FORMALDEHYDE AND WATER ADSORPTION
ON ACTIVATED CARBON FIBERS BY AIR OXIDATION

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1. Introduction

In recent years, indoor air pollution becomes more and more serious. The concentration of many pollutants in indoor air is higher than that in atmosphere. Formaldehyde and other aldehydes are main pollutants in indoor air. Formaldehyde is a kind of poison. High concentration of formaldehyde can cause a series of symptoms such as headaches, nausea even can cause to death etc [1]. So it is necessary to take some measures to remove formaldehyde and other aldehydes from indoor air. So far, the most widely used method for air purification is adsorption by AC (activated carbon) and ACF (Activated carbon fiber). ACF is a novel and fibrous adsorbent, which has been developed during the 1970s. Its properties are better than traditional granular or powered AC because of its larger adsorption capacity, higher surface areas and fast adsorption and desorption speed. But the adsorption capacity of ACF prepared by traditional physical or chemical activated methods for formaldehyde is not as large in ambient air, because the surface properties of ACF are hydrophobic, while formaldehyde is a kind of polar molecule.

After air oxidation, the adsorption capacity of ACF for formaldehyde can be enhanced remarkably. In this research paper, the influence of air oxidization to ACF on formaldehyde was investigated from several aspects. Because formaldehyde solution was used in this experiment, water adsorption was also studied.

2. Experimental

2.1 Sample Preparation

Sample preparation was carried out in the continuous vertical synchronism carbonization and activation apparatus designed by the staffs in our laboratory.

Activated carbon fibers used here were prepared in a large apparatus mentioned above, steam as activation agent. The precursor was cellulose carbon fiber. The resultant sample was designated as ACF0. The specific surface area of ACF0 is 1269 m^2/g. The static adsorption amount of ACF0 for formaldehyde and water is 588.22 ml/g and 452.87 ml/g respectively.

Air oxidized samples were prepared in the same apparatus, but smaller than that mentioned above. ACF0 reacted with air at different temperature, time and air flow rate. The influence of different oxidization conditions on the formaldehyde and water adsorption properties was investigated.

2.2 Determination of nitrogen adsorption isotherms

A Micrometrics ASAP accelerated surface area and porosimetery apparatus (Micrometrics Ins. Corp.) was used for volumetric measurement nitrogen adsorption isotherms at 77.4K. The relative pressure was from 10^{-6} to 1.

2.3 FTIR analysis of samples

A Bio-Rad FTS-15/20 (Texas Instrument Corp., USA) IR spectrometer was used to measure the infrared spectra of the ACFs and to identify their chemical functionality. Data acquisition was performed automatically using standard software. The samples were ground with an agate mortar and pestle (15~20 min) and mixed with ground KBr powder; this was subsequently subtracted from the measured sample spectrum. For a typical run, 20 scans were obtained at a resolution of 4 cm^{-1}, the slope of the spectrum was 400~4000 cm^{-1}.

2.4 Formaldehyde and water adsorption

The static adsorption capacity of formaldehyde and water was determined by the desiccator's method, the dynamic adsorption of samples for formaldehyde and water determined by nitrogen bubbling method in the DuPont Instruments 951 Thermogravimetric Analyzer. Before the determination, all samples were degassed over 24 h at 105 .

3. Results and discussion

3.1 *Static and dynamic adsorption for formaldehyde and water adsorption on samples*

The adsorption capacity of air oxidized samples for formaldehyde and water was determined and compared with that of untreated sample. The influence of air oxidation condition on their adsorption was also investigated in details.

Figure 1 showed the effect of different air oxidation temperature, oxidation time and air flow rate on the yield of samples. With the increasing of oxidation temperature and time, the yield of all samples decreased. But the effect of air flow rate on the yield showed the opposite tendency.

Figure 2 showed the effect of different air oxidation temperature, oxidation time and air flow rate on static adsorption amount for formaldehyde and water. From the figure, it can be inferred that with the oxidation temperature increased from 300 to 420 , the static adsorption amount of oxidized samples for formaldehyde and water also increased obviously (Fig. 2-a). But when oxidation temperature was further increased to 450 , the adsorption amount decreased drastically. The sample oxidized at 420 exhibited the highest adsorption capacity for formaldehyde and water. In comparison with the untreated sample ACF0, its adsorption capacity for formaldehyde and water was improved remarkably. Fig. 2-b showed that the static adsorption amount of samples for formaldehyde and water decreased when the oxidation time increased from 1 hour to 4 hours, while there was a little increasing after the 5 hours' oxidation. So the valuable oxidation time should be 1 hour because the yield of 5 hours' oxidation sample was too low. Figure 2-c showed the best air flow rate was 150 ml/min. All these phenomena can be explained as following: in oxidized fibers, many polar groups are present primarily in the form of carboxylic acids, which can be identified from the FTIR spectrums mentioned below. So it can be inferred that due to the dipole interaction, the adsorption properties of oxidized samples for formaldehyde and water were improved.

Fig 3 illustrated the dynamic adsorption/desorption curves of formaldehyde and water on the untreated and air oxidized ACFs. The dynamic adsorption curves showed that with the increasing of air oxidized time, the dynamic adsorption capacity of samples decreased gradually. The sample of A-420-1h showed the highest adsorption capacity.

3.2 *Nitrogen adsorption isotherms of samples*

Figure 4 showed the nitrogen adsorption isotherms of the samples oxidized and untreated. All the three isotherms of the samples presented type I isotherm, which indicated that the controlled pores of all the three samples were micropores [2]. It also showed that the sample of A-420-1h-150 had higher adsorption amount of nitrogen than that of A-420-1h-200, which can be inferred that the sample of A-420-1h-150 had higher specific surface area than the sample of A-420-1h-200. This phenomenon corresponded to the adsorption capacity for formaldehyde and water shown in Fig. 2. In Fig. 2, the sample of A-420-1h-150 showed the highest adsorption amount for formaldehyde and water than any other sample. It illustrated that the samples with higher specific surface area had relatively higher adsorption capacity than that with lower specific surface area.

3.3 *FTIR spectrums of samples*

Figure 5 showed the difference in infrared adsorption of the sample as-received (ACF0) and the oxidized samples. Two characteristic peaks appeared in the spectra of all oxidized samples and were appropriately labeled at $\sim 1200 cm^{-1}$ and $\sim 1560 cm^{-1}$ respectively, while there weren't obvious peaks in the spectrum of as-received sample ACF0. Peaks at $\sim 1200\ cm^{-1}$ implied that there was carboxylic acids in the surface and bulk of air oxidized samples [3,4,5]. Peaks at $\sim 1560\ cm^{-1}$ were illustrated as C=C aromatic stretching and quinones. The intensity of peaks was different in different oxidized samples' spectra [3,4,5]. The peaks in the spectrum of A-420-1h were the most strong and A-350-1h showed the weakest peaks. All those showed that air oxidation could produce oxygen-containing functional groups at the edge of the graphitic planes of ACFs. But it is impossible to obtain quantitative information from the FTIR scans performed.

4.Conclusions

After air oxidization, the adsorption capacity of ACFs for formaldehyde and water were determined by static method and dynamic method. It was illustrated that the adsorption properties of treated samples were improved in comparison with untreated ACF. The porous structure parameters were investigated using nitrogen adsorption at 77.4k. The results showed that the samples with high surface areas had high adsorption capacity for both formaldehyde and water. Different treatment temperature and treatment time also affected the adsorption properties of ACF. FTIR spectra showed that there were carboxylic acid and quinones et al. oxygen-containing functional groups in the samples oxidized by air, which were attributed to the excellent adsorption capacity for formaldehyde and water.

References

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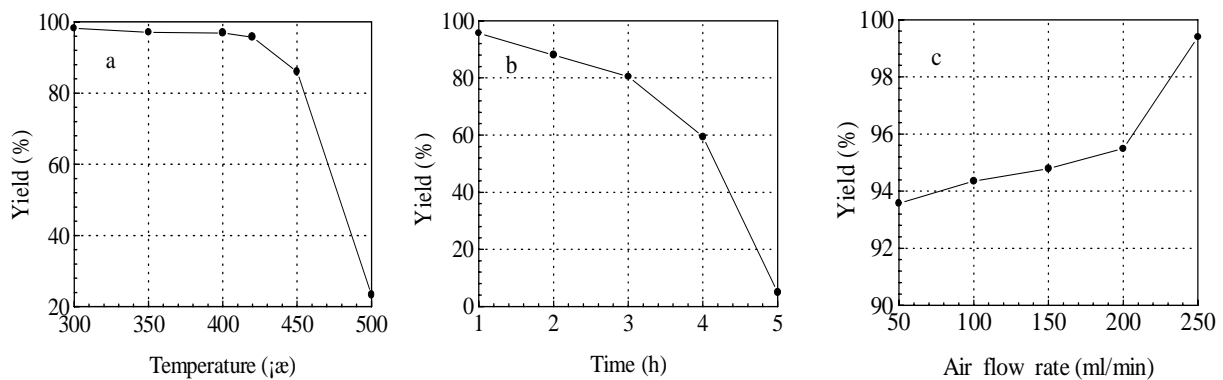
Fig 1 Effect of air oxidation condition on yield
a. temperature and yield   b. time and yield   c. air flow rate and yield
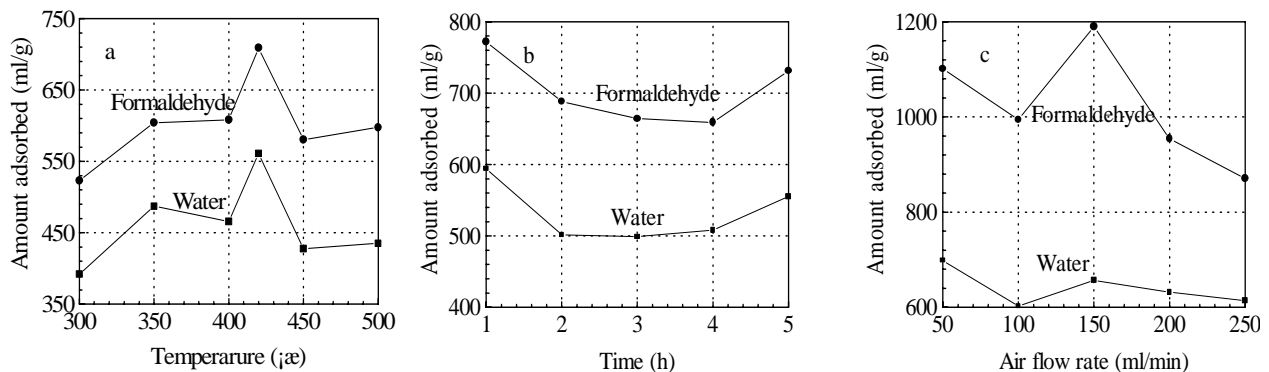

Fig 2 Effect of air oxidation condition on the static adsorption amount for formaldehyde and water
a. temperature and adsorption amount   b. time and adsorption amount c. air flow rate and adsorption amount
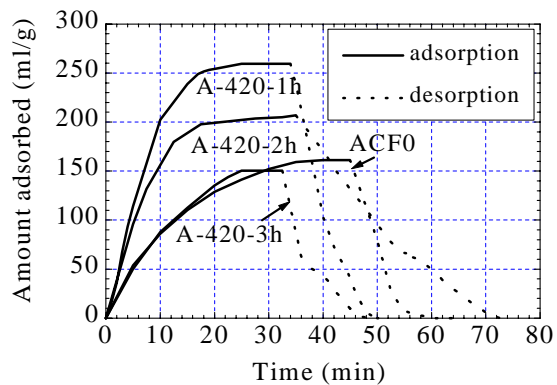
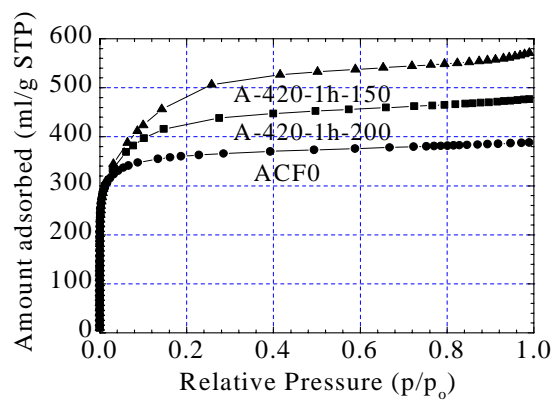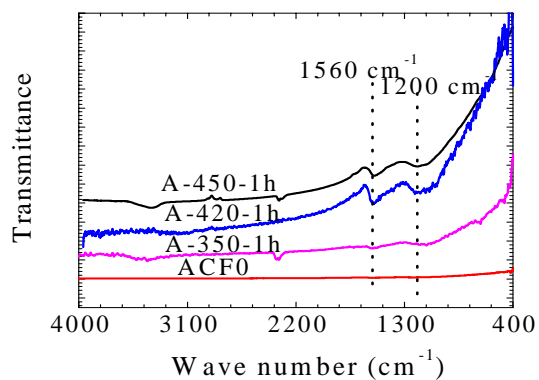Fig 3 Dynamic adsorption/desorption curves of samples
for formaldehyde and water

Fig 4 Nitrogen adsorption isotherms of samples

Fig 5 FTIR spectra of samples