Preparation of Calcium Chloride Composite Adsorbents for Woodchip by Carbonization Porosity

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Abstract. In order to improve the mass transfer performance of calcium chloride based composite adsorbents, calcium chloride was embedded in wood chips by soaking, and then the calcium chloride wood chips were carbonized to form holes. SEM images and elemental analysis show that at a charring temperature of 700 °C, the composite adsorbent prepared by charring calcium chloride sawdust has a developed pore structure, and calcium chloride is evenly dispersed in the adsorbent. The adsorption properties of the composite adsorbent to ammonia gas were shown to be 0.204, 0.253 and 0.285 kg/kg at evaporation temperature of -5 °C and condensation temperature of 40 °C at adsorption time of 5, 10 and 15 min, respectively. SCP(refrigeration power per unit mass sorbent) is 868.96, 540.02 and 405.16 W/kg, respectively, with average adsorption rates of 6.79 * 10^-4, 4.22 * 10^-4 and 3.17 * 10^-4 kg/kg/s, respectively, At the same time, the expansion and agglomeration of calcium chloride were solved.

1. Introduction
Adsorption refrigeration system does not use Freon working quality, does not consume high-grade energy, has a simple structure, and has the advantages of energy conservation and emission reduction. It has become a topic for scholars in various countries to compete for research in recent years[1]. However, adsorption refrigeration technology still has problems such as low refrigeration power per unit mass adsorbent, small cyclic adsorption amount, and slow adsorption rate[2]. The key to solve the above problems is to develop a adsorption cooling working pair with low regenerative temperature and high heat transfer and mass transfer performance. The research and development of high efficiency adsorbents is the core of high performance adsorption refrigeration.

The adsorption agent composed of silica gel and water has the advantage of low regeneration temperature, but the absorption of silica gel is low and generally does not exceed 20 %. Metal chlorides, such as calcium chloride, have a large amount of adsorption on ammonia gas, but they are prone to expansion and agglomeration during use, and increase in mass transfer resistance. For the above problems, the more commonly used solution is to prepare composite adsorbent[3] And ... That is, metal chlorides(CaCl2, BaCl2, SrCl2, etc.) embedded in their micropores to prevent metal chlorides from bulging during desorption [4]. At present, the research on this compound adsorbent is relatively popular in the world[5], has developed some high-performance adsorbents, such as SWS-1L, SWS-2L and so on. This simple composite method solves the expansion and agglomeration of metal chlorides, but due to the limitation of the carrier, the content of calcium chloride in this composite adsorbent is small, and its adsorption is limited by the content of calcium chloride.
Activated carbon prepared by the above compound method and carbonization activation method. Inspired, this paper intends to prepare adsorbent with high mass transfer properties by means of carbonization. The specific method is to soak the sawdust in a calcium chloride solution. After drying, the mixture is carbonized at high temperatures. By charring, the sawdust has a developed pore structure to improve the mass transfer of the adsorbent. If heated graphite or metal powder is added to the mixture and then carbonized, the carbonized adsorbent not only has a developed pore structure but also has a high thermal conductivity. In this paper, calcium chloride composite adsorbent of sawdust was prepared by carbonization, and the properties of adsorbent were tested by ammonia adsorption. The addition of thermal conductive materials was written in subsequent papers.

2. Experiment

2.1 Raw materials
Fir sawdust 20-35 head; Calcium chloride, powder, pure analysis; Deionized water; Starch; Dry boxes; Pipe furnace and so on.

2.2 Performance testing
The performance test is mainly the test of the adsorption capacity and adsorption rate of the composite adsorbent to ammonia gas. The test is completed on the self-made ammonia adsorption laboratory. The diagram of the laboratory is shown in Figure 1. In Figure 1, Valve 5 is used to adjust the pressure in the tank 3 and to release air. Valve 8 is connected to the vacuum pump. The test station mainly includes gas tanks, adsorption beds and test instruments. The adsorption bed is a flange structure, which facilitates the replacement of the sample. The tank volume is 2309.158 CM3 and the adsorption bed volume is 80.99 CM3. The absolute pressure of the tank is 354.76 KPa, which is the pressure corresponding to the evaporation temperature of -5 °C.

![Fig. 1 Adsorption test device](image)

In addition, the microscopic morphology(SEM image) and the distribution of elements of the sample were observed by scanning electron microscopy(instrument model: HITACHI S-4800); BET surface area and aperture tested by the adsorption instrument ASI Q MO002-2; The crystallinity of calcium chloride is tested by an X-ray diffractometer(model: PANalytic X’pert Pro MPD).

3. Results and analysis
It can be seen from Fig. 2 and Fig. 3 that the carbonized composite adsorbent has developed pore structure and calcium chloride is evenly dispersed in the composite adsorbent. This shows that the high-temperature charring method can create a rich pore structure to improve mass transfer. At the same time, due to the uniform distribution of calcium chloride and the developed pores of the adsorbent, on the one hand, the uniform distribution prevents the clotting of calcium chloride, and on the other hand, the pores provide space for expansion.

The X-ray diffraction of the adsorbent is shown in Figure 4. As can be seen from Figure 4, the carbonization temperature of 700 °C results in partial crystallization of calcium chloride in the adsorbent, with a crystallization of 25.1 %. The crystallization of calcium chloride can adversely affect
the adsorption performance, and the carbonization temperature is the biggest determinant of the crystallinity of calcium chloride. Therefore, the emphasis of this study is to determine the relationship between the crystallinity of calcium chloride.

It can be seen from Fig. 5 that the adsorption of ammonia gas by composite adsorbent increases with the adsorption time, but the increase decreases. At adsorption times of 5, 10, 15 and 30 min, adsorption times were 0.204, 0.253, 0.285 and 0.38 kg/kg. Adsorption time corresponding to 1, 2, 3 and 4 H was 0.511, 0.658, 0.722 and 0.774 kg/kg. The adsorption of 5, 10, 15 and 30 min accounted for 26.32 %, 32.71 %, 36.81 % and 49.11 % of the 4 H adsorption, respectively. This shows that the adsorption rate of the adsorbent to ammonia gas is relatively fast at the beginning, and this characteristic is particularly suitable for adsorption refrigeration because of the short operating cycle of each cycle. carbonization temperature in the adsorbent.

4. conclusion
In this paper, a new method and new technology for preparing calcium chloride wood chip matrix composite adsorbent are developed by means of high-temperature charring.

(1) SEM images and elemental analysis show that the calcium chloride sawdust composite adsorbent prepared by charring method under vacuum has developed pore structure, and calcium chloride is evenly dispersed in the adsorbent.

(2) The adsorption properties of the composite adsorbent to the ammonia gas are shown to be 0.204, 0.253 and 0.285 kg/kg at evaporation temperature of -5 °C and condensation temperature of 40 °C at adsorption time of 5, 10 and 15 min, respectively; The SCP is 868.96, 540.02 and 405.16 W/kg, respectively.

Acknowledgments
This work was supported by the financial support by the Social Development Project of Dongguan (NO.20185071401605), the Special Fund for science and Technology Development of Guangdong
Province in 2017(Grant NO.2017A010104014), the Natural Science Foundation of DGUT (NO. ZJ20180524), and the Service team of DGUT (NO.GC200104-47).

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