotechnol.* 2016, 7, 1141–1155. [CrossRef] [PubMed]
- 46. Zhang, C.; Ding, X.; Wu, S. The Microstructure Characterization and the Mechanical Properties of Electrospun Polyacrylonitrile-Based Nanofibers. *Nanofibers Prod. Prop. Funct. Appl.* **2011**. [CrossRef]
- 47. Wu, M.; Wang, Q.; Li, K.; Wu, Y.; Liu, H. Optimization of stabilization conditions for electrospun polyacrylonitrile nanofibers. *Polym. Degrad. Stab.* **2012**, *97*, 1511–1519. [CrossRef]
- 48. Dias, J.M.S.; Costa, V.A.F. Adsorption heat pumps for heating applications: A review of current state, literature gaps and development challenges. *Renew. Sustain. Energy Rev.* **2018**, *98*, 317–327. [CrossRef]
- Bonaccorsi, L.; Calabrese, L.; Freni, A.; Proverbio, E. Hydrothermal and microwave synthesis of SAPO (CHA) zeolites on aluminium foams for heat pumping applications. *Microporous Mesoporous Mater.* 2013, 167, 30–37. [CrossRef]
- Sing, K.S.W.; Everett, D.H.; Haul, R.A.W.; Moscou, L.; Pierotti, R.A.; Rouquérol, J.; Siemieniewska, T. REPORTING PHYSISORPTION DATA FOR GAS/SOLID SYSTEMS with Special Reference to the Determination of Surface Area and Porosity (Recommendations 1984). *Pure Appl. Chem.* 1985, 57, 603–619. [CrossRef]
- 51. Demir, H.; Mobedi, M.; Ulku, S. A review on adsorption heat pump: Problems and solutions. *Renew. Sustain. Energy Rev.* **2008**, *12*, 2381–2403. [CrossRef]
- 52. Calabrese, L.; Bonaccorsi, L.; Bruzzaniti, P.; Proverbio, E.; Freni, A. SAPO-34 based zeolite coatings for adsorption heat pumps. *Energy* **2019**, *187*, 115981. [CrossRef]



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