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A New Composite Adsorbent Material for Water Moisture Adsorption

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Abstract

The paper describes a new type of composite absorbent material with high water moisture absorbing capacity. The composite material has a high water moisture uptake ability. The composite adsorbent is made of high porosity materials with strong capillary effect to hold the liquid. The purpose of the work is to investigate composite materials of KCOOH and silica gel. The optimised composite materials of KCOOH and silica gel with specific ratio of KCOOH is presented in the paper. The manufacturing process, water uptake and energy density etc. are also discussed. The material can be used for wide range of applications including chemical energy storage, dehumidification and water harvest.

Keywords: Moisture adsorption, composite absorbent, salt, high porosity

Introduction

Solid absorbent materials such as silica gel, activated carbon etc. are featured with high porosity with limited capacity of water moisture absorption and without lyolysis which is favourable, while salts including inorganic salt such as $CaCl_2$, and organic salt such as KCOOH, have higher capacity of water moisture absorption than solid absorbent materials. However, these salts with unavoidable lyolysis effect is always not acceptable.

It is possible to combine both adsorbent materials and salts to synthesise composite materials with high water moisture uptake and without dissolution. According to the research work of Yu. I. Aristov [1], S Nakabayashi [2], and JY Wang [3], the potential risk of dissolution still exists [4] and is required to have further investigated.

In fact, the inorganic salts such as CaCl2, LiCl, LiBr, CaBr$_2$ [5-8], Na$_2$SO$_4$ [9] and LiNO$_3$ [10] are the only selected materials for this research and most of composite materials previously investigated contain less than 50% salts which means less moisture absorption capacity.

In this paper, the initial description includes the composite materials based on silica gel, and inorganic salt KCOOH, which is featured with no corrosion for almost every typical materials, such as aluminium, iron and copper etc. And also, the composite materials contain salt proportion higher than 50%, some even higher than 75%, which means it has larger water moisture uptake capacity and also a strong absorb capability at low humidity level. The paper also described the comparison of the silica gel with KCOOH based composite materials.

Preparing the manuscript
Instruments

In the project, used instruments (the technique data is shown in **Table 1**) include:
- Constant Temperature & Humidity Test Chamber, ZH-TH-408, Dongguan City Sailham Equipment Co. Ltd.
- Electronic scale - FC204, Shanghai Precision Scientific Instrument Company.
- Electronic thermometer and hygrometer - DWS508D, Beijing Yaguang Instrument Co., Ltd.

Materials

The basic materials including silica gel and KCOOH, the details of the two materials are shown in **Tables 2** and **3**.

Composite Adsorbent Preparation

After long term field tests and laboratory experiments, the optimum composite adsorbent with an ideal ratio of KCOOH has been obtained, and also, the specific micro surface structure and the designed process of the preparation were found. This paper is based on the optimum adsorbent with 66% mass ratio of KCOOH. The optimum adsorbent has lower risk of lyolysis/dissolution effect and higher absorbing capacity of moisture at

Table 1. Technical data of Constant Temperature Humidity Test Chamber.

Temperature	-20 - 150ºC
Temperature resolution accuracy/distribution accuracy	0.1ºC/±2.0ºC
Temperature accuracy	±0.5ºC
RH	20%-98%

Table 2. Silica Gel.

Designation of silica gel	Particle diameter, μm	Specific surface area, m2/g	Pore size, nm	Pore volume ml/g
Mesoporous silica gel	300-500	300–400	8–10	0.75–1.0

Table 3. Potassium Formate: KCOOH.

Chemical Formula	Molar Mass	Density g/cm³	Melting Point	Appearance	Solubility In water
KCOOH	84.12	1.908	167.5°C	Colourless Crystal	331 g/100 mL (25°C), 657 g/100 mL (80 °C)

the same time. The preparation procedure is shown in **Figure 1**.

As shown in **Figure 1**, firstly, mixed KCOOH with silica-gel, the raw materials used were indicated in **Tables 2** and **3**. Drying 100g of silica-gel at 110°C for 4 hours, then mixed it with 200g KCOOH. Then put the mixture on a large surface for adsorbing moisture in the environment at 26°C with relative humidity of 60%. After 24 hours, put the sample in oven and dried at 150°C for 2 hours. The dried sample was then exposed to the
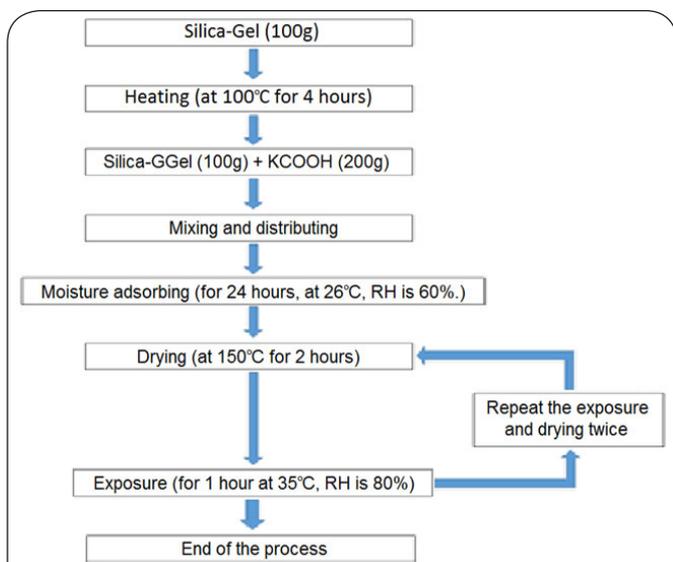
environment at RH 80% with temperature at 35°C for 1 hour. The sample dried at 150°C for 1 hours, then repeated the above process of exposure and drying for another two times.

Results and discussion
Equilibrium Adsorption Capacity

The equilibrium adsorption capacities of the composites at different temperature were estimated. These results were generated at the atmospheric pressure.

During the test, the samples of silica-gel and the composite adsorbent of silica gel with KCOOH (SG/KCOOH) are put into the Constant Temperature Humidity Test Chamber with temperature at 80°C, moisture content was 0.01kg/(kg dry air) until there is no weight change of samples. The samples were then exposed into various environment with four different temperature (15°C, 20°C, 30°C, 40°C) and relative humidity (30%, 50%, 70%, 90%) for a period of time to adsorb the moisture until there is no weight change of the samples. The water uptake, X (kg/kg), can be calculated as:

$$X = \left(m - m_{dry} \right) / m_{dry} \qquad (1)$$

Where:

m – the total mass of the adsorbent including the mass of the adsorbed water vapour;

m_{dry} – the mass of adsorbent before adsorption.

The mass m and m_{dry} are measured with the Electronic scale and the water uptake X is obtained via equation $X=(m-m_{dry})/m_{dry}$ (1).

It is shown that the water uptake X remains stable at different temperature. **Figure 2** and **Table 4** show the relation between water uptake and relative humid level of the environment when the air temperature is 20°C.

Table 4 and **Figure 2** illustrate the differences between equilibrium water uptake (X) of silica-gel and SG/KCOOH in the RH range of 30% - 90%. It is clear that SG/KCOOH showed much higher equilibrium water uptake against silica-gel in
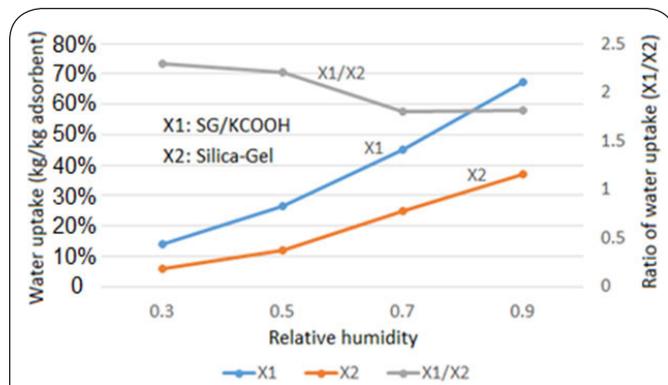

Figure 1. The Procedure of Preparation of composite adsorbent.

Figure 2. Equilibrium water uptake of silica gel and SG/KCOOH at 20ºC.

Table 4. Equilibrium water uptake of SG/KCOOH(X_1) and silica-gel (X_2) against relative humidity.

Relative Humidity	X_1	X_2	X_1/X_2
30%	0.14	0.061	2.3
50%	0.266	0.121	2.2
70%	0.45	0.25	1.8
90%	0.675	0.371	1.82

the whole range of relative humidity level. When the relative humidity were at different level of 30%, 50%, 70% and 90%, the SG/KCOOH showed an improvement over silica-gel of 230%, 220%, 180% and 185%, respectively.

It shows an interesting characteristic that the lower relative humidity level, the better improvement of equilibrium water uptake (X) of SG/KCOOH over silica-gel, it is because of the fact that the adsorption process of the composite adsorbent is the combination of both physical adsorption and chemical absorption, the latter one is more effective against the former one in lower humidity level than in higher condition.

Obviously, the water absorbing capacity at low humidity is more meaningful and useful in the real application, such as air dehumidification and energy storage.

Thermal energy storage density

Thermal energy storage density is described as one unit thermal energy stored inone unit of materials mass, it can be expressed as:

$$q_{sed} = \frac{Q}{m_{dry}} = q_{st} \cdot (x_h - x_l) \quad (2)$$

Where:

q_{sed} –energy storage density, kJ/(kg adsorbent);
Q – thermal energy input during desorption or released during absorption, kJ;
q_{st} –adsorption heat, kJ/kg;
x_h– the water content of adsorbent after adsorption, kg/kg adsorbent;
x_l – the water content of adsorbent after desorption, kg/kg adsorbent.

The adsorption heat could be calculated according to formula (3) or further formula (4), which is the variation of formula(3). The relationship of *lnp*&1/T can be worked out through a series of adsorption isometric line at different temperature. Where:

$$q_{st} = RT^2 \left(\frac{\partial \ln \ln p}{\partial T} \right)_x \quad (3)$$

$$q_{st} = -R \left(\frac{\partial \ln \ln p}{\partial \left(\frac{1}{T} \right)} \right)_x \quad (4)$$

P – pressure, kPa;
q_{st} – adsorption heat, kJ/ mol;
R – gas universal constant, J/(mol·K);
T – temperature, K;
X – water uptake, kg/kg adsorbent.

Figure 3 and **Table 5** show the adsorbent heat released in different air humidity conditions. It is based on the open system, in the desorption process, temperature was 80°C and moisture content was 0.01kg/(kg dry air), both silica gel and SG/KCOOH went through the air with stable temperature and different relative humidity level.
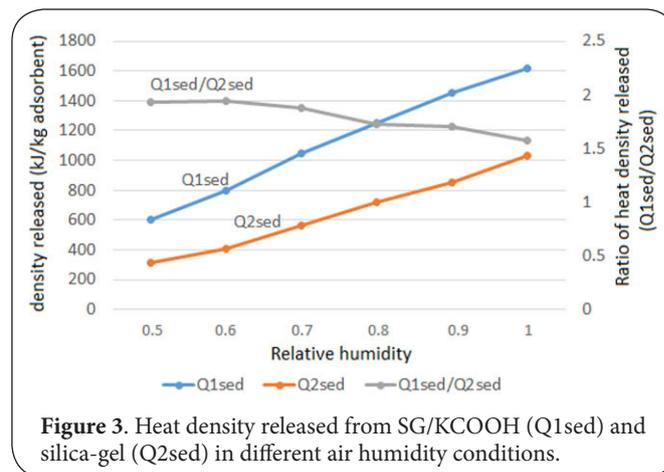

Figure 3. Heat density released from SG/KCOOH (Q1sed) and silica-gel (Q2sed) in different air humidity conditions.

Table 5. Heat released from SG/KCOOH (Q1sed) and silica gel (Q2sed) under different air humidity conditions.

Relative Humidity	$Q1_{sed}$	$Q2_{sed}$	$Q1_{sed}/Q2_{sed}$
50%	600	310	1.93
60%	795	410	1.94
70%	1050	560	1.88
80%	1250	720	1.73
90%	1450	850	1.7
100%	1620	1030	1.57

Compared with SG/KCOOH and silica-gel, the data result represents the undoubtable tendency of the improvement of energy storage density from the low humidity condition to high humidity condition. The maximum energy storage density of SG/KCOOH was about 1600 kJ/kg, which was much higher than the normal closed system based on the composite adsorbent of silica-gel and inorganic salts, such as LiCl, which was about 254Wh/kg [4]. This does not mean that the SG/KCOOH shows a higher energy storage density than other composite adsorbent. This is mainly because of the fact that the open system only uses the dehumidified air as heat source to avoid heat transfer process required for the closed system, which also causes some ineffectiveness.

Conclusion

In conclusion, this paper described a development of a composite material consists silica-gel and KCOOH (SG/KCOOH). The process of preparing the composite adsorbents was presented in detail, and the water uptake of both composite adsorbent and silica-gel were tested in the project. The energy storage density and water uptake were discussed and the results showed that the composite adsorbent has great improvement on both parameters. It is noticed that the water uptake improvement of SG/KCOOH is similar with other composite adsorbent based on inorganic salts, such as LiCl, $CaCl_2$, $CaBr_2$, etc. [5-8], it can be easily understood as the composite adsorbents share the same basic mechanism, it is called the combination of chemical absorption and physical adsorption. The energy density of SG/KCOOH is higher than other composite adsorbents used in the closed system.

Overall, the new composite adsorbent based on KCOOH is similar with other inorganic based composite adsorbent in water uptake and energy storage etc., but SG/KCOOH is not corrosive and compatible with almost all metals which is preferred for real application, especially when the potential lyolysis/dissolution effect is taken into account. Under the consideration of the lyolysis/dissolution effect, KCOOH also shows less potential risk, the mechanism of which is required to have further study.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

Authors' contributions	YY	YZ	SR
Research concept and design	✓	✓	✓
Collection and/or assembly of data	✓	✓	✓
Data analysis and interpretation	✓	✓	✓
Writing the article	✓	✓	✓
Critical revision of the article	✓	✓	✓
Final approval of article	✓	✓	✓
Statistical analysis	✓	✓	✓

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