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A Review on Development of Heat and Mass Transfer Enhancement in Adsorption Heat Exchangers

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Abstract: As an environment-friendly approach for low-grade thermal utilization, adsorption technology has received more and more attention since it can have a plethora of applications, such as thermal energy storage, heat pumps and carbon dioxide capture etc. The performance of this technology is highly affected by the heat and mass transfer efficiency in the adsorption heat exchangers. This minireview is focused on recent studies and investigations on performance improvement of the adsorption heat exchangers, especially on the improvement of the thermal conductivity of adsorbents, the reduction of the thermal contact resistance, and the improvement of the heat exchange area. Discussion on the future research required to improve the heat and mass transfer performance was presented. These technologies and results are expected to provide insights and guidance for performance improvement of both adsorption heat pumps and adsorption thermal energy storage systems.

Keywords: Adsorption heat exchanger, Heat and mass transfer enhancement, Thermal conductivity, Thermal contact resistance

1. INTRODUCTION

Adsorption heat pump (ADHP) system, as an environment-friendly technology, has been paid more and more attention due to its advantages in the utilization of low-grade thermal energy. The ADHP system mainly depends on the principle that some solid adsorbents (such as zeolite, activated carbon, etc.) have different adsorption capacities for some refrigerants (such as water, ammonia, etc.) at different temperatures and pressures. The heating/cooling capacity of an ADHP system is produced by the thermal effects that occur inside the adsorbent-refrigerant working pairs during the adsorption or desorption process.

Compared with the vapor compression heat pump systems, the ADHP systems can be driven by low-grade heat sources without using a compressor, which can minimize the electricity consumption (mainly used to drive water pumps, fans, etc.). ADHP system may not use traditional refrigerants, such as chlorofluorocarbon (CFC), hydrochlorofluorocarbon (HCFC) and hydrofluorocarbon (HFC). The ozone depletion potential (ODP) and global warming potential (GWP) are 0. Compared with the absorption heat pump (ABHP) systems, ADHP systems have no risk of crystallization and can be driven by lower temperature heat sources. For example, adsorption refrigeration systems using silica gel-water as working pair can be driven by 55°C -90°C heat source to produce cold water at 5°C -15°C.

However, due to poor heat and mass transfer performance inside the adsorption heat exchangers, ADHP systems have low efficiency and large size. These have been the main technical challenges to be faced in the large-scale application of ADHP systems.

The efficiency of the heat and mass transfer in an adsorption bed is mainly affected by the conduction and the convection insides. as shown in Fig. 1, the overall thermal resistance in the adsorption bed depends on four parts:

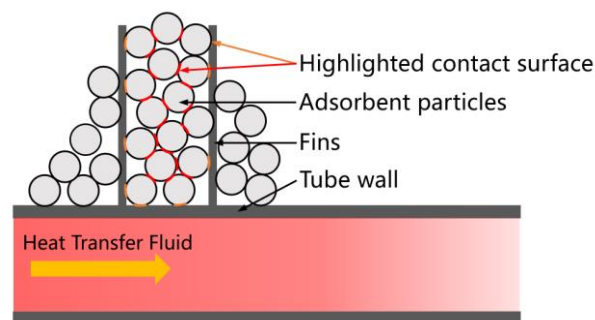


Fig. 1. Images of an adsorption heat exchanger configuration

(a) The convective heat transfer coefficient between the heat transfer fluid and the tube wall of the heat exchanger. The convective heat transfer coefficient can be increased simply by increasing the flow rate of heat transfer fluid, and the proportion of thermal resistance on this side is small.

(b) The thermal conductivity of the metal wall of the heat exchanger. The thermal resistance in this part is usually negligible and can be controlled by controlling the type of metal and the thickness of the wall.

(c) The thermal contact resistance between adsorbent particles and metal tube wall of the heat exchanger. This is one of the main parts of the total thermal resistance of the adsorption heat exchanger. At the interface between the adsorbent particles and the metal wall, the thermal contact resistance can result in a great temperature gradient[1].

(d) The internal thermal resistance of the adsorbent, including the thermal resistance of the adsorbent particles themselves and the thermal contact resistance between the particles. With the porous structure, the thermal conductivity of the adsorbent is poor, and its internal thermal resistance is usually large.

In order to improve the step of the ADHP toward commercialization, researchers around the world have put forth many measures to optimize the performance of adsorption beds, especially to improve the heat and mass transfer efficiency of the adsorbate in the adsorption bed.

Several materials and techniques have been proposed, such as composite adsorbents, fixed beds, adsorbent coatings, fin-type adsorption beds and porous adsorption beds. As shown in Fig. 2, in general, the total heat transfer performance of the adsorption bed can be improved by increasing the thermal conductivity of the adsorbent, reducing the thermal contact resistance and increasing the heat transfer area.

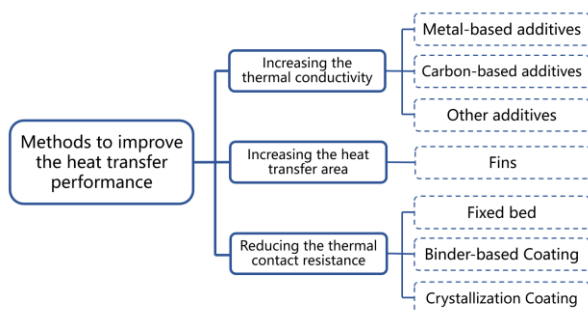


Fig. 2 Methods to improve the heat transfer performance

In this manuscript, a minireview of the recent research and development focused on the field of adsorption heat exchangers optimization is presented. This paper summarizes and compares the advantages and disadvantages of each technology, which will be quite conducive to the design and optimization of adsorption heat exchangers, and also beneficial to the efficiency improvement of the ADHP systems and the adsorption heat storage systems. In addition, it covers mainly and usually scattered information about adsorption heat exchangers optimization, and can be used as a guide for new researchers to this field.

2. INCREASING THE THERMAL CONDUCTIVITY OF ADSORBENTS ITSELF

Increasing the thermal conductivity of adsorbents itself to reduce the internal thermal resistance of adsorption bed plays a crucial role to improve the performance of ADHP systems. In commercially available ADHP systems, commonly used adsorbents include zeolite, silica gel, activated carbon, etc. Due to their porous structure, the thermal conductivity of these materials is usually low, and there is also a relatively large thermal contact resistance between the adsorbent particles. The effective thermal conductivity of zeolite is only about $0.07\text{--}0.13 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ [2]. The low heat and mass transfer rate in the adsorption bed, resulting in long adsorption/desorption time and specific cooling/heating power[3].

To enhance the thermal conductivity of adsorbents, a variety of methods are adopted in the past few decades. Technically, many researchers have chosen to combine adsorbents with other additives with higher thermal conductivity to prepare composite adsorbents. The common additives are metal-based materials and carbon-based materials.

2.1 Metal-based additives

Many recent pieces of research have been focused on composite adsorbents with metal-based additives, such as metallic powder[4, 5], aluminum foam[6-9] (as shown in Fig. 3) and activated alumina[10, 11] etc. Guilleninot et al.[6] first proposed to prepare composite materials by

zeolite and the metal foam bonded by copper foil to improve the heat transfer performance of zeolite. It is found that the effective thermal conductivity is greatly improved, which is helpful to reduce the size of the adsorption heat exchanger. Hu et al.[7] proposed a composite adsorbent made of zeolite particles and aluminum foam to enhance heat and mass transfer for adsorption refrigeration. The zeolite particles are encased in the pores of foam aluminum. Compared with normal zeolite particles or powder, the effective thermal conductivity of the zeolite/foam aluminum composite adsorbent is increased to $2.89 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. This composite adsorbent was used in a mass recovery adsorption refrigeration system driven by engine exhaust heat. When the composite adsorbent thickness is set to 5 mm and the cycle time is 8 min, the system specific cooling power (SCP) reaches the maximum value of $642 \text{ W}\cdot\text{kg}^{-1}$ and the coefficient of performance (COP) is 0.24. In a short cycle time, the COP and SCP of the adsorption refrigeration system using composite adsorbents are significantly higher than those of the adsorption system using ordinary zeolite as adsorbent.

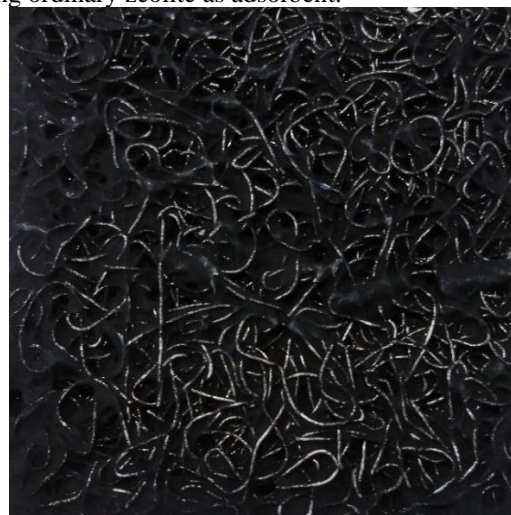


Fig. 3 aluminum foam filled with Maxsorb III

Mohammed et al.[8, 12] reported a study on the composite adsorbent that combined silica gel particles with high-porosity aluminum foam. The effect of pores per inch (PPI) of the foam, silica-gel particle size and bed height on the performance of adsorption heat exchanger was studied experimentally and numerically. Under typical working conditions. By using composite adsorbent, the overall effective thermal conductivity of the adsorption bed was enhanced from 0.198 to $5.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. It was found that aluminum foam with 20 PPI for adsorption cooling applications can deliver an SCP of $827 \text{ W}\cdot\text{kg}^{-1}$ and a COP of 0.75. Zhang et al.[10] studied the low-temperature heat storage system with composite adsorbent which impregnated the LiCl in the activated alumina. Their TGA-DSC results showed that the energy storage density of the composite adsorbent can reach $1041.5 \text{ kJ}\cdot\text{kg}^{-1}$ at the temperature of 20°C and relative humidity of 80% with a charging temperature of 120°C . Askalany et al.[5] added iron, copper and aluminum particles with different mass concentrations to activated carbon. The composite adsorbent with aluminum as filler shows higher thermal conductivity than the mixture with copper or iron as filler. The author conducted a mathematical model to study the effect of the metallic

fillings on COP and SCP of adsorption cooling system. As the concentration of the metallic fillings increases, the thermal conductivity of the composite adsorbent and the SCP of the adsorption cooling systems increases, but the COP of the system decreases. It was reported that when using aluminum fillings by about 30%, the system cycle time was reduced by 50%, and SCP was increased by 100%, but the COP was reduced by 22%. The metal-based additive with high thermal conductivity helps to reduce the internal thermal resistance of the adsorption bed, but it will increase the heat capacity of the composite adsorbent, which usually comes together with high sensible heat consumption. The extra heat input will result in low COP in the adsorption refrigeration/heating systems. Therefore, it is more suitable for adsorption thermal energy storage systems rather than cooling/heating systems[13].

2.2 Carbon-based additives

The thermal conductivity of adsorbents can also be enhanced by carbon-based additives, such as expanded natural graphite (ENG)[14-16], carbon nanotube (CNT)[17, 18] and activated carbon fiber (ACF)[19, 20]. ENG is prepared by electrochemical and chemical (oxidation) treatment of natural graphite to force the crystal lattice to separate and produce abundant micropores[21]. Wang et al.[14] added the ENG treated by sulfuric acid (ENG-TES) into the active carbon. The highest effective thermal conductivity of the composite adsorbent has been increased by 150 times, reaching $34.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. Simultaneously, the thermal diffusivity is also increased to 72 times that of untreated activated carbon. Generally, higher thermal diffusivity means higher thermal conductivity and smaller thermal capacity. For the real application of adsorbents in an adsorption refrigeration system, the COP of the ADHP system was improved with the increase of the concentration of the ENG. Jiang et al.[16] compared different composite adsorbents for two-stage adsorption refrigeration. The result shows that the ENG treated with sulfuric acid can improve the SCP effectively. For $\text{CaCl}_2\text{-BaCl}_2\text{-NH}_3$, the addition of ENG-TSA improves SCP by 76.9% than that of ENG. It is mainly because that the heat and mass transfer inside the adsorption bed has been greatly improved, which effectively shortens the adsorption/desorption time of the adsorbent.

ACF is a kind of fiber-shaped material with a diameter of 5-10 μm . It has high porosity and a well-defined porous structure, and its specific surface area can reach $2000 \text{ m}^2\cdot\text{g}^{-1}$, thermal conductivity can reach $150\text{--}1100 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which makes it an ideal choice for composite adsorbent materials[22]. Wang et al.[19] developed a novel $\text{CaCl}_2\text{-ACF}$ composite adsorbent to improve the performance of the air-to-water systems. The water uptake performance of $\text{CaCl}_2\text{-ACF}$ composite adsorbent is up to $1.7 \text{ g}\cdot\text{g}^{-1}$, which is three times more than the $\text{CaCl}_2\text{-silica gel}$ composite adsorbent under the same test condition. Alyousef et al.[23] experimentally investigated three-bed adsorption solar cooling system. In this three-bed system, ammonia was used as the refrigerant, $\text{MnCl}_2\text{-ACF}$ composite adsorbent was used in two adsorption beds and $\text{BaCl}_2\text{-ACF}$ composite adsorbent was used in a low-temperature adsorption bed.

The results indicated that the SCP of the system is about $100 \text{ W}\cdot\text{kg}^{-1}$, which is two times more compared with conventional coolers.

CNT is a kind of allotrope of carbon with a cylindrical nanostructure. It has extraordinary thermal conductivity, mechanical and electrical properties, which makes it a good candidate for composite matrix material with enhanced heat transfer performance. Yan et al.[18, 24] prepared a composite adsorbent made of CaCl_2 and multi-wall carbon nanotubes for the ADHP system. The authors evaluated the adsorption capacities of the composite adsorbent and analyzed the chemical reaction steps between the adsorbent and refrigerant. The experimental results showed that the maximum adsorption amount of ammonia refrigerant is $0.86 \text{ g}\cdot\text{g}^{-1}$. The thermal conductivity of the composite adsorbent was $1.52 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, while that of the CaCl_2 used in the experiment was $0.17 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is increased by 794%. Moreover, the addition of CNT into the CaCl_2 can avoid the agglomeration and as a result, prevent the performance attenuation, improve the stability of the system.

3. REDUCING THE THERMAL CONTACT RESISTANCE BETWEEN ADSORBENT AND HEAT EXCHANGER

Besides the internal thermal resistance of the adsorbent itself, the performance of the heat and mass transfer inside the adsorption bed is also significantly influenced by thermal contact resistance between the adsorbent and the heat exchanger. The thermal contact resistance will cause a huge temperature gradient near the metal walls in the adsorption heat exchangers[1]. In order to enhance effective contact, three main techniques are investigated to improve system performance, namely fixed bed, binder-based coating bed [25, 26] and crystallization coating bed[27, 28]. Ref. [29] summarized and compared the main features of the solutions that were used to reduce the thermal contact resistance between adsorbent and heat exchanger in the literature.

3.1 Fixed bed

Fixed bed, a basic way to reduce thermal contact resistance, usually directly fills adsorbent materials in the gaps inside heat exchangers without using a binder. The adsorbent particles, which are randomly distributed in the gaps between the fins, are not in close contact with the metal wall, and there are many gaps. The effective contact area between the adsorbent particles and the heat exchanger walls, as well as the among the adsorbent particles, is very limited[30]. As a result, such a configuration presents a poor effect of reducing thermal contact resistance. On the other hand, thanks to the voids inside the fixed bed, the internal vapor transportation is quite good and the flow resistance is small, so the mass transfer efficiency is high enough[29].

3.2 Binder-based coating bed

The binder-based coating bed is an effective way that can contribute to the improve the heat transfer improvement between the adsorbent and the metal walls. In this method, the binders are used to consolidate the adsorbent particles on the metal walls of the heat exchangers. The addition of the binder makes the adsorption bed compact

and therefore obtains good heat transfer efficiency. Generally, the following processes are needed: firstly, the adsorbent and the binder are mixed in a specific ratio. During this stage, some other solvents or reagents will also be added to obtain a homogeneous and stable mixture. After that, the obtained slurry is evenly covered on the surface of the heat exchanger fins and compacted by a press. Finally, the mixture is heated and dried at a certain temperature until the slurry is consolidated over the fins surface to avoid falling off during the cycle. Therefore, binders, reagents, and manufacturing methods play critical roles in the heat and mass transfer performance of the final heat exchangers. In addition to using a press, there are other ways to fix the adsorbent on the metal wall, such as dip-coating, spray coating, spin coating and drop-coating. Each of these technologies has its characteristics and is suitable for different materials and purposes. With these treatments, the adsorbent material can be tightly bonded to the metal surface, thereby the thermal contact resistance is effectively reduced. Li et al.[31] reported that for the same adsorption material, the conductivity of the binder-based coating bed is 4 times that of the fixed bed.

Nevertheless, the reduction of the voids in the adsorption bed will reduce the flow path of the refrigerant gas and prevent it from entering the microporous structure of the adsorbent. Therefore, it will increase the mass transfer resistance, slow down gas transport, and reduce the mass transfer efficiency inside the adsorption bed. El-Sharkawy et al.[25] developed and characterized consolidated composite adsorbents with Maxsorb III as adsorbent, ENG as additive and polyvinyl alcohol as binder. The authors experimentally studied the ethanol adsorption equilibrium uptakes performance and thermal conductivity of the adsorbents coating. The results show that the increase in the proportion of ENG in the composite material can increase the thermal conductivity of the composites, and the maximum can reach $0.74 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is about 11 times that of the original Maxsorb III, but with the addition of polyvinyl alcohol, the adsorption equilibrium capacity of ethanol onto composite material decreased. When the material composition ratio is 70% Maxsorb III, 20% ENG and 10% polyvinyl alcohol, the adsorption uptake is $8.9 \text{ g} \cdot \text{g}^{-1}$, which is only 74% of the original Maxsorb III.

3.3 Crystallization coating bed

It is also a potential way to reduce the thermal contact resistance by directly crystallizing and fixing the adsorbent on the metal wall of the heat exchanger. In this way, a very thin adsorbent layer can be obtained on the surface of the heat exchangers. Adsorbent molecules are closely attached to the metal wall, which makes the contact area large and the thermal contact resistance low. Meanwhile, there is no need to use binders when manufacturing the crystallization adsorption bed, which will not negatively affect the adsorption capacity of the adsorbent material, and the adsorbent can be uniformly crystallized on the surface of the adsorption bed. With this thin crystallized layer, the adsorbent is fully exposed to refrigerant vapor, so the mass transfer resistance of the crystallization coating bed is smaller than that of fixed

beds and binder-based coating beds.

Atakan et al.[28] performed an experimental study, which crystallized zeolite on copper and stainless steel fibrous plates by substrate heating synthesis method, and characterized the properties of the coatings by X-ray diffraction (XRD) laser microscopy and thermogravimetry (TGA). It is found that the thickness of the zeolite layer and the material of the wall are the key factors affecting the heat and mass transfer performance of the coating bed. Tatlier et al.[32] used microwave heating to crystallize zeolite on the stainless steel surface and characterized its performance. Compared with the traditional heating methods, the microwave heating used in this study can heat the material faster and more evenly during the synthesis process, and the crystallization rate of the zeolite is also higher.

On the contrary, only when the thickness of the adsorbent layer is very low, the adsorbent molecules can be tightly attached to the wall surface. With the increase of thickness, the risk of adsorbent shedding due to the mechanical stressing induced by thermal expansion of the metal wall during the adsorption/desorption cycle will increase. Moreover, in the crystallization adsorption bed, the adsorbent is dispersed on the surface of each fin of the entire heat exchanger, the quality of adsorbent per unit volume is very low, resulting in a low adsorption capacity of the whole adsorption bed. Simultaneously, the metal-adsorbent ratio is high, resulting in low system efficiency when used in adsorption heating or cooling applications.

Improving the internal heat transfer efficiency of the adsorption heat exchanger can be conducted through the above-mentioned several different configurations aiming at reducing the thermal contact resistance. On the contrary, it must also be pointed out that the method of reducing the thermal contact resistance poses limitations in refrigerant vapor transmission efficiency because the over-compacted adsorbent layer will reduce the free paths and increase the mass transfer resistance. In the optimization design of the adsorption heat exchanger, it is necessary to comprehensively consider the internal heat transfer and mass transfer efficiency. Consideration should be given to carefully find the proper balance between these two parameters to improve system performance.

Meanwhile, other parameters, such as the type of metal material, the form of the tube wall, and the thickness of the coatings, have an important influence on the performance of the ADHP system. These parameters also need to be carefully optimized in the design. During the heating-cooling cycle, due to thermal stress and metal volume expansion, the adsorbent coatings may have problems such as poor contact, cracks or even shedding. In order to obtain a stable and satisfactory adsorption heat exchanger, detailed investigations and studies of the stability of the coatings are necessary in the following work.

4. INCREASING THE SURFACE AREA OF THE HEAT EXCHANGER SYSTEM

Apart from reducing the internal thermal resistance of the adsorbent, expanding the heat transfer area of the adsorption heat exchanger is also used in the ADHP system to provide high heat transfer capacity. Larger

contact areas between the adsorbent and the adsorption bed will enlarge the heat transfer area per unit volume and shorten the heat transfer path, thus enhancing the heat transfer between them. For such consideration, researchers are committed to the modeling and experimental testing of the designs and configurations of some new adsorption heat exchangers. The common methods investigated include the plate-finned[33-35], spiral plate[36] and pin-fin bed[3].

The finned tube heat exchanger is a popular candidate for adsorption bed structure because of its simple structure and low manufacturing cost. Usually, a cylindrical pressure vessel is used as the outer shell, and there are multiple tube-fin heat exchangers inside. Many fins are welded to the tube to increase the heat transfer surface. The heat transfer fluid flows in the tube, and the adsorbent material is filled around the tube and between the fins. Sharafian et al.[33] evaluated the performance of nine different existing adsorption heat exchangers used in waste-heat driven adsorption cooling systems for vehicle air conditioning and refrigeration. Consequently, the finned-tube adsorption bed had the best performance. Meanwhile, optimizing the fin spacing and fin height is a practical solution to improve the heat and mass transfer rate in the adsorption bed. Louajari et al.[34] evaluated the effect of finned cylindrical tubes on the performance of a solar-driven adsorption refrigeration system using activated carbon/ammonia as the working pair. The results showed that the use of an adsorption bed with external fins can improve the mass of the adsorbent cycled in the system. The maximum temperature of the adsorption bed with fins can reach 97°C, while the maximum temperature of the adsorption bed without fins is only 77°C. The maximum COP increased from 0.075 to 0.111 after using the adsorption bed with finned tubes. The performance of the solar adsorption refrigerating machine with fins was higher than the one without fins. When the fin width is equal to half of the diameter of the cylindrical tube of the adsorption bed, better performance can be observed. Critoph et al.[37] built and tested laboratory prototype of a fast cycle adsorption refrigerator with carbon-aluminium laminate adsorbent and ammonia refrigerant. The cooling COP is about 0.44. Chang et al.[38] used flat tube heat exchanger to increase the heat transfer area and improve the heat transfer capacity for adsorption cooling system with silica gel as the adsorbent. When the temperatures of chilled water, cooling water and hot water are 14°C, 30°C and 80°C respectively, the COP of 0.45 and the SCP of 176 W·kg⁻¹ could be achieved.

However, different adsorption heat exchanger designs and configurations will lead to different adsorbent-tube wall contact areas, metal to adsorbent mass ratio, adsorbate-adsorbent contact area, and heat loss to the environment, which in turn affects the heat and mass transfer performance of the heat exchanger. Finned tubes can increase the heat exchange area inside the adsorption heat exchanger, but the large heat capacity ratio of metal fins and tubes will have a non-negligible negative impact on the COP and SCP of the ADHP systems. The COP and SCP are directly related to the mass ratio of the adsorbent material and the metal. In the ADHP system cycle, the adsorption heat exchangers are constantly is

heated or cooled alternately. The greater the mass fraction of metal, the greater the sensible heat loss of the system, and the lower the thermodynamic efficiency of the ADHP system, which has been verified for several different adsorbent-refrigerant working pairs [39, 40]. Moreover, the added fins will also occupy the precious space that could have been filled with adsorption materials. Compared with similar structures without fins, the mass of adsorbent per unit volume will be reduced, and thereby the heating or cooling capacity of the ADHP system will be reduced.

Therefore, when designing the adsorption bed, consideration should be given to ensuring a sufficient heat exchange area while minimizing the metal to adsorbent mass ratio. It should also be noted that the fact of increasing the tube diameter and fins increases the weight and manufacturing cost of the heat exchanger. In future work, further detailed investigations are required for the optimal balance of all these parameters, the technical and economic analysis of the adsorption heat exchanger should also be carried out.

5. CONCLUSION

Adsorption technology is an eco-friendliness and energy-saving technology that can be applied for many purposes. Recently, researchers showed great interest in improving and optimizing its disadvantages such as low efficiency and large size. The efficiency of the adsorption systems is closely connected with the heat and mass transfer rate in the adsorption heat exchanger. Whether in the desorption or adsorption process, high heat and mass transfer efficiency are always essential. This minireview summarizes different technologies and configurations for improving heat and mass transfer efficiency in adsorption heat exchangers. These techniques can be grouped as (a) increasing the thermal conductivity of adsorbent itself by adding additives with high thermal conductivity; (b) reducing the thermal contact resistance between the adsorbent and the metal wall of the heat exchanger through the adsorbent coating layer; (c) increasing the heat exchange area through different heat exchanger structures.

Although many types of composite adsorbents and advanced heat exchanger designs have been proposed, the world has not seen any large-scale commercial applications that use adsorption technology to replace traditional vapor compression technology. In the future, more studies may still be needed to reduce the negative impact of additives or binders on the adsorption capacity of the adsorbents. Efforts should also be made to find a balance between heat transfer efficiency and mass transfer efficiency to avoid the increase of internal mass transfer resistance caused by over-compacted structures. Simultaneously, the negative impact of excessive metal-adsorbent ratio on the performance of ADHP cooling or heating systems cannot be ignored, but such heat exchangers are more suitable for thermal energy storage systems.

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