

Review

An Overview of Developments In Silica Gel Matrix Composite Sorbents for Adsorption Chillers with Desalination Function

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Abstract: Adsorption cooling technology is a promising alternative to replace conventional solutions. However, adsorption chillers still need to be improved in terms of performance parameters. One of the most important factors affecting their efficiency is the characteristics of the adsorbent, which should have the highest adsorption capacity and enable efficient heat transport in the bed. The objective of this paper is to present current developments in the field of composite sorbents with silica gel matrix as modern and very promising materials and then perform a detailed analysis of them. The paper summarises the methods of synthesis of composite sorbents and the current knowledge concerning these materials. The analysis focuses on a comparison of the available data, particular taking into account the types of matrixes, so that the analysis provides a clear and qualitative basis for further research. As a result of exploring the state of the art, this subject is found to be insufficiently described; therefore, these materials are comprehensively analysed in terms of their properties and the impact of their use on the COP (coefficient of performance) and SCP (specific cooling power) of adsorption chillers. Based on the analysis of the literature, the most promising directions for further research are also indicated.

Keywords: adsorption; adsorption cooling; adsorbents; composite sorbents; silica gel; inorganic salts; additive; adsorption capacity; heat transfer; coefficient of performance



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1. Introduction

Demand for electricity is increasing along with the growth of the global economy and population. In mid-November 2022, the world's population surpassed 8 billion, reaching a threshold that is extremely important for the world. This is another incentive to increase energy conservation in every possible area, especially as the global population is predicted to be almost 9.7 billion in 2050 [1] and electricity consumption might increase by 50% by 2050 compared with 2020 [2]. One of the most important areas comprises HVAC (heating, ventilation and air conditioning) systems, which account for approx. 40% of the total energy consumption of an average commercial building [3]. Bearing in mind the scale, reducing the energy consumption of this kind of system will make a very significant difference to the global energy situation and reduce carbon dioxide emissions into the atmosphere. Taking into consideration only the refrigeration sector, it is estimated that it accounts for approx. 20% of the global electricity consumption [4]. In 2019, the International Institute of Refrigeration reported that there are approx. 2.6 billion air-conditioning units in operation [4]. Most commonly, these are solely electric-powered compressor units that use synthetic refrigerants. Cooling is one of the most important utilities used in many industries, including the food, pharmaceutical, energy, chemical and heavy industries. At the same time, it should be noted that the enormous amount of energy in the form of low-temperature heat (<90 °C) is dissipated into the atmosphere. It is estimated that up to 50% of the energy consumed in the industrial sector worldwide may be discharged into

the atmosphere as waste energy [5]. Although efforts are being made by industrial plants to recover the maximum amount of energy, harnessing heat at such low temperatures is a challenge. Its utilisation provides an opportunity to increase the energy efficiency of the existing and new systems and to reduce primary energy consumption. A very effective and promising option for its utilisation is to supply waste low-temperature heat to equipment using the adsorption and desorption phenomena. Such devices include adsorption chillers, adsorption heat pumps, adsorption desalination systems, energy storage systems, gas cleaning systems and gas storage systems. The phenomenon of vapour adsorption on the surface of a sorbent and thus adsorption cooling production was discovered in 1848 by Michael Faraday [6]. However, work on the development of this technology was stepped up in the 1990s as a result of signing the Montreal Protocol (1987) and the Kyoto Protocol (1997), which restricted the use of greenhouse gases and gases with high ozone-depleting potential.

Adsorption chillers are powered by low-temperature heat of 50–90 °C (even below 50 °C), which is their key advantage [7,8]. Adsorption chillers can simultaneously produce chilled water, as a result of heat being removed from it in the evaporator, and desalinated water by evaporating the water twice, first in the evaporator, then in the adsorbent bed, and condensing the already pure distilled water inside the condenser. Then, although the cooling capacity drops even by 60% [9], the technology becomes unrivalled in its functionality combined with zero environmental impact during its use. The operating principle of an adsorption chiller is based on thermal compression so they consume very little electricity. Adsorption chillers are very easy and inexpensive to operate compared with traditional systems [10]. The main advantage and the reason why there is so much hope for the wide deployment of adsorption cooling technology is that these units can be powered by low-temperature heat in the form of, e.g., waste heat and heat derived from solar or geothermal energy with very low electricity consumption, required only to drive pumps and automation systems. Cooling using adsorption and desorption phenomena is a more sustainable method than conventional technologies. Adsorption chillers are devices with zero ozone depletion potential and zero global warming potential [11]. The cooling cycle in them resembles the conventional one, but it is thermal compression that takes place instead of mechanical compression. Consequently, a number of further advantages of adsorption cooling technology can be identified, which include the presence of only a small number of moving parts, resulting in low vibration and high reliability, and the easy operation of the chiller combined with low noise emissions [10,12,13]. A unique advantage of adsorption cooling systems is that they use natural refrigerants instead of chlorofluorocarbons (CFCs) or hydrofluorocarbons (HFCs), which can be used in conventional chillers [14].

The commercialisation of adsorption cooling technologies will significantly reduce electricity consumption and reduce emissions of greenhouse gases and ozone-depleting gases. The implementation of technologies that enable the production of chilled water without the need for using fossil fuels is particularly important not only due to their environmental friendliness, but also for geopolitical considerations. Adsorption cooling technology is still not widely used because of some disadvantages resulting from the nature of its operation, which include a low COP (coefficient of performance) of up to 0.6 in most cases and low SCP (specific cooling power) of up to 200 W/kg [15]. Considering only the parameters mentioned above, adsorption technology cannot compete with conventional cooling units whose COP is several times higher.

A chilled-water production technology, seemingly similar to adsorption, is the absorption technology. Both belong to the same group of sorption technologies, but in the case of absorption chillers, the cooling effect is generated by using a chemical compressor. Absorption chillers can be operated with low-temperature heat, but usually at a higher temperature than adsorption chillers. An important advantage of absorption chillers is continuous operation, which is a challenge with adsorption chillers which then require appropriate system design. The most commonly used working pairs in absorption cooling technology are water/lithium bromide ($\text{H}_2\text{O}/\text{LiBr}$) and ammonia/water ($\text{NH}_3/\text{H}_2\text{O}$). Commercially available absorption chillers are characterised by a slightly higher COP than

adsorption chillers, usually ranging from 0.7 to 0.85. Unlike adsorption chillers, there is a risk of crystallisation of lithium bromide salt and device failure with absorption technology.

The implementation of adsorption cooling technology is possible in many variants. It can be used in cooperation with a cogeneration system, thus creating a trigeneration [16–18] or multigeneration source [14]. A system integrating an adsorption chiller with a CHP (combined heat and power) unit offers the possibility of saving 15–20% in primary energy [18]. There are also systems where a turbine is located between the evaporator and the condenser [19]. This makes it possible to generate electricity. An exceptionally interesting configuration is the combination of solar collectors with an adsorption unit. The issue of operating an adsorption system with solar heat has been widely studied. It has been described in several references [10,11,20–23], among others. Interesting implementations are also possible in data centres where it is necessary to cool servers while at the same time generating low-temperature heat [12,24]. Adsorption chillers were considered for use in cars [25], locomotives [26] and ships [27]. Due to its unique advantages, this technology is often referred to as one that might be used in space vehicles. The use of adsorption technology for water desalination is an additional benefit, particularly relevant for a group of potential customers in countries where access to fresh water is limited and the climate is warm. The topic of adsorption desalination has been addressed in [8,28–33], among others.

The present paper addresses the issue of improving the performance of adsorption chillers by focusing on achieving this effect through the use of innovative materials, most notably composite materials with a silica gel matrix. These materials are characterised by better properties than pure silica gels that are most commonly used today, but still remain relatively inexpensive and accessible. The main objective of this paper is to review the developments in the scientific community related to the synthesis and application of these materials as a means to improve the performance of adsorption chillers at a low cost, which is required for their commercialisation. This review organises the opportunities that the use of composite materials can provide in this regard, and identifies prospects for further research.

2. Adsorption Chillers—An Overview

2.1. Theoretical Background

In a general sense, adsorption is a surface phenomenon that involves the accumulation of a fluid (adsorbate) in an interfacial layer. It can also be defined differently as a change in the concentration of the adsorbate on the surface of the sorption material (adsorbent) [34]. This phenomenon occurs due to the adhesion of the adsorbate to the surface of the adsorbent [35]. The extent of adsorption, i.e., the amount of adsorbate adsorbed, depends on the properties that characterise the sorbent material, which primarily include the size with pore volume and the specific surface area of the adsorbent. Adsorption is divided into physical and chemical adsorption. Physical adsorption is an easily reversible process that is based on the interaction of intermolecular forces (e.g., van der Waals forces) and electrostatic forces between the adsorbate molecules and the adsorbent surface [6,8,36]. In chemical adsorption, ionic or covalent bonds are formed between the adsorbate and the adsorbent [10]. The process is based on the sharing or transferring of electrons alone between molecules or on breaking them into radicals or atoms and forming bonds [37]. In contrast to physical adsorption, the bonds formed during chemical adsorption are difficult to break, so the process is hardly reversible. The heat of chemical adsorption is higher than the heat of physical adsorption [10]. Furthermore, in chemical adsorption a single layer of adsorbent is formed on the surface of the adsorbent, whereas in physical adsorption multiple layers can be formed [34].

Adsorption chillers use physical adsorption, one of the reasons being its reversible nature. The process of adsorption starts when the adsorbate vapours interact with the adsorbent surface. The adsorption process can be long and lasts at most until an adsorption equilibrium state is reached, which depends on the operating conditions of the system and the properties of the sorbent [8,18,38]. The ideal equilibrium state with reference to

the design of the unit occurs when the pressure in the evaporator is equal to that in the condenser and the temperature inside the entire bed is the same. In practice, the process must be designed so that a pressure difference exists between the heat exchangers because of the need to force the refrigerant flow in order to achieve a higher cooling capacity [18].

The adsorption process can be described by isotherms that characterise the flow of the process. The most popular isotherm models include the Dubinin–Astakhov (DA), Thoth, Freundlich, Langmuir and Brunauer–Emmett–Teller (BET) isotherms [34,39]. The shape of isotherms has been classified by the International Union of Pure and Applied Chemistry (IUPAC). Six types of isotherms are determined depending on the mode of adsorption. The characteristic feature of sorbents for which adsorption is represented by a type I isotherm is hydrophilicity at low pressures. Furthermore, the type I isotherm is characteristic of microporous adsorbents [40,41]. The type II isotherm characterises adsorption during which the binding forces between the adsorbate and the adsorbent are strong. In the case of type III isotherm, the bonds are weak and the adsorption described by a type III isotherm occurs much less frequently than a type II isotherm. Both type II and type III isotherms are characteristic of macroporous adsorbents. In the case of adsorption described by isotherms IV and V, the characteristic feature is the hydrophobicity of the material in the low pressure range, with the former occurring when the bonds are strong and the latter when the bonds are weaker and observed less frequently than the type IV isotherm. The graphs of type IV and V isotherms sometimes have a hysteresis loop associated with the phenomenon of capillary condensation. Type VI isotherms are characteristic of the multilayer adsorption process [40].

2.2. Principle of Operation of an Adsorption Cooling System

A typical adsorption cooling system consists of three basic components, i.e., an evaporator, an adsorbent bed and a condenser. In the bed, which is filled with a porous sorption material, the phenomena of adsorption and desorption alternately occur. In the first stage of the cycle (A-B), initial isosteric heating of the bed with heat Q_{h1} takes place. The pressure in the bed increases to the value of P_{cond} . Then, with a further supply of heat energy Q_{h2} to the bed, isobaric endothermic desorption of the refrigerant is carried out (B-C). The temperature inside the bed rises to T_{des} . The desorbed adsorbate vapour leaves the bed and is condensed in the condenser. Once the desorption process is completed, isosteric cooling of the bed begins before the adsorption process (C-D). The pressure in the bed then drops to the P_{eva} value. Isobaric exothermic adsorption of the adsorbate then takes place (D-A). During the adsorption of the refrigerant on the adsorbent, the heat of adsorption Q_{ads} is released in the bed as a result of the conversion of the latent heat of the refrigerant vapours into sensible heat. Consequently, the bed is cooled to a temperature of T_{ads} . The cooling effect is achieved in the evaporator by absorbing the heat of vaporisation. A simplified flow diagram of the adsorption/desorption cycle in an adsorption chiller is shown in Figure 1.

An adsorption chiller, like any technical appliance, can be characterised by performance parameters, which primarily include COP and SCP. The coefficient of performance is the ratio of the enthalpy of adsorption and the enthalpy of desorption [42]. It is interpreted as a measure of the energy conversion efficiency of the system; in practical applications it is defined as the ratio of the cooling capacity and the total thermal power (the quotient of the energy that was received in the evaporator and the energy supplied in the process of desorption of the refrigerant) [10]. Although there is a limit to the achievable theoretical COP value [42], there are many possibilities to approach it from the typical COP value of adsorption chillers.

The cyclic operation of the thermal compressor and the low heat transfer coefficient of the sorbent account for the low COP value and relatively low SCP value of adsorption chillers [43]. Methods to improve these are being researched and developed by groups of researchers around the world. The large-scale implementation of adsorption cooling technologies is disadvantaged by the higher unit price and larger size and weight as compared

with competing technologies or the most commonly used conventional equipment with the same cooling capacity [14].

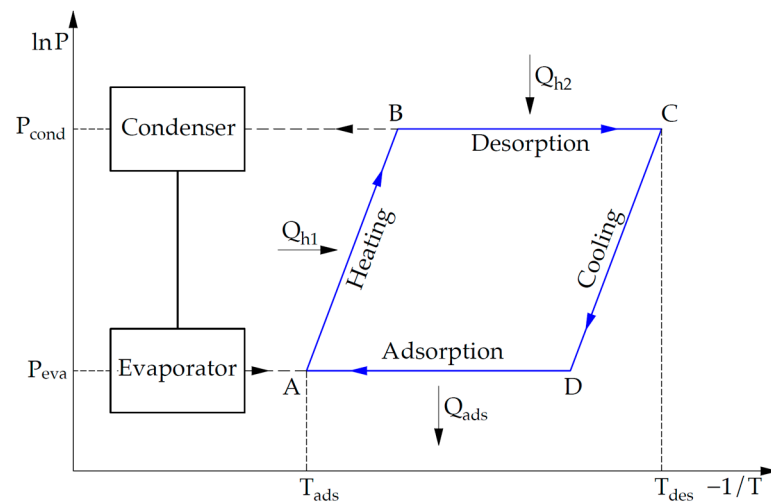


Figure 1. Simplified flow diagram of the adsorption/desorption cycle in an adsorption chiller.

2.3. Improvement of Performance Parameters of Adsorption Chillers

Adsorption cooling technology has developed greatly in recent years in many areas as a result of research work carried out by scientific teams in many research centres around the world. The low performance characteristics, including low COP, are often cited as the main disadvantage of adsorption chillers. It is true that a typical COP of adsorption systems (up to 0.6) is lower than that achieved for traditional mechanical compressor chillers (around 3–5) or even absorption chillers, especially those operated by steam (around 0.7–1.4). However, it should be borne in mind that the heat supplied to adsorption chillers can be almost entirely free.

Performance values of adsorption chillers are determined by a number of factors, the main ones being the operating parameters of the chiller and its design. Over many years, researchers have developed, tested and described many methods to improve performance parameters of adsorption chillers. These methods can be divided into those for which the application involves structural changes and those that only require changes in the operating parameters of the device. The former include increasing the number of beds, the use of multiple compression stages, modifications to the design of heat exchangers or changes related to the sorption material, while the latter occur when operating parameters are modified, such as flow rates and temperatures in the chilled, cooling and hot water circuits. In general, methods for improving performance parameters can be grouped according to the following division:

- Improvement of adsorbent properties that are beneficial for their use in adsorption chillers;
- Modification in the design of the heat exchanger in the adsorbent bed;
- Optimisation of the operating parameters of the adsorption unit;
- Modification in the cooling system, e.g., by using two or more adsorbent beds, using multistage systems, using either one or more refrigerant evaporation stages and using a redesigned cooling cycle.

2.3.1. Optimisation of Operating Parameters of an Adsorption Chiller

The performance of an adsorption chiller depends on many factors and is the result of correlations between many operating parameters, including flow rate and temperature in the chilled, cooling and hot water circuits. In many publications, researchers have presented correlations between the individual operating parameters and performance parameters. A few of these are summarised below.

- A higher heat-source temperature results in a higher COP and higher cooling capacity. This increase can generally be limited to temperatures of approx. 80–90 °C [44–46].
- A lower condenser cooling water temperature with constant heating and chilled-water temperatures results in higher SCP and COP values [45].
- A higher chilled-water temperature at the evaporator inlet has a positive effect on the cooling capacity value and COP of the adsorption chiller under constant heating and chilled-water temperatures [46].
- A higher chilled-water flow rate results in an increase in COP and cooling capacity [47].
- A higher heating-water flow rate results in an increase in cooling capacity and a decrease in COP [47].

Research into the optimisation of operating conditions can be carried out in the form of experimental studies or numerical simulations. The first method allows for verification in the actual system, but it is very time-consuming and expensive, and also limited in terms of the number of verifiable operating configurations of the adsorption chiller. A modern method of optimisation is to perform it using neural networks [48]. An exceptionally interesting development towards optimising the operation and increasing the efficiency will be to simulate the operation of an adsorption chiller using its digital twin. Such studies have already been presented in [49], among others. The implementation of such solutions will make it possible to quickly predict the operating parameters under different conditions.

2.3.2. Modification in the Design of Heat Exchanger in the Bed

Design changes include modifications to the design of the heat exchangers in the system, primarily in the adsorbent bed. The search for the most advantageous design of the heat exchanger in the bed is related to the need to intensify heat exchange between the exchanger material and the sorbent. Many options have been developed to achieve better heat transfer by increasing the surface area of the exchanger. The focus has been on modifications in classically used exchangers, including the use of fins, the search for the optimum height [15,50,51], thickness [52], shape [51] and distance between them [15,51–53]. Numerous numerical simulations and experimental work have been carried out by a number of researchers in this area, the results of which have been presented in publications [15,50–53], among others. Different types of heat exchangers have been considered, such as finned-tube heat exchangers with ring-shaped fins, plate-fin heat exchangers, flat-tube heat exchangers and others [15]. Heat exchange in the bed occurs primarily by conduction and convection [54]. Approximately 25% of the total thermal resistance relates to heat exchange at the interface between the heat exchanger and the sorption material [55]. Reducing its impact on the performance of the unit can be achieved by coating the surface of the heat exchanger in the bed with a sorption material [56]. The possibilities of using binders and their effect on sorption capacity and heat transfer increase were analysed in [56–61].

2.3.3. Multibed Adsorption Chillers

Adsorption chillers with a single adsorbent bed are rare, mainly for experimental studies in a laboratory environment. In design practice, multibed chillers are used because of the higher stability of cooling production and higher cooling capacity as compared with a single-bed unit [37]. Multibed systems also have a higher efficiency in low-temperature heat recovery [62]. Chua et al. carried out a simulation study of an adsorption chiller with four and six beds. The authors obtained an increase in the efficiency for waste heat recovery of 70% for the four-bed unit compared with the two-bed unit, and 40% for the six-bed unit compared with the four-bed unit [62]. Saha et al. achieved heat recovery higher by 35% in a three-bed chiller compared with a two-bed chiller. They also reported that the chilled-water temperature for the three-bed chiller was more stable than for the two-bed one [45]. In [63], Sztékler et al. compared test results for a three-bed chiller and compared its performance parameters with a two-bed chiller. They indicated that when the desorption temperature is higher than 75 °C, the COP is higher for the three-bed chiller in comparison with the

two-bed unit. The maximum COP improvement was 16% for a heating-water temperature of 85 °C [63].

2.3.4. Multistage Chillers

Adsorption chillers with more than one vapour compression stage are a good solution for achieving high efficiency at low temperature (although the achievable COP will be higher for a single-stage chiller). Such systems work well when the heat supply source temperature is below 70 °C. A large number of stages is a particularly recommended solution when the difference between the evaporator and condenser pressures is more than 20 kPa [64]. Multistage chillers can recover heat at a lower temperature than single-stage chillers. According to the results published by Mitra et al. [65], desorption is theoretically possible in a two-stage adsorption chiller at a temperature of 42–48 °C, and in a single-stage chiller at 48–62 °C [65].

2.3.5. Process Modifications to Adsorption Chiller Operation

Process changes include, among other factors, modification in the cooling cycle and the selection of appropriate duration of the processes of adsorption and desorption, and of the preheating and cooling of the beds. The basic adsorption cooling cycle is characterised by very low efficiency [66]. In order to improve it, modifications to the cycle are used. The simplest is heat recovery to prevent heat loss or enable more efficient heat utilisation [37,46,67,68]. Another method is mass recovery, whereby the pressure in the beds is either reduced or increased before the relevant phases of the cycle by connecting them directly to each other [7,37,69,70]. More complicated methods include thermal wave cycle, forced convection thermal wave cycle and cascade cycle [36,66,71–73]. The selection of the correct duration of adsorption, desorption and preheating and cooling of the beds has a very significant impact on the performance parameters of adsorption cooling systems [74]. It depends on the operating conditions of the unit [44]. A number of studies have found that COP increases with increasing cycle length while for SCP there is a point at which its maximum is reached [75]. For example, Sztékler et al. [75] investigated an experimental adsorption unit operating in two-bed mode with the pair silica gel (with copper added) and water. For the longest time of 600 s, they obtained the highest COP value of 0.6. The highest SCP value of 148.87 W/kg was recorded for a cycle time of 300 s [75]. Chang et al. [47] tested a single-bed adsorption chiller with silica gel–water as the working pair during which the maximum COP of 0.53 was obtained at the 6th minute of the cycle (the cycle lasted 7 min) and the maximum cooling capacity between 4 and 5 min [47]. In other publications, it was also demonstrated that the performance parameters are positively influenced by the shortening of desorption relative to adsorption [76]. Glaznev and Aristov [76] reported that the desorption process can take place 2.2–3.5 times faster than the adsorption process.

2.3.6. Selection of the Working Pair

An important aspect from the point of view of chiller performance is the appropriate selection of the adsorbent–adsorbate working pair [77]. The choice of working pair depends primarily on the application of the adsorption unit because, firstly, adsorbates are designed to operate under different conditions and, secondly, each adsorbent–adsorbate pair is characterised by different properties, e.g., adsorption heat, regeneration temperature or adsorption capacity. Among other factors, the choice of working pair is influenced by the temperature of the chilled water, the temperature of the heat source and the pressure nature of the system [77]. The characteristics of the individual working pairs are described in a later section.

2.3.7. Improving the Properties of Adsorbent Materials

This paper is devoted to collecting and describing the achievements to date in the search for low-cost and accessible adsorbents that show improved adsorption capacity and boost heat transfer within the bed. The focus is on composite materials based on

silica gel impregnated with inorganic salts. However, due to the vast range of issues related to adsorbents, it is worth directing more attention to the possibilities for improving their properties. Therefore, in this section the authors describe some known methods of improving the properties of sorption materials that are of crucial importance with regard to the adsorption chiller requirements.

Sorption materials have a unique impact on the performance of any adsorption cooling system. A poor performance by such a system is typically caused by poor mass flow and heat transport through the bed as well as the low adsorption capacity of the sorbents [10]. The highest heat resistance in a bed occurs in the sorption material [52]. The very low thermal conductivity of porous adsorbents prevents efficient heating and cooling in the bed. The poor effective thermal conductivity in the sorbent is due to its porosity and the fact that the voids between the grains are filled with a static gas [56,78,79]. The selection of the adsorbent is therefore particularly important. It is necessary to seek a compromise between a high sorption capacity and a good thermal conductivity of the material. There is ongoing research in the field of materials engineering aimed at finding sorbent materials with the best possible adsorbate adsorption capacity and the highest possible thermal conductivity coefficient. Another interesting direction of research into composite sorbents includes considerations on combining the most common adsorbents to form composites, such as activated carbon with zeolite or activated carbon with silica gel and CaCl_2 salt [80]. The topic of composite sorbents with a silica gel matrix is described in more detail in a later section.

Improved heat transfer in the bed can be achieved by reducing the grain size of the adsorbent, compacting the bed (reducing the volume occupied by the sorbent) or coating the sorption material onto metal foams [55,79,81]. However, the aforementioned methods imply achieving inferior mass exchange [55]. One way that has been considered for achieving better heat transfer with only a slight deterioration in mass transfer is by admixing the sorbent with a material that has a higher thermal conductivity coefficient than the sorbent itself. Many researchers have taken action in this area. Different types of additives in the form of powder, chips, filings or chunks have been considered, and the most favourable ratio of additive to sorbent has been sought [81–83]. For example, Demir et al. [81] published results on the addition of metal pieces (aluminium, copper, brass and stainless steel) to silica gel. Askalany et al. [82] verified the effect of the addition of aluminium, copper and iron in the form of filings to activated carbon with a mass fraction of 10 to 30%. Sztékler et al. [83] investigated the effect of additions of powdered aluminium, copper and carbon nanotubes to silica gel on the kinetics of water vapour sorption and adsorption capacity by the materials prepared. A particularly interesting issue was addressed by Eun et al. in the two parts of their publication [84,85], which are devoted to analysing the issue of consolidation of adsorbent composite blocks composed of silica gel and expanded graphite. Thus, the authors addressed simultaneously the issue of additives resulting in improved heat transfer to the sorbent and the consolidation of the bed resulting in a reduced volume filled with a static gas with very low thermal conductivity. Different conditions of manufacturing of composite blocks (moulding pressure) and different fraction percentages of expanded graphite (20–40%) were used [85]. It was found that the addition of graphite improved heat transport in the entire composite block, which was above $10 \text{ W m}^{-1} \text{ K}^{-1}$ (by way of comparison, a bed filled with silica gel only has a thermal conductivity of $0.17 \text{ W m}^{-1} \text{ K}^{-1}$) [84], and the use of a consolidated composite block improves cooling capacity as compared with a granular silica gel bed [85]. The selection of the optimum moulding pressure and fraction of expanded graphite is crucial for mass and heat transport in the bed. In this study, the authors considered a silica gel block with a 30% fraction of expanded graphite moulded at a pressure of 8 MPa to be optimal [84,85].

A very interesting composite sorption material is a combination of powdered silica gel with additives improving thermal conductivity and with a binder. A study on this type of composite sorbents was carried out by Hua et al. and published in [86]. The authors prepared composite materials based on silica gel with the addition of nano-copper, alu-

minium nano-oxide, carbon nanotubes and graphite powder, and the polyvinylpyrrolidone (PVP) binder. The samples were found to have higher thermal conductivity than pure silica gel, with the greatest improvement observed for the addition of nano-copper, achieving up to 185% increase. It was also found that the adsorption properties deteriorated only slightly [86]. Younes et al. [87] reported the results of a study on consolidated RD-type silica gel powder with the addition of four binders: hydroxyethyl cellulose (HEC), polyvinyl alcohol (PVA), PVP and gelatine. The sorption and thermal properties of the resulting composite materials were investigated for different weight fraction percentages of the additives. It was found that 2% additive had the best sorption properties among the additives with other mass fractions, and had almost no effect on the sorption capacity relative to the parent material. The addition of PVP at a mass fraction of 2% resulted in a 32% increase in thermal conductivity compared with pure silica gel [87].

3. Adsorbents, Adsorbates and Working Pairs—An Overview

3.1. Adsorbents

As shown in the previous section, improving the performance of adsorption chillers is a very broad issue. One of the biggest challenges in this area is work on finding adsorbents with properties that are particularly relevant to the sorption processes that take place. These include in particular a relatively high thermal conductivity coefficient and good sorption capacity.

Adsorbents are hydrophilic porous sorption materials with a strongly developed specific surface area. They should be hydrophilic at lower temperatures and exhibit hydrophobic characteristics at higher temperatures [8]. The characteristics defined for an adsorbent meeting the requirements necessary for achieving maximum adsorption chiller performance are [8,10,36,88,89]:

- Good affinity of the adsorbent to the adsorbate;
- Low regeneration temperature (evaporation of the adsorbate from the surface of the adsorbent);
- Adsorption capability of the adsorbate at low temperatures and low relative pressures;
- Large specific surface area;
- High porosity;
- High thermal conductivity coefficient;
- Ability to maintain stability of properties over time;
- Ability to adsorb a maximum amount of adsorbate per unit mass of sorbent;
- Nontoxicity;
- Nonflammability.

In addition, the adsorbent should also be characterised by an adequately high mechanical strength [56]. It should also be readily available and inexpensive. One of the key characteristics of sorption materials is porosity. Pursuant to the IUPAC classification, pores are divided according to their width into micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm) [90]. Inside mesopores, multilayer adsorption occurs while the interior of macropores is completely filled with the adsorbate [91].

The sorbents most commonly used in practice today are characterised by good sorption properties, but do not provide adequate heat transport in the bed. A porous sorbent material is characterised by a low thermal conductivity coefficient, and when considering heat transport in the bed, one must also take into account the voids between the adsorbent grains that are filled a static gas, further increasing the overall thermal resistance of the bed. Although it does not positively affect heat transport, porosity is important from the point of view of the diffusivity of refrigerant vapours.

3.1.1. Silica Gel

Silica gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is the most commonly used adsorbent in adsorption chillers. It is an amorphous and synthetic silica derived from colloidal silica combined with particles of hydrated SiO_4 [6]. The structure of silica gel consists of spherical particles ranging in

size from 2 to 20 nm [92]. The widespread use of silica gel in adsorption technologies is due to the combination of its relatively good sorption properties with good market availability and low price. Silica gel can form a working pair with water. Furthermore, it can be used in devices with desalination function. Silica gels are characterised by good mechanical properties, which are essential considering the durability of the preservation of the original properties, but they are poor heat conductors as their thermal conductivity coefficient is most often in the range $0.13\text{--}0.17\text{ W m}^{-1}\text{ K}^{-1}$ [93]. In addition, they are thermally stable and ensure the possibility of regeneration at low temperatures, ranging from $55\text{ to }140\text{ }^{\circ}\text{C}$ [8]. Regeneration of an adsorption chiller bed filled with silica gel occurs at temperatures below $90\text{ }^{\circ}\text{C}$ [94]. The specific surface area of silica gels is typically between 100 and $1000\text{ m}^2/\text{g}$ [6]. There are different types of silica gels classified according to the size of the pores. These include type A, type B, type RD and type 3A silica gel [91,95]. The basic properties of selected commercially available silica gels are shown in Table 1. Silica gel is most commonly used in the form of irregularly shaped grains or sphere-like grains with a size of 1–4 mm [56]. Figure 2 shows SEM (scanning electron microscope) images of typical silica gels used in adsorption chillers.

Table 1. Commercially available silica gels.

	Specific Surface Area (m^2/g)	Pore Volume (cm^3/g)	Source
Silica gel Fuji Davison Type A	650	0.36	[92]
Silica gel Fuji Davison Type 3A	606	0.45	[92]
Silica gel Fuji Davison Type RD	650	0.35	[92]
Silica gel Type-RD 2560, Fuji Silysia	636.4	0.314	[90]
Silica gel Type-A5BW, KD Corporation	769.1	0.446	[90]
Silica gel Type-A++, Mayekawa	863.6	0.476	[90]
Silica gel Davisil Grade 646	300	1.15	[96]
Silica gel Grace SP2-8506	340	0.9	[97]

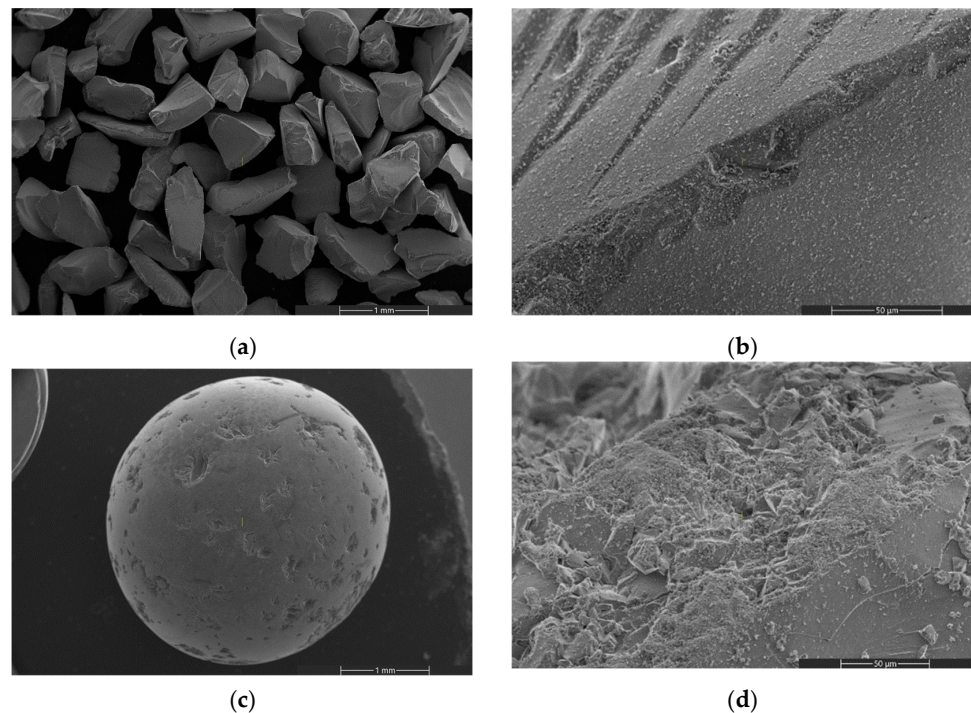


Figure 2. SEM images of silica gels: (a) irregularly shaped (80 $\times$); (b) irregularly shaped (2000 $\times$); (c) spherically shaped (80 $\times$); (d) spherically shaped (2000 $\times$).

As a very attractive and widely used sorbent, silica gel is often investigated in adsorption chillers and selected for commercial applications. Additionally, methods to improve its properties are widely studied. Wang et al. [68] presented the proposals put forward in this regard so far. An interesting economic analysis was presented by AL-Hasni and Santori [98] in which they compared the cost of 1 kW of cooling considering the use of different adsorbents including modern ones. It was concluded that none of them could compare with silica gel in terms of economic viability due to its price, which ensures the most inexpensive cooling production [98]. Examples of using silica gel in working pair with water in an adsorption chiller are presented in Table 2 together with the basic system parameters.

Table 2. Examples of adsorption cooling units using silica gel/water working pair.

Location	Working Pair	Cooling Capacity (kW)	COP (-)	Heat-Source Temperature (°C)	Source
Cracow, Poland	Silica gel–water	1.1	0.6	75–85	[75]
Tokyo, Japan	Silica gel–water	3.54	0.34	55	[99]
Shanghai, China	Silica gel–water	8	0.4	85	[100]
Messina, Italy	Silica gel–water	10	up to 0.6	65–85	[101]

3.1.2. Zeolites

Zeolites are defined as microporous aluminosilicate minerals formed from tetrahedral crystals of aluminium silicate [6,41]. Depending on their origin, they can be divided into natural and artificial. There are about 40 types of natural zeolites [6]. In terms of porosity, uniformity of pore size distribution and purity, synthetic zeolites perform better [6]. To date, more than 150 types of synthetic zeolites have been developed, and each is characterised by different properties and therefore performs best under specific conditions, e.g., depending on the regeneration temperature [6,41]. In practice, the most commonly used zeolites are molecular sieves 4A, 5A, 10X and 13X [6]. Because of their favourable sorption properties, zeolites can be used in adsorption chillers supplied with both low-temperature heat and medium-temperature heat. Desorption of water from the surface of the most commonly used zeolites is carried out at relatively high temperatures of 175 to 370 °C, which therefore limits their use to some extent [8]. However, there are zeolites being developed that require lower temperatures for desorption. Like silica gel, zeolites have a poor effective thermal conductivity of 0.07 to 0.13 W m^{−1} K^{−1}, but they are more stable [102,103]. The thermal conductivity of zeolites can be increased by creating zeolite composite materials, e.g., aluminium foam/zeolite composite materials or mixtures of zeolites with materials with a higher thermal conductivity coefficient [104]. Zeolites have good adsorption capacity. For example, zeolite 13X, which is popular in cooling applications, is characterised by a sorption capacity determined for water per unit mass of sorbent of 0.23 g/g [105]. An increase in adsorption capacity even by several times can be achieved by synthesising composite materials, such as combining zeolites with lithium chloride (LiCl) or calcium chloride (CaCl₂) [106]. For example, Chan et al. [107] investigated a composite with zeolite 13X and calcium chloride, for which up to 420% increase in adsorption capacity was achieved in comparison with pure zeolite 13X. By means of simulations, the effect of using the composite on the performance parameters of the adsorption chiller was also assessed, and an 81% higher COP and 34% higher SCP were achieved in comparison with a bed of pure zeolite 13X [107]. Zeolites can be modified according to the properties relevant to a specific application, e.g., by changing the Si/Al ratio and thereby influencing material characteristics including hydrophilicity

(when the ratio decreases, the adsorption capacity of the sorbent increases) [41]. Currently, particular attention is given to aluminophosphates (AIPOs) and silica-aluminophosphates (SAPOs) [108]. These are materials similar to zeolites, characterised by a lower regeneration temperature in the range 60–100 °C and a high water adsorption capacity [102]. Popular commercial materials are those developed by Mitsubishi Plastic Inc. AQSOA®. Among others, AQSOA-Z02 is expected to replace silica gel in adsorption chillers. Youssef et al., showed in an experimental study that using it instead of silica gel can improve SCP by 180% [39]. One example of zeolites operating at <100 °C is also FAM-Z01, which has a water sorption capacity per sorbent unit of 0.17 g/g. Its regeneration can take place at 50–85 °C [109]. Figure 3 shows SEM images taken for commercially available and zeolite molecular sieves used in adsorption systems.

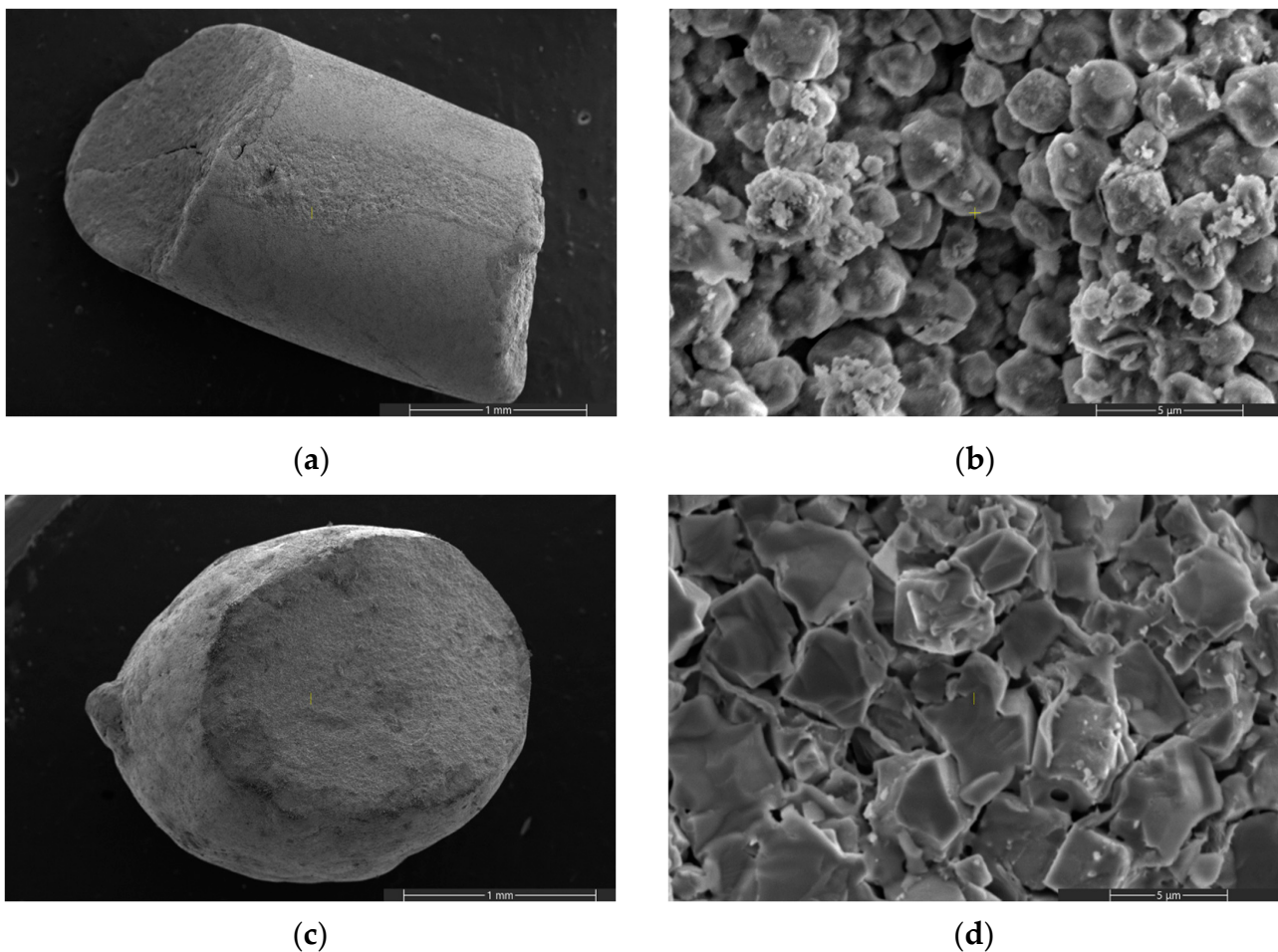


Figure 3. SEM images of zeolite molecular sieves: (a) 13X (120×); (b) 13X (20,000×); (c) 4A (130×); (d) 4A (16,000×).

3.1.3. Activated Carbon

The use of activated carbon as an adsorbent is very common due to its microporous structure and attractive adsorption capacity [95]. Activated carbon can be formed by carbonisation of materials of natural origin, such as wood, coal or peat, at high temperatures of 700–800 °C [6]. After the carbonisation process, the carbon still needs to be activated by air or steam gasification in order to develop the specific surface area [110]. Regeneration of an adsorption chiller bed filled with activated carbon takes place at temperatures above 100 °C [56]. Activated carbons are characterised by a low effective heat transfer coefficient and an adsorption capacity per unit mass of sorbent of approx. 0.3 kg/kg [111]. The specific

surface area of activated carbons ranges from 500 to 1500 m²/g [91]. Figure 4 shows SEM images taken for commercially available activated carbon.

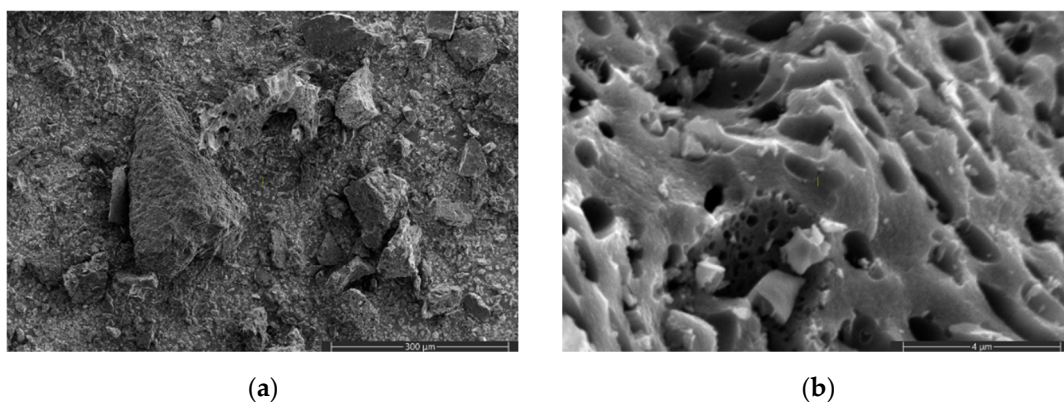


Figure 4. SEM images of activated carbon: (a) activated carbon (480 $\times$); (b) activated carbon (32,000 $\times$).

3.1.4. Metal–Organic Frameworks

The most commonly used adsorbents in the form of various types of silica gels or zeolites are relatively good materials that have been proven in industrial applications. Their most serious disadvantages are poor heat conductivity and poor adsorption properties at low relative pressures [112]. Some of the most promising types of modern adsorbents being considered for application are metal–organic structures (MOF). MOFs structurally consist of metal ions linked by organic ligands [56]. They are characterised by extremely high porosity, a large pore volume and a highly developed specific surface area of 1000–10,000 m²/g, and the ability to finely control pore size and keep the size constant [112–114]. Recently, many researchers have focused on synthesising organometallic structures and analysing the possibility of using them in adsorption cooling systems. For example, aluminium fumarate, MIL-100 (Al), MIL-101, CAU-10-H and HKUST-1 have been selected for use in adsorption refrigerators [57,115]. Among others, Elsayed et al. [116] investigated the possibility of using aluminium fumarate in an adsorptive desalination system. Aluminium fumarate is particularly attractive because of its low desorption temperature, high water adsorption capacity, large pore surface area and the possibility to produce it on a mass industrial scale through an easy synthesis process [116,117]. Ma et al. [118] used simulation to determine the properties of the MIL-101–ethanol working pair, obtaining ethanol adsorption per unit mass of adsorbent equal to as large as 1.2 kg/kg. Saha et al. [119] determined the sorption properties of MIL-101Cr paired with ethanol and found that its adsorption capacity was as large as 1.1 g/g at 30 °C. Further, MIL-101Cr paired with water can achieve an adsorption capacity of 1.43 g/g [120]. Dakkama et al. performed tests in a system of desalination and chilled-water production with a single-bed chiller and CPO-27 (Ni)-water pair where the system was fed with seawater, achieving a COP of 0.9 [121]. Even though MOFs are superior to other types of sorbents, they are not currently widely used in cooling due to their high cost.

3.2. Adsorbent–Adsorbate Working Pairs

Adsorbents should be described considering the adsorbates with which they form a working pair. An ideal adsorbate should have the following characteristics [88,89,91]:

- High latent heat per unit volume;
- Low evaporation temperature;
- Small particle size;
- Low viscosity;
- Low specific heat;
- High thermal conductivity;
- Small volume in liquid state;

- Chemical and thermal stability;
- No negative impact on the environment;
- Nontoxicity and nonflammability.

In practice, it is impossible to find an adsorbate that meets all of the above requirements. The most commonly used adsorbates are water, ammonia, ethanol and methanol. Water is an exceptional adsorbate due to its obvious environmental friendliness and good thermal properties. It is characterised by thermal stability and high latent heat of vaporisation of 2258 kJ/kg [91,122]. A disadvantage of using water as an adsorbate affecting the design aspects of adsorption chillers is the need to operate the system under vacuum conditions. Water is most commonly used when silica gel or zeolite is the adsorbent. Methanol is toxic and highly flammable, requiring special care and attention [10]. It has inferior thermodynamic properties compared with water. Among other things, it is characterised by an approximately twice lower heat of vaporisation [91]. However, it enables the production of chilled water with a temperature below 0 °C. Ammonia works in systems where overpressure conditions must prevail [102]. It is characterised by the lowest thermal stability of the adsorbates discussed [10]. Like methanol, it is toxic [110].

Appropriate selection of the working pair is extremely important from the point of view of chiller efficiency. The course of adsorption and desorption in which the performance parameters of the adsorption chiller depend is related to the sorption kinetics, the shape of the isotherms and the value of the isosteric heat of adsorption [32]. These factors vary depending on the working pair used. The heat of adsorption is a particularly important characteristic in terms of the operating conditions of the equipment as the amount of heat required for the desorption process depends on it. The most commonly used working pairs are silica gel with water, zeolite with water and activated carbon with methanol [72].

The working pair most often chosen is silica gel–water. It is characterised by a high heat of adsorption of approx. 2800 kJ/kg and a low desorption temperature of approx. 50 °C to 120 °C (typically 60–90 °C) [91,123]. When using the silica gel–water pair, it is not possible to produce chilled water with a temperature below 0 °C. The combination of silica gel and water requires maintaining low pressure in the system as the working pressure for this pair is 0.01–0.3 bar [36]. The adsorption capacity of water on the surface of silica gel depends on the pore width of the sorbent [8]. Ng et al. [8] reported obtaining the highest water adsorption capacity for silica gel with a pore width of 0.8–1 nm (up to 0.2 kg/kg) [8]. In adsorption cooling technologies, zeolites are most commonly used in pair with water, but they can work with all of the most common refrigerants. The zeolite–water working pair is distinguished by its high adsorption capacity [102]. Its characteristic feature is its high desorption temperature of 250–300 °C [123]. Water adsorption can occur at temperatures below 80 °C [66]. The heat of adsorption for zeolite–water pair is approx. 3300–4200 kJ/kg [6,36]. As with the silica gel–water working pair, it is impossible to produce chilled water with a temperature below 0 °C. The working pressure in a system with zeolite–water working pair should be 3.4–8.5 bar [36]. Due to the high heat of adsorption and high desorption temperature, a longer cycle time is required for this pair [91]. In contrast, the activated carbon–methanol working pair is characterised by a low heat of adsorption of 1800–2000 kJ/kg [91]. Regeneration of the bed in this case occurs at a temperature of approx. 100 °C, up to a maximum of 120 °C (above 150 °C, an increase is observed in the catalytic properties of activated carbon in the reaction of converting methanol to dimethyl ether) [81,124]. The use of the activated carbon–methanol pair makes it possible to produce chilled water with a temperature below 0 °C, but in this case it is necessary to maintain vacuum conditions in the system [36,91]. According to a literature review, the highest methanol adsorption is obtained for Maxsorb-III activated carbon and is 1.24 g/g [125]. The working pressure in a system with the activated carbon–methanol working pair is 0.01–0.35 bar [36]. On the other hand, the combination of activated carbon and ethanol enables regeneration of the bed at temperatures below 100 °C [126]. In [126], El-Sharkawy et al. analysed the combination of Maxsorb-III activated carbon with ethanol and obtained an adsorption capacity of 1.2 kg/kg. Activated carbon can also be combined

with ammonia. Regeneration of the bed then occurs at temperatures even above 200 °C and the working pressure in the system is 3–16 bar [36,91]. The heat of evaporation for this pair is equal to 2000–2700 kJ/kg [123]. The overpressure improves the performance of the system. However, this working pair is not frequently used due to the toxicity of ammonia and the fact that ammonia is incompatible with copper [6,91]. Activated carbon can also work with refrigerants such as R-32, R-134a, R-507A, n-butane and CO₂ [95]. A little-known working pair is also formed by combining activated alumina with water. The heat of evaporation for this pair is 3000 kJ/kg [123]. Regeneration of the activated alumina bed is carried out at temperatures between 120 and 260 °C [8]. In [102], the authors compared working pairs for their use in adsorption cooling and heating systems. For air-conditioning purposes, the sorbents AQSOA®-FAM-Z02 and the composites silica gel with LiBr and silica gel with CaCl₂ were selected as the most promising for working with water [102].

Many authors have published thorough literature reviews regarding the possible working pairs for adsorption cooling. Among others, Shabir et al. [95], Askalany et al. [6], Freni et al. [102], Wang et al. [91], Younes et al. [110], Boruta et al. [58] and Shmroukh et al. [127] have published comprehensive reviews of working pairs. From time to time, new review publications on this topic are published in order to update the current knowledge and present the latest developments.

4. Sorption Composite Materials with Silica Gel

In the 1990s, a new type of composite sorbents was reported in the form of adsorbents impregnated with inorganic salts and characterised by a significantly higher adsorption volume compared with their porous matrix. Since then, research in this area has been intensified, the effect of which were results obtained for different salts with different mass fractions in the composite. Research into the new composite sorbents has also been carried out in actual adsorption systems. This publication focuses exclusively on the analysis of the available knowledge in the field of silica gel composite adsorbents because the authors considered this material to be the most promising porous matrix, requiring the most attention.

Figure 5 shows the change in the number of publications and citations since the beginning of the 21st century on the topic of composite adsorbents, but with a silica gel matrix. The graph confirms the topicality and interest in the topics concerned. A very clear trend can be seen towards an increase in citations year to year. Although the highest number of publications on this topic was produced in 2012, there is now a clear upward trend, which means that interest in the topic of composite sorbents with a porous matrix in the form of silica gel will increase in the years to come.

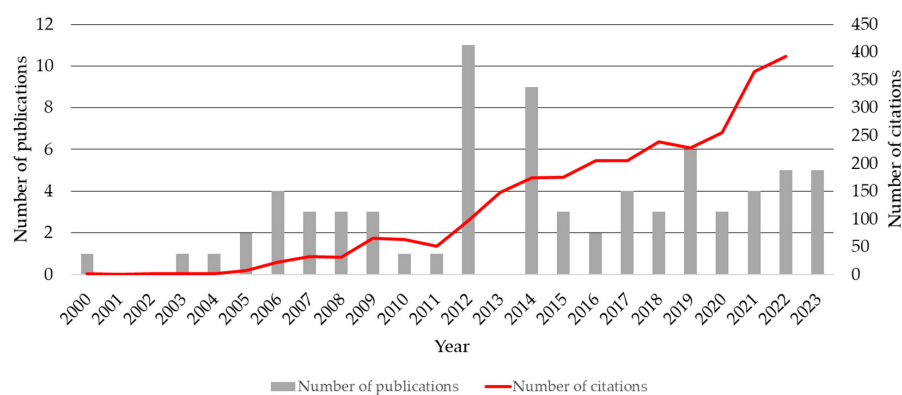


Figure 5. Number of publications and citations since the beginning of the 21st century in the field of composite adsorbents with a silica gel matrix [128].

The problem of explaining what sorption composite materials are essentially relates to the basic definition of composite materials, according to which they are materials composed of two or more materials with different properties. A more detailed analysis of this issue

requires the division of sorption composite materials into several separate areas. The first approach is to focus mainly on improving the effective heat transfer in the bed. The second approach is to focus on improving adsorption of the adsorbate. Being composed of two types of materials with a wide spectrum of properties, composite materials enable the synthesis of materials with properties tailored to the conditions under which the system will operate [129]. One of the types of composite materials is sorbents that include a hygroscopic substance in addition to the porous matrix. These materials are formed by combining the parent porous material and an inorganic salt that is impregnated inside the pores of the porous material [130]. As a result, a sorbent characterised by exceptionally high water adsorption per unit mass of the sorption material is obtained. This includes the SWS (selective water sorbents) family of materials which are characterised by a significantly higher adsorption capacity compared with the most commonly used silica gel [131].

4.1. Methods of Synthesis

The synthesis of porous composite materials with inorganic salts is not very complicated, but requires careful selection of the porous matrix and the salt content of the solution. The process of synthesis involves impregnating the porous matrix with an inorganic salt solution. It is usually preceded by drying of the impregnated sorbent to completely desorb water from the pore surface [132]. Impregnation is followed by filtration and drying of the composite until no change in material mass is observed [133,134]. Impregnation can be divided into two types, dry and wet. Dry impregnation involves using only such an amount of salt solution that is equal to the previously determined pore volume of the porous material being impregnated. The advantage of this method is the rapid penetration of the solution into the solid phase and the lack of need to use drainage of excess water after the process. The dry method, however, requires prolonged soaking in the salt solution in order to evenly distribute the salt ions in the porous matrix. Wet impregnation occurs when the volume of the solution is larger than the pore volume of the porous sorbent being impregnated [134,135]. It is then necessary to remove the excess solution by filtration or vacuum drying [134,136]. Sorbents are typically impregnated with a single-component salt solution, but impregnation with a two-component solution is also possible. The advantage of such a solution is that the properties of the composite synthesised can be more accurately matched to the conditions in which it will be operating [134].

One of the most serious problems occurring after the synthesis of composite sorbents is the blockage of adsorbate flow through the pores or a reduction in pore volume relative to the pore volume of the base material. For wet impregnation, the problem of salt deposition on the outer surface of the sorbent material has also been noted. In this regard, Gong et al. [137] presented the solution they used, which involved placing the composite under conditions of high humidity (90%) and constant temperature so that the salt would take up water, transform into a solution and flow onto the sieve [137]. Yu et al., in turn used vacuum filtration to remove excess salt during the testing described in [138]. However, as a result of the treatment of the material after impregnation, the mass fraction of salt in the material is reduced [137,138]. Therefore, it seems that the best solution is to properly design the material synthesised and optimise the inorganic salt content [138]. It should be noted that the properties of composite sorbents change depending on the content and type of salt in the base material. Among others, in [139], the authors verified the influence of salts (CaCl_2 , CuSO_4 , MgSO_4 and Na_2SO_4) and their mass fractions on the sorption properties of the composites obtained.

4.2. Mechanism of Adsorption

The mechanism of sorption inside composite sorbents differs from classical adsorption on silica gels and other adsorbents. Such a high sorption capacity is due to the interactions between the refrigerant and the salt in the pores of the sorbent. Adsorption on the surface of the matrix plays the least important role, accounting for 3–5% of the total sorption. Two

mechanisms are important, absorption of solids (responsible for 10–15% of sorption) and absorption of liquids (responsible for approx. 80% of sorption) [140].

In general, the mechanism of sorption for composite sorbents consists in the first place of physisorption, then the formation of salt hydrates, then salt solution filling partially or completely the pores [140]. If the porous matrix being impregnated is a mesoporous material, then according to analyses, a salt crystalline phase is formed inside the mesopores, usually with a size close to the pore diameter. Water sorption then leads to the formation of stable crystalline hydrates ($\text{salt} \cdot n\text{H}_2\text{O}$ where $n = \text{const.}$). In the case of microporous matrices, the formation of crystalline hydrates has not been observed [139].

4.3. Overview of Tests and Materials Tested

The first reference to the synthesis of silica gel composite sorbents and studies of their properties concerned the SWS-1L material composed of silica gel impregnated with sodium chloride (CaCl_2) and dates from 1996 [133]. This material has subsequently been studied very extensively. In [131], tests were performed for SWS-1L, among others, and its water adsorption capacity was estimated to be 0.75 g/g. In the same study, SWS-1S, SWS-2L(32) and SWS-2L(57) materials were also investigated by determining their properties and estimating the performance parameters of the adsorption chiller in which they would be used [131]. More information is provided in Table 3. In [130], Saha et al. presented the results of a simulation study to verify the impact of using the SWS-1L composite in a two-bed adsorption chiller in comparison with a commercially available typical RD-type silica gel. Water was used as the adsorbate. The authors indicated that the COP for the system with SWS-1L is up to 0.45 and increases with increasing heat-source temperature (up to 90 °C), which is a difference in comparison with silica gel, which reaches a maximum COP of 0.35 at approx. 75 °C. The effect of desorption temperature on cooling power was also tested. It was found that for both filling types, the cooling power increased with higher desorption temperature. Nevertheless, it was noted that when the regeneration temperature was between 60 and 75 °C, pure silica gel enabled higher cooling power. At higher temperatures, the composite adsorbent made it possible to achieve higher power. Furthermore, the authors verified the effect of cycle length on the COP and average cooling power. The COP value increases monotonically for both types of adsorbent beds. Using SWS-1L, a maximum COP of approx. 0.54 was obtained. The cooling power did not increase monotonically. The maximum power for the adsorption chiller using SWS-1L and silica gel RD was obtained when the cycle time was approx. 500 s and approx. 300 s, respectively [130]. Freni et al. experimentally tested the SWS-1L material together with a binder coated on a finned-tube heat exchanger in a single-bed chiller. The authors obtained an SCP of 150–200 W/kg and a COP of 0.15–0.3 depending on the operating conditions [141]. Resticcia et al. in their publication [129] presented the results of experimental tests performed for an adsorption chiller with a single bed filled with SWS-1L material and compared the results with those obtained from simulations. The results proved that the use of CaCl_2 -impregnated silica gel enables a significant increase in the COP, up to 0.6 [129]. Aristov [142] analysed the adsorption dynamics for SWS-1L, among others. For example, he determined the effect of the composite grain size on the adsorption rate. It turned out that the fastest adsorption was obtained for the smallest grain sizes of 0.355–0.425 mm [142]. Gong et al. [143] presented the results of a simulation analysis comparing the performance of chillers with a bed filled with pure silica gel and a bed filled with silica gel with added lithium chloride (LiCl). It was shown that the cooling capacity was 28.6% higher for the chiller with the composite material. It was found that a chiller with the bed filled with composite sorbent used more thermal energy in the process of desorption [143]. In [138], Yu et al. presented the results of a study on the search for optimal conditions for impregnating silica gel with LiCl salt. The authors used silica gel A (pore size 2–3 nm) and silica gel C (pore size 8–10 nm). After the process of impregnation, it was determined that silica gel C, which is characterised by larger pore size and volume, had a higher mass concentration of LiCl salt [138].

In publication [144], Zheng et al. analysed the properties of silica gels (microporous, type A and mesoporous) impregnated with inorganic salts LiCl, LiBr and CaCl₂. As a result, nine different materials were obtained. Table 3 summarises the results obtained by the authors. The authors noted that for the composite with a microporous matrix (pore size of 2–3 nm), worse sorption properties were obtained, which is probably due to flow blockage. In contrast, for mesoporous and B-type silica gels, the amount of adsorption increased by 2–3 times [144]. The above conclusion was also confirmed by Cortés et al. in their publication [145] where they described an analysis of the properties of composites composed of silica gel and inorganic salts, such as LiBr, CaCl₂ and MgCl₂. A mesoporous silica gel with an average pore size of 8.2 nm was used for the synthesis. The results showed that after the synthesis of the composite material with the hygroscopic salt, the specific surface area and porosity of the material decreased compared with pure silica gel matrix, and this reduction is greater with increasing mass fraction of inorganic salt. Three composites were prepared with silica gel and 17% fraction of LiBr, CaCl₂ and MgCl₂ salts, of which the highest adsorption was measured for silica gel with the additive and was 0.33 g/g per unit mass of sorbent. Silica gel with the addition of 33% CaCl₂ salt was also investigated. A water uptake of 0.85 g/g was obtained [145].

Silica gel with the addition of LiCl can be used in working pairs with alcohols (methanol or ethanol). In [146], Gordeeva et al., conducted a study determining the properties of the commercial silica gel KSK impregnated with LiCl being in working pair with methanol. A methanol adsorption amount of 0.6 g/g was obtained. The performance of an adsorption chiller using this working pair was also checked and a COP of up to 0.41 and an SCP of up to 290 W/kg were obtained [146]. Maggio et al. [147] modelled an ice maker with a working pair combining a composite adsorbent in the form of mesoporous silica gel with a LiCl salt content of 29.5% with methanol. A COP of 0.33 was obtained (an increase by almost 100% compared with activated carbon) [147]. Lu and Wang [148] presented the results of tests on a two-bed adsorption chiller with heat and mass recovery operating with a composite-methanol pair (the composite material is mesoporous silica gel with 14% mass fraction of LiCl salt). The authors obtained a maximum COP of 0.41 and its value depended on heat/mass recovery and cycle time [148]. Further, Gordeeva et al., in their publication [149] presented the results of a study for a composite adsorbent in the form of silica gel impregnated with LiCl salt, determining its properties and the performance parameters of an adsorption chiller that uses it in the bed. A composite methanol adsorption capacity of 0.6 g/g was obtained. Tests for the adsorption system were carried out by simulation and with the use of an actual laboratory chiller. In the first case, a COP of 0.72 was obtained while for the laboratory system a COP of 0.32–0.4 and an SCP of 210–290 W/kg were obtained [149]. In turn, in [97], Gordeeva and Aristov analysed the sorption of ethanol on composite sorbents impregnated with various salts. They used the wet impregnation method and then dried the material at 200 °C. LiCl and LiBr were selected as the most promising salts for impregnation, and composites impregnated with these salts achieved ethanol adsorption of 0.41–0.68 g/g depending on the salt and type of silica gel. For LiBr-impregnated silica gel used in an adsorption chiller for air conditioning, a COP of 0.66 was calculated [97].

However, the working pair that is most commonly studied is the combination of composite sorbent and water. Freni et al. [150] performed laboratory-scale tests of an adsorption chiller using the SWS-8L (silica modified by calcium nitrate) composite sorbent. The tests were performed for cycle times ranging from 8 to 30 min. An increase in COP was observed with increasing cycle time, with a maximum of 0.41, while the maximum SCP of 389 W/kg was obtained for a cycle time of 10 min. With the cycle time increasing beyond 10 min, the SCP progressively decreased. It was found that the optimal parameters were obtained for cycle times of 15–20 min [150]. Daou et al. [151] synthesised composite materials in the form of microporous/mesoporous silica gel impregnated with calcium chloride solutions at different concentrations of 10–50 wt%. Sorption properties were tested depending on humidity, and it was found that an improvement in sorption properties was noticeable from

a relative humidity of 70%. It was noted that silica gels impregnated with solutions with concentrations above 30% can be regenerated at 70 °C [151]. Bu et al. [152] demonstrated that a silica gel composite impregnated with CaCl_2 aqueous solution with different salt contents adsorbs more water with increasing humidity. The authors also confirmed that after impregnation of the microporous silica gel, the capacity and rate of adsorption did not increase with increasing concentration of the CaCl_2 aqueous solution and, under certain conditions, decreased relative to the base material. The opposite conclusions were obtained for mesoporous silica gels. The team selected the sample that had the most favourable properties and verified its properties using a laboratory adsorption chiller. It was found that as a result of using the composite sorbent, the COP and SCP increased by 23% and more than 300%, respectively, compared with pure silica gel [152]. Daou et al. [153] experimentally compared the performance of a single-bed adsorption chiller with the bed filled with pure microporous silica gel. The authors reported obtaining a COP 25% higher for the composite compared with pure silica gel [153]. In [154], Tanashev et al. checked the thermal conductivity coefficients of various composite materials with a matrix of mesoporous silica gel KSK impregnated with salt solutions of CaCl_2 (42 wt%), LiBr (48 wt%) and MgCl_2 (33 wt%). The thermal conductivity of dry SWS materials is 0.13–0.16 $\text{W m}^{-1} \text{K}^{-1}$. The thermal conductivity increases for each of the tested materials as the amount of adsorbed water increases, typically reaching values of 0.4–0.5 $\text{W m}^{-1} \text{K}^{-1}$, and for SWS-1L even above 0.5 [154]. In [155], Xin et al. investigated composites based on a silica gel matrix with the addition of CaCl_2 , LiCl , MgCl_2 and ZnCl_2 salts. It was found that the greatest improvement in the amount of adsorbed water was obtained for CaCl_2 and LiCl salts [155]. As mentioned in an earlier section, Gong et al. [137] presented a method to prevent excess salts from remaining in the composite material and investigated the adsorption equilibrium for a composite material with silica gel matrix and LiCl additive (13 wt%). A maximum water uptake by the composite material of 0.702 g/g was determined [137]. Wang et al. [156] described the synthesis and tests of the properties of composite sorbents in the form of mesoporous silica gel impregnated by the wet method with solutions of several salts (CaBr_2 , MgBr_2 , MgSO_4 , CaCl_2 and $\text{Al}(\text{NH}_4)(\text{SO}_4)_2$) in salt weight fractions of 15, 30 and 50 wt%. It was found that the best adsorption capacity of 109% was obtained for the addition of CaCl_2 salt at a mass fraction of 50 wt%. It was also reported that the highest adsorption rate was obtained for the addition of MgBr_2 and CaCl_2 salts, and desorption can take place at temperatures below 90 °C [156]. Further, Zhang et al. developed a material with a porous matrix in the form of a mesoporous silica gel impregnated with LiCl salt. They reported that up to 300% higher adsorption capacity could be achieved compared with microporous silica gel [157]. Subsequently, in [158], the authors performed a study for a desalination adsorption system using the sorption material described in [157] and obtained an SDWP (specific daily water production) rate 1.2–2.1 times greater than when using microporous gel. Xie et al. in publication [159] presented the characteristics of a new silica gel composite with carbon nanotubes impregnated with a 40% CaCl_2 solution. An adsorption capacity of 0.665 g/g (almost 500% higher than pure silica gel) was determined for the synthesised material. The thermal conductivity of the composite was 0.664 $\text{W m}^{-1} \text{K}^{-1}$ [159].

To clearly present and compare the available silica gel matrix composite sorbents along with their properties, most of the materials described are summarised in Table 3. Additionally, for some composites, the performance parameters of the adsorption aggregates that worked with them, determined experimentally or by simulation, are included in Table 3.

4.4. The Authors' Own Research

This publication is a presentation of what has been achieved so far in the field of composite materials based on silica gel impregnated with inorganic salts. The authors' research team is conducting research on composite sorbents. A continuation of this paper will be the presentation of the authors' research results concerning the work on composite materials in the form of silica gels impregnated with various salts and the verification of their properties in actual systems and simulation models.

Table 3. Summary of composite adsorbents with their properties and parameters of the adsorption equipment in which they were used.

Material	Porous Matrix	Addition	Percentage of Salt (%)	BET Specific Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	Water Uptake (g/g)	Synthesis Procedure	Desorption Temperature (°C)	COP in Adsorption Chiller	SCP in Adsorption Chiller (W/kg)	Source
SWS-1L	Silica gel KSK	Inorganic salt CaCl ₂	33.7	-	-	0.8	Dry impregnation by saturation of mesoporous silica gel KSK with CaCl ₂ solution and drying at 150 °C.	80–100	max. 0.54	-	[130]
KSK *	Mesoporous silica gel	-	-	-	1	0.1	-	-	approx. 0.5 (model, for a desorption temp. of 95 °C)	-	[131,133]
KSM *	Microporous silica gel	-	-	-	0.35	approx. 0.16	-	-	-	-	
SWS-1L	Silica gel KSK	Inorganic salt CaCl ₂	33.7	-	-	0.75	Silica gel granules were filled with a solution of appropriate inorganic salts and dried to constant weight at 200 °C.	-	0.79 (model, for a desorption temp. of 95 °C)	-	
SWS-1S	Silica gel KSM	Inorganic salt CaCl ₂	21.7	-	-	approx. 0.25		Temperatures of 70–130 °C were tested	0.53 (model, for a desorption temp. of 90–100 °C)	-	
SWS-2L	Silica gel KSK	Inorganic salt LiBr	32	-	-	-			-	-	
SWS-2L	Silica gel KSK	Inorganic salt LiBr	57	-	-	-			0.8 (at a desorption temp. of 95 °C)	-	
SWS-1L	Silica gel KSK	Inorganic salt CaCl ₂	33	-	-	-	Saturation of the pores of silica gel KSK with 40% CaCl ₂ solution and then drying to constant weight at 200 °C.	80–100	0.6 (at a heat-source temperature of 90–95 °C)	20	[129,133]
SWS-1L	Silica gel KSK	Inorganic salt CaCl ₂ with added binder (25 wt%)	33.7	-	-	-	-	90–100	0.15–0.30	150–200	[141]
SWS-1L	Silica gel KSK	Inorganic salt CaCl ₂	33.7	-	-	0.63	-	80	0.39	510	[160]
SWS-2S	Silica gel KSM	Inorganic salt LiBr	-	-	-	0.25	-	-	-	-	[140,161]
SWS-3L	Silica gel KSK	Inorganic salt MgCl ₂	-	-	-	0.72	-	-	-	-	[140,161]
SWS-4L	Silica gel KSK	Inorganic salt LiCl	-	-	-	0.7	-	-	-	-	[140,161]
SWS-5L	Silica gel KSK	Inorganic salt MgSO ₄	-	-	-	0.65	-	-	-	-	[140,162]
SWS-6L	Silica gel KSK	Inorganic salt NaSO ₄	-	-	-	0.62	-	-	-	-	[140,162]

Table 3. Cont.

Material	Porous Matrix	Addition	Percentage of Salt (%)	BET Specific Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	Water Uptake (g/g)	Synthesis Procedure	Desorption Temperature (°C)	COP in Adsorption Chiller	SCP in Adsorption Chiller (W/kg)	Source
SWS-7L	Silica gel KSK	Inorganic salt CuSO ₄	-	-	-	0.58	-	-	-	-	[140,162]
SWS-8L	Silica gel KSK	Inorganic salt Ca(NO ₃) ₂	-	-	-	0.42	-	-	-	-	[140,163]
SGA *	Microporous silica gel	-	-	706	0.4	-	-	-	-	-	[144]
SGB *	Silica gel type B	-	-	487	0.82	-	-	-	-	-	
SGC *	Mesoporous silica gel	-	-	395	0.93	-	-	-	-	-	
SGA/LiCl	Microporous silica gel	Inorganic salt LiCl	20	296	0.18	-	Saturation of silica gel with an aqueous salt solution for 24 h, then a vacuum filter was used and the samples were dried for at least 4 h (to constant weight) at 120 °C.	-	-	-	
SGB/LiCl	Silica gel type B		36	205	0.46	-		-	-	-	
SGC/LiCl	Mesoporous silica gel		39	219	0.53	-		-	-	-	
SGA/LiBr	Microporous silica gel	Inorganic salt LiBr	27	148	0.08	-		-	-	-	
SGB/LiBr	Silica gel type B		42	127	0.26	-		-	-	-	
SGC/LiBr	Mesoporous silica gel		48	143	0.36	-		-	-	-	
SGA/CaCl ₂	Microporous silica gel	Inorganic salt CaCl ₂	19	327	0.20	-		-	-	-	
SGB/CaCl ₂	Silica gel type B		37	180	0.44	-		-	-	-	
SGC/CaCl ₂	Mesoporous silica gel		41	165	0.42	-		-	-	-	
Silica KSK *	Mesoporous silica gel KSK	-	-	260	1	-	-	-	-	-	[150,164]
SWS-8L	Mesoporous silica gel KSK	Ca(NO ₃) ₂	-	60	0.24	0.2–0.3	Dry impregnation by saturation of mesoporous silica gel with an aqueous solution of calcium nitrate (45 wt% of salt). The material was dried at 200 °C.	90–95 °C	0.18–0.41 (depending on cycle time)	190–389 (depending on cycle time)	
SG *	Silica gel type C (pore size 2–3 nm)	-	-	348	0.99	0.088	-	-	-	-	[138]
-	Silica gel type B (pore size 2–3 nm)	LiCl (10% solution)	6.5	-	-	-	First, the silica gel was dried at 120 °C. The silica gel was then immersed in aqueous LiCl solutions of 10–40% at 25 °C for 12 h. The sample was then dried to constant weight at 120 °C.	-	-	-	
-		LiCl (20% solution)	19.8	-	-	-		-	-	-	
-		LiCl (30% solution)	24.3	-	-	-		-	-	-	
-		LiCl (40% solution)	25.6	-	-	-		-	-	-	
SLi10	Silica gel type C (pore size 2–3 nm)	LiCl (10% solution)	11.4	293	0.91	0.467		-	-	-	
SLi20		LiCl (20% solution)	24.0	242	0.75	0.87		-	-	-	
SLi30		LiCl (30% solution)	35.1	204	0.65	1.19		-	-	-	
SLi40		LiCl (40% solution)	43.6	179	0.55	1.2		-	-	-	

Table 3. Cont.

Material	Porous Matrix	Addition	Percentage of Salt (%)	BET Specific Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	Water Uptake (g/g)	Synthesis Procedure	Desorption Temperature (°C)	COP in Adsorption Chiller	SCP in Adsorption Chiller (W/kg)	Source
-	Mesoporous silica gel KSK	-	-	350	1	-	-	-	-	-	[132]
SWS-9L	Mesoporous silica gel KSK	LiNO ₃	34.5	-	-	0.22	Drying of silica gel at 200 °C for 2 h. Then saturation of the silica gel with LiNO ₃ solution at 25 °C and drying to constant sorbent weight at 200 °C.	-	-	-	
SCa17	Mesoporous silica gel	Inorganic salt CaCl ₂	17	-	-	0.33	Impregnation with an aqueous salt solution and drying at 120 °C.	-	-	-	[145]
SCa33	Mesoporous silica gel	Inorganic salt CaCl ₂	33	-	-	0.85		-	-	-	
SG *	Silica gel	-	-	481	0.844	0.444	-	-	-	-	[137]
SG + LiCl	Silica gel	Inorganic salt LiCl (50% solution)	13	350	0.613	0.702	Silica gel was dried in a vacuum dryer at 85 °C, and then a salt solution was added in the chamber and heated. The whole was then kept at room temp. for 24 h to saturate the matrix. The composite was dried at 120 °C to dry mass. This was followed by a procedure of removing excess salt (at 30 °C, RH 90%).	-	-	-	
-	Mesoporous silica gel *	-	-	529	0.806	approx. 0.17	-	-	-	-	[165]
-	Mesoporous silica gel	Inorganic salt CaCl ₂ (10% solution)	-	-	0.698	approx. 0.44	First, the silica gel was dried at 120 °C in an oven and then cooled in a vacuum dryer. Then the silica gel was immersed in a salt solution. During impregnation, the temperature was 25–80 °C and implementation lasted 1–8 h.	-	-	-	
-	Mesoporous silica gel	Inorganic salt CaCl ₂ (20% solution)	-	-	0.567	0.53		-	-	-	
-	Mesoporous silica gel	Inorganic salt CaCl ₂ (30% solution)	-	-	0.529	approx. 0.6		-	-	-	
-	Mesoporous silica gel	Inorganic salt CaCl ₂ (40% solution)	-	-	0.395	0.74		-	-	-	

Table 3. Cont.

Material	Porous Matrix	Addition	Percentage of Salt (%)	BET Specific Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	Water Uptake (g/g)	Synthesis Procedure	Desorption Temperature (°C)	COP in Adsorption Chiller	SCP in Adsorption Chiller (W/kg)	Source
SA0 *	Mesoporous silica gel	-	-	300–400	0.75–1.0	0.02 (RH 20%) 0.059 (RH 50%) 0.019 (RH 20%)	-	90	0.22	41.5	[152]
SB0 *	Silica gel type B	-	-	450–600	0.5–0.8	0.072 (RH 50%) 0.047 (RH 20%)	-	-	-	-	
SC0 *	Microporous silica gel	-	-	≥600	0.35–0.45	0.228 (RH 50%) 0.157 (RH 20%)	-	-	-	-	
SA50	Mesoporous silica gel	Inorganic salt CaCl ₂ (50% solution)	37.75	-	-	0.376 (RH 50%) 0.156 (RH 20%)	Silica gel was dried to constant weight at 120 °C. It was then cooled in a vacuum chamber to ambient temperature. The silica gel was impregnated with a 50% CaCl ₂ salt solution with deionised water for 48 h at 25 °C. The sample was washed with deionised water to remove salt from the surface and dried to constant weight at in a vacuum dryer at 120 °C.	90	0.27	128.3	
SB50	Silica gel type B		41.3	-	-	0.376 (RH 50%) 0.07 (RH 20%)		-	-	-	
SC50	Microporous silica gel		23.08	-	-	0.214 (RH 50%) 0.084 (RH 20%)		-	-	-	
SA20	Mesoporous silica gel	Inorganic salt CaCl ₂ (50% solution)	15.38	-	-	0.234 (RH 50%) 0.07 (RH 20%)		-	-	-	
SB20	Silica gel type B		14.09	-	-	0.232 (RH 50%) 0.047 (RH 20%)		-	-	-	
SC20	Microporous silica gel		5.18	-	-	0.172 (RH 50%)		-	-	-	
SG	Mesoporous silica gel	-	-	417.18	0.884	-	-	-	-	-	[157]
LiCl@SG_30	Mesoporous silica gel	Inorganic salt LiCl	29.5%	-	-	up to 0.74	First, the porous matrix was dried at 150 °C. The matrix was then mixed with a LiCl solution (dry impregnation). After mixing, the material was left at room temperature for 24 h and then dried in an oven at 150 °C for 12 h.	-	-	-	

* Reference silica gel in the individual papers.

5. Discussion

The results of the literature survey on composite materials with a matrix being silica gel have revealed a very high potential for these materials. The data collected in Table 3 represent in detail the current state of knowledge in this field. They can be analysed by considering above all two main aspects, i.e., the sorption properties and the influence on the performance of the adsorption chiller.

The dot plot in Figure 6 shows the increasing values of the water sorption capacity of selected composite samples. They have a silica gel matrix (different types of silica gel) and were impregnated with solutions of different inorganic salts with different salt concentrations (as a result of different salt concentrations in the impregnating solution and different synthesis methods, the samples have different mass fractions of salts in the composite, which affects their properties).

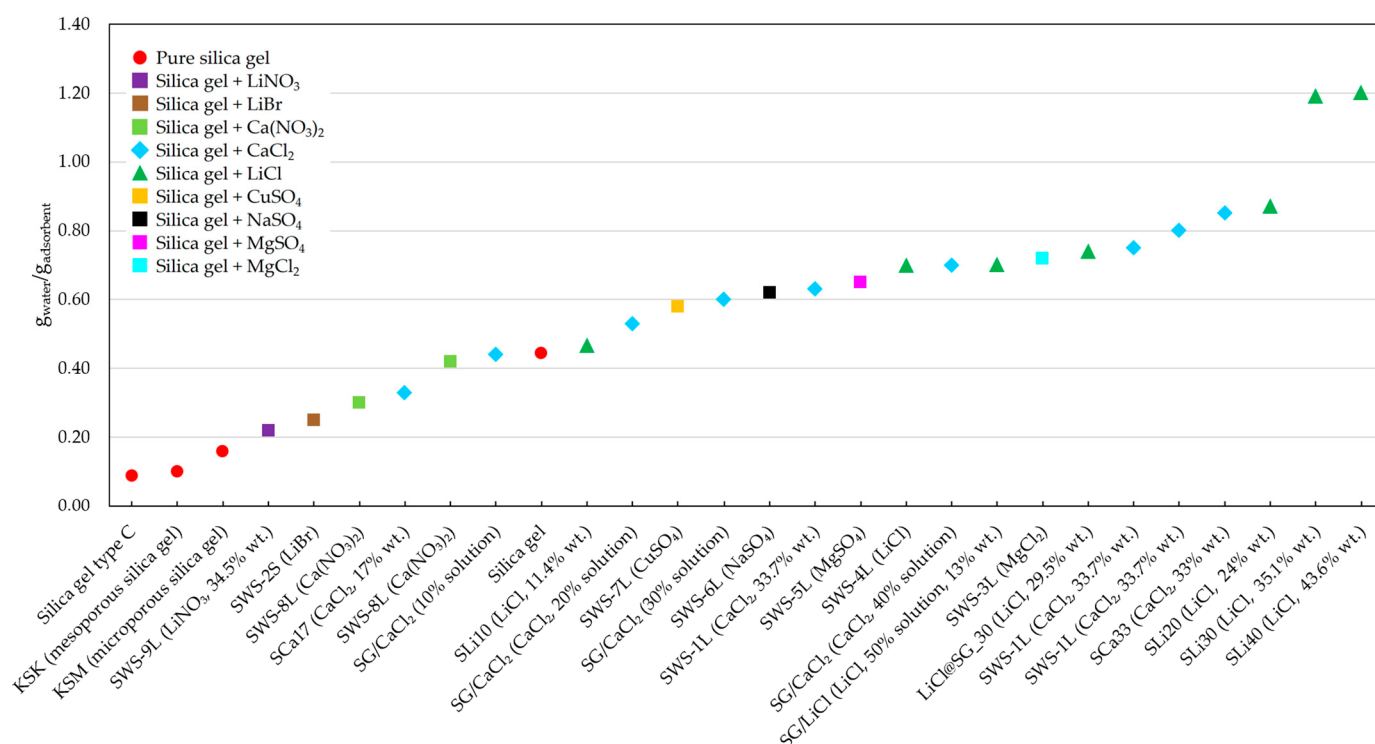


Figure 6. Overview of composite materials concerning water sorption capacity [66,130–133,137,138, 140,145,150,157,160–165].

Based on the graph shown in Figure 6 it was found that it is clearly possible to improve the sorption capacity after impregnation with inorganic salts. Two salts in particular stand out—CaCl₂ and LiCl—these are the most commonly used in the synthesis of composite sorption materials. However, the improvement is not obvious. As shown in Figure 6, it is not always apparent. This is mainly due to the type of silica gel used and the salt content of the composite material. This aspect is described in more detail later in this section. For a clear comparison, Figure 6 also includes water adsorption values for different silica gels (reference material with no salt added). An analysis of Figure 6 provides a general overview of the available materials and provides a good basis for the planning of subsequent studies, including the determination of the appropriate direction thereof. An exact comparison is not possible due to the different conditions under which the synthesis of the composite sorbents takes place.

The increase in adsorption of water can also be analysed based on the graph shown in Figure 7 in which the bar chart shows the percentage increase in the selected composite materials in relation to the reference material (the pure silica gel that provided the pore matrix for the material synthesised).

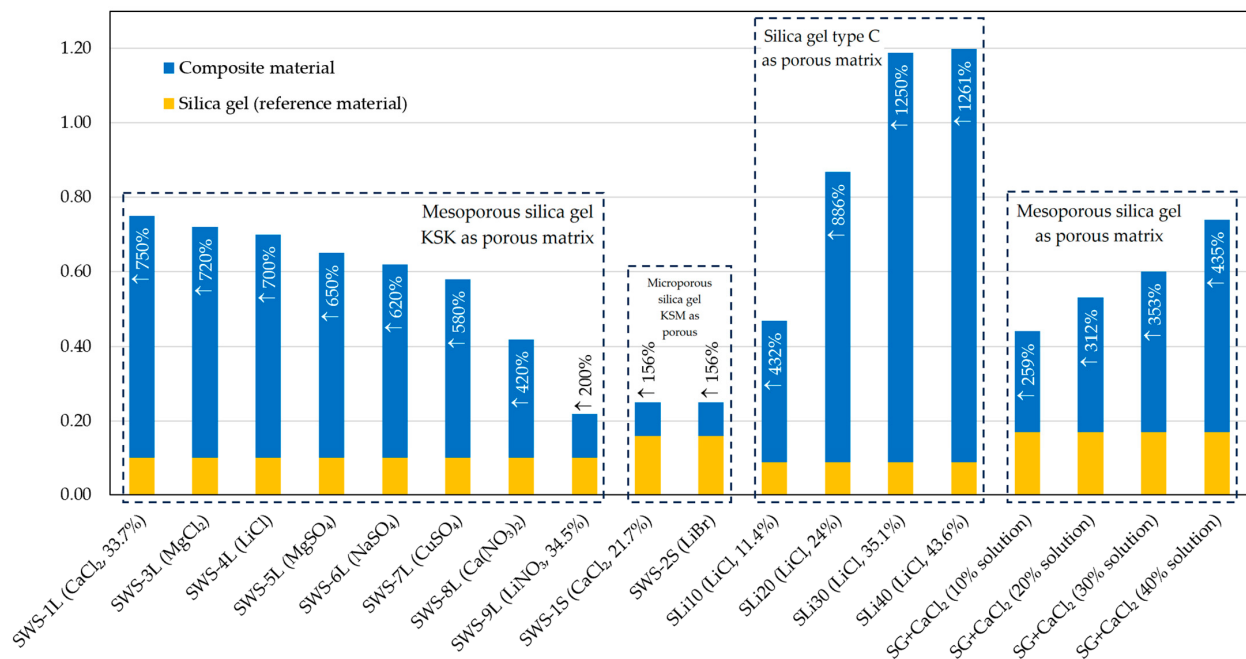


Figure 7. Bar chart showing the magnitude of the increase in the amount of water adsorbed by the composite sorbents relative to the porous matrix (reference material) [131–133,138,140,161–163,165].

Based on Figure 7, it can be seen that the maximum increase of 1261% was obtained for the composite sorbent with a matrix of mesoporous silica gel impregnated with a LiCl salt solution (mass fraction in the composite equal to 43.6 wt%). In general, impregnation with LiCl salt solutions resulted in the greatest increase in adsorption compared with the base material. Furthermore, it was noted that the largest increase was obtained for the mesoporous silica gel matrix and the smallest for the microporous silica gel.

The second line of analysis of the literature study is the comparison of the adsorption chiller performance parameters achievable with each composite sorption material. However, this analysis is limited by the relatively small amount of data. Figure 8 shows the COP values (measured during simulation or experimental studies) for some composite materials with silica gel as a porous matrix.

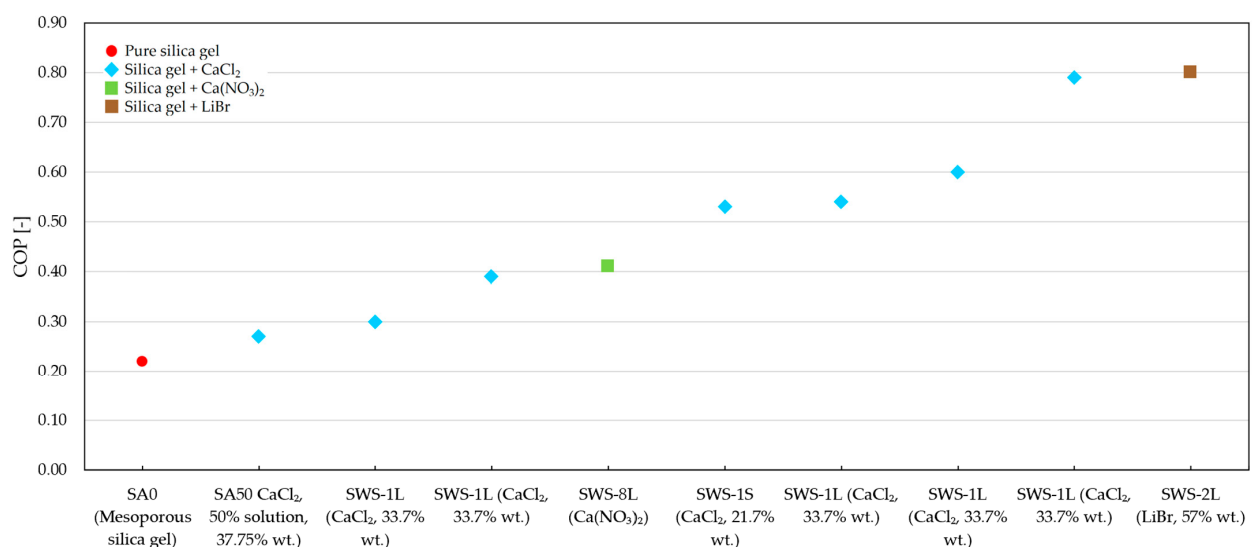


Figure 8. Summary of COP values of adsorption chillers using each composite sorbent [129–131,133,141,150,152,160,164].

The achievable COP values vary and can depend on:

1. The operating parameters of the adsorption chiller (primarily the cycle time, the hot, cooling and chilled-water temperatures and the water flow rates in the hot, cooling and chilled-water circuits);
2. The methods of synthesis and the materials/substances used in the synthesis that directly affect the properties of the composite sorbent.

Nevertheless, despite the many factors influencing the cooling coefficient of performance, the available data were collected in the form of a dot plot to show the high potential for the use of such materials in adsorption chillers. A maximum COP of 0.8 was obtained for SWS-2L (according to Table 3, this material has a matrix in the form of mesoporous silica gel KSK impregnated with LiBr salt that has a mass fraction in dried composite of 57 wt%) [131]. A slightly lower COP of 0.79 was obtained for SWS-1L (according to Table 3, this material has a matrix of mesoporous silica gel KSK impregnated with CaCl_2 salt, whose mass fraction in the composite after drying is 33.7 wt%) [131]. In both cases described above, the bed was filled with granules of the composite material. The performance of an adsorption chiller is certainly strongly influenced by the fraction of salt in the composite. However, this correlation is not apparent in Figure 7. Due to the different operating conditions of the systems subjected to simulation or experimental tests, it is not possible to assess the influence of this factor. To do so, it would be necessary to compare the results obtained for a system operating under the same or similar operating conditions. This aspect must certainly be taken into account in further studies.

Impregnation with inorganic salts yields very promising results in terms of improved material properties and, consequently, improved performance by adsorption systems. However, this improvement is not noticeable for every composite material. It is very important to correctly choose the porous matrix and method and conditions of the synthesis. Microporous silica gel does not always have better sorption properties after impregnation. In general, silica gel with a pore size of 2–3 nm is not suitable for impregnation. In the case of type B silica gels and mesoporous silica gels, the sorption properties improve as the concentration of the salt solution increases.

The most important parameters in the development of composite sorbents are the mass concentration of the impregnating solution and the structure and pore size of the matrix. These parameters have a strong influence on the properties of the composite synthesised. Also very important are the parameters of the impregnation process, e.g., in the case of matrix preparation, these are the temperature and drying time, then the conditions for saturating the matrix with the salt solution and finally the drying parameters. In the case of wet impregnation, it is also important to remove excess salt from the surface of the composite sorbents. Yu et al. [138] further considered the ratio of the impregnating solution to the solid being impregnated. The authors emphasised that the higher the ratio, i.e., the more salt solution there is relative to the porous matrix, the higher will be the salt content in the composite material [138]. Wu et al. in their publication [165] indicate that the impregnation temperature has a strong influence on the properties of the sorbent, and that as the temperature increases, the sorption capacity increases. They also confirm that an increase in the salt concentration in the solution results in an increase in the amount of adsorbed water per unit mass of sorbent. Furthermore, the authors report that the amount of adsorbed water was higher with longer impregnation times [165]. In [140], Aristov emphasises that the properties of the synthesised composite material are influenced by five factors [140]:

- Chemical nature of the impregnating substance;
- Concentration of salt in the impregnating aqueous solution;
- Chemical nature of the porous matrix;
- Porosity of the matrix;
- Process conditions for the synthesis of the composite material.

Based on the results, it was also deduced that the content of salt in the matrix influences the desorption temperature. With increasing salt concentration, desorption at lower temperatures is possible, as shown, e.g., in [151]. The issues described above are reflected in the summary of composite materials presented in Table 3.

Based on the literature review, it was found that the typical synthesis comprises five steps:

1. Preparation of a salt solution with appropriate mass concentration;
2. Drying of the porous matrix to remove water (Aristov [140] suggests 120–180 °C);
3. Wet or dry impregnation of porous matrix with salt;
4. Drying of the composite material to remove water (Aristov [140] suggests 120–150 °C);
5. Possible treatment of the material after synthesis.

This indicates that the state of knowledge concerning the mechanism of impregnation of different types of silica gels with inorganic salts is good. In publications that consider the topic of composite adsorbents with a silica-ionic gel matrix, the most common main objective was to determine the properties of the material. Verification of the influence of the use of this type of sorbents on the operation of the adsorption chiller, including primarily its performance parameters, occurred much less frequently. Only in a few publications have authors focused on investigating the influence of the operating parameters of an adsorption chiller with a bed filled with a composite adsorbent on the performance parameters. A thorough analysis of the operation of adsorption chillers using sorption materials with the most promising properties should be the subject of further research to enable easy and certain implementation of such materials in commercial systems.

6. Conclusions

The results of the literature survey carried out in the preparation of this paper indicate that there is now a large body of knowledge about sorption materials for adsorption chillers. The properties of many sorbents are characterised in detail and their influence on the performance of adsorption cooling systems has been determined. Nevertheless, it has been noted that although the knowledge enriched for decades regarding sorption materials is at a very high level, there are still some gaps regarding extremely promising materials, such as composite sorbents with a porous matrix in the form of silica gel. Composite materials are a very interesting development because of the possibility of combining the characteristics of more than one material in one material. This is very essential, especially for sorbents used in adsorption chillers.

This paper comprehensively compiles information on silica gel-based composite adsorbents from all available papers that were analysed in the literature review. The authors noted that topics related to the synthesis of silica gel composite sorbents and, above all, studies on actual systems or simulations are relatively rarely addressed. Several research groups have performed experimental or simulation studies assuming the use of these composites and indicating the unique potential of these materials compared with other available adsorbents. However, there is still a lack of complete studies that are necessary for the easy application of these materials in commercial adsorption refrigerators. This publication aims to bring together all the knowledge on silica gel-based composite adsorbents in a clear and detailed manner, in order to guide further research in this field and to present the current state of knowledge indicating further research objectives on the topic.

Silica gel is the most commonly used sorption material in the adsorption cooling technology. Impregnation with an inorganic salt solution will improve the sorption capacity and influence other parameters. The current state of knowledge indicates that water sorption can increase by up to more than twelve times. It is also possible to improve the thermal conductivity coefficient. Studies on the impact of using composites in adsorption chillers have indicated that the COP and SCP can increase significantly. A maximum COP of 0.8 was obtained for SWS-2L, which was a silica gel impregnated with a LiBr salt solution, with a postsynthesis salt mass fraction of 57 wt% [131]. A slightly lower COP of 0.79 was

obtained for SWS-1L, which was a silica gel-based composite impregnated with CaCl_2 salt with a postsynthesis salt mass fraction of 33.7 wt% [131].

In summary, the state of knowledge concerning the sorption materials discussed is relatively high considering the research on the synthesis and sorption properties of composite sorbents with a silica gel matrix. In the publications, the authors mainly focus on impregnation with CaCl_2 salt. Further, more detailed research is needed on the use of different salts, in order to determine their effects on both sorption and thermal properties. Experimental or simulation studies on determining the performance of adsorption devices using composite sorbents will be very important. An interesting and very topical direction would be to use a digital twin for this purpose. This publication presents the available knowledge on the synthesis and properties of composite materials with a silica gel matrix. Numerous factors affecting the synthesis effect of composite sorbents are highlighted, including the appropriate choice of silica gel, the concentration of salt in the impregnating solution and the choice of inorganic salt.

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