Effect of different pretreatment methods on pore structure of activated carbon

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Abstract. The effects of pretreatment on the pore structure of activated carbon were studied by the methods of water washing, acid washing, alkali washing and a combination of acid washing and alkali washing. It can be known from experiments that water washing has a cleaning effect on activated carbon, while acid washing helps to open the micropores of activated carbon and improve its porosity. Sodium hydroxide solution has an etching effect on activated carbon, which can increase the porosity and average particle size of activated carbon. All the pretreatment methods in this article can improve the adsorption capacity of activated carbon for nitrogen, and the pretreatment by dilute hydrochloric acid is tested to be the most effective.

1. Introduction
Manganese dioxide is a kind of microwave absorbing material with dielectric loss. Its dielectric constant decreases with the increase of frequency. The tangent of dielectric loss angle is relatively stable within 2 GHz~18 GHz. Liu Shunhua [1] added manganese dioxide into quartz / carbon black composite and ABS resin / carbon black respectively, which greatly improved the microwave absorption performance of the material. Cui Xiaodong [2] used manganese dioxide as a matching layer material, designed two-layer absorbing materials such as manganese dioxide / carbon type, and achieved good results. Jiao Yajun [3] designed a three-layer structure of absorbing material, its impedance matching layer also uses manganese dioxide, the middle layer uses nickel zinc ferrite, the bottom layer uses graphite, and prepared a flat absorbing material with both absorbing and carrying performance requirements.

Activated carbon absorbing material can be used as a kind of resistance, China civil aviation university of wrinkle spring rain [4] using activated carbon fiber, glass fiber cloth and epoxy resin could be prepared for composite absorbing material in 4.2 GHz ~ 18 GHz frequency range has good absorbing properties, reflectivity are less than 10 db, if the resistor type activated carbon and manganese dioxide composite dielectric type, theory can form a more absorption mechanism of the absorbing material, to some extent compensate for the single absorbing band narrow absorbent shortcomings. Now the minimum reflectance is -26.6 GHz. The highly developed pore structure of activated carbon has a certain effect on the scattering of electromagnetic wave. Manganese dioxide itself loss tangent changes little with the frequency, is a stable broadband absorbent. Zhao et al. [5]
studied the wave absorbing properties of activated carbon fiber blanket film and vertically arranged carbon fiber composites. The results showed that the elemental configuration of the activated carbon fiber felt film had a great influence on the composite materials, and the smaller the interlayer spacing and interlayer width. Zou et al. [6] prepared activated carbon fiber polymer composites by mold pressing method, and it was found that the content of activated carbon fiber was important to the absorption rate of the composites. In the frequency range of 5.8 GHz ~18 GHz, it has good absorption performance and reflectivity is less than -10 dB.

In order to make use of the adsorption capacity of activated carbon to prepare the composite absorbent, the effects of different pretreatment methods on the pore structure of activated carbon were studied in this paper.

2. Pretreatment method
Activated carbon ash removal methods are selected raw materials, physical removal and chemical removal of three, most of which use physical and chemical methods, chemical removal is considered to be the last method. That is, different chemical reagents were used to remove the ash from the activated carbon, and the physical and chemical characteristics of the surface of activated carbon were changed to improve its adsorption performance. Şahin et al. [7] with two-step pretreatment (ZnCl₂ - HCl) at high temperature in physical activation method of preparation of activated carbon from acorn shell, increasing concentration impregnant, it also improved the physical properties such as specific surface area, the biggest BET specific surface area, pore volume and the width of the DFT hole activated carbon is 1779 m²/g, 0.927 cm³/g and 1.688 nm, respectively.

Water washing, acid washing, alkaline washing and alkaline washing after acid washing were adopted. In the pretreatment process, the specific conditions are as follows: AC1 - without treatment, AC2 - distilled water washing, AC3 -1.5 mol/L diluted hydrochloric acid washing, AC4 -1.5 mol/L NaOH alkaline washing, AC5 - acid washing + alkaline washing (1.5 mol/L diluted hydrochloric acid + 1.5 mol/L NaOH); The temperature of the water bath was 85 °C and the treatment time was 2 hours. Among them, pickling and alkaline washing pretreatment method is to pickling the activated carbon, after many times of cleaning and filtration with sodium hydroxide for alkaline washing. Dolas et al. [8] studied the specific surface area and pore structure of activated carbon in pistachio shell using ZnCl₂ and HCl as impregnating solution, and the results showed that the pore structure of activated carbon treated has been developed to a great extent. Yakout et al. [9] prepared activated carbon with olivine as raw material and phosphoric acid as activator. The higher the phosphoric acid concentration is, the higher the surface and the higher the total pore volume of the carbon will be produced. Zhao et al. [10] prepared simulated sulfur-containing precursor by adding elemental sulfur to petroleum coke, and synthesized activated carbon with high surface area. The results show that elemental sulfur can change the surface chemical properties of activated carbon, and the amount of KOH decreases. Therefore, when the elemental sulfur is used as the pretreatment agent, the amount of activator KOH should be increased correspondingly, so that the activated carbon has developed porosity.

3. Result analysis
The activated carbon after pretreatment was washed and filtered for many times, then put into the blast drying box and dried for 24 hours at 85 °C. The specific surface area, pore volume and pore distribution were measured by NOVA 1000e high-speed automatic surface ratio and porosity analyzer and AutoPore IV 9500 mercury injection instrument. The results are shown in Figure 1-5.
Figure 1. Nitrogen adsorption desorption isotherms of activated carbon.

Figure 1 for activated carbon nitrogen isothermal adsorption stripping, hysteresis loop is found five kinds of activated carbon, according to the IUPAC puts forward six isotherm category, the activated carbon was nitrogen isothermal adsorption stripping I sorption isotherm and IV type isotherm types. At low pressure, the adsorption amount of nitrogen increases rapidly, indicating that the activated carbon has more pores. The order of nitrogen adsorption capacity of activated carbon was AC3 >, AC5 >, AC4 >, AC2 >, AC1, indicating that the order of specific surface area of several pretreated activated carbon was AC3 >, AC5 >, AC4 >, AC2 > AC1. When the relative pressure of the activated carbon pretreated by pickling, alkaline pickling, acid pickling and alkaline pickling was close to 1, the isotherm appeared at the corner and curved upward, indicating that the activated carbon pretreated by these three types of activated carbon had pores with diameter greater than 50 nm. The adsorption capacity of activated carbon to nitrogen was improved by water washing, acid washing and alkaline washing. Among them, the method of treating activated carbon with dilute hydrochloric acid is the most effective. Alkaline washing can also remove some ash, but it is not as good as pretreatment with dilute hydrochloric acid. The specific surface area of activated carbon after pickling was smaller than that of activated carbon after pickling.

Figure 2. Specific surface area.
It can be seen from Figure 2, Figure 3 and Figure 4 that the pore volume and specific surface area of activated carbon gradually increase with the decrease of the average pore diameter of activated carbon. Compared with the untreated AC1 and 3.748 nm, the average pore diameter of the washable activated carbon AC2 showed little change, while the specific surface area increased, indicating that the washable activated carbon could clean it and had little effect on the pore diameter of the activated carbon. The average pore size of AC3 decreased significantly, the BET specific surface area changed the most, increased by 15.7% compared with that before treatment, and the pore volume ratio increased by 25.8% compared with that before treatment, indicating that the treatment of activated carbon with dilute hydrochloric acid could not only remove ash content, but also open the activated carbon holes to produce more micropores. Alkaline washing can remove activated carbon partial ash, open the role of holes, so that the pore volume increased, the average pore size also increased, indicating that alkaline washing can increase the average pore size of activated carbon in a certain way.
Figure 5. Pore size distribution.

Water washing pretreatment method can significantly reduce the pore content of activated carbon with pore size less than 20 m, but it has no obvious effect on the pore size greater than 20 m. The pretreatment of activated carbon with hydrochloric acid has obvious effect on the pores with pore size less than 10 m, and the content of these pores increases greatly. However, for holes with an aperture between 10 m and 20 m, the effect is not as obvious as that with a diameter less than 10 m, and the content of holes greater than 40 m decreases. Due to the erosive effect of NaOH, the pore diameter of activated carbon is less than 20 m, but for the pore diameter of more than 20 m, it has an increasing effect. Therefore, NaOH has a reaming effect on large pores. In the activated carbon treated by pickling first and alkaline washing later, the pore size less than 10 m also decreased, and the content of macropore also increased.

4. Conclusions
The washing method has a cleaning effect on activated carbon, but some water remains.

The pretreatment methods of pickling and alkaline washing have great influence on the pore structure of activated carbon.

Alkaline washing is conducive to expanding macropores of activated carbon and reducing the content of micropores. By Pickling it can reduce the size of activated carbon particles and increase the pores of activated carbon, so as to increase the specific surface area of activated carbon. The BET specific surface area of activated carbon can be increased by 15.7% after pickling.

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