

Chlorine Adsorption of Activated Carbons, Carbon Molecular Sieves and Carbon Nanotubes†

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Activated carbon, carbon molecular sieves and carbon nanotubes as ordered porous carbon materials, which have huge surface areas and special developed holes are investigated and compared by their chlorine adsorption properties in this paper. The adsorption properties of chlorine are investigated by pressure composition temperature instrument and characterized by X-ray diffractometer, Fourier transform infrared spectroscopy and scanning electron microscopy. The data is obtained at a temperature range of 273 K-323 K and pressure is in the range of 0-0.35 MPa. Among the three porous carbon materials, carbon nanotubes is most efficient in adsorption of chlorine and the adsorption capacity can reach 37.51 % at temperature 30 °C and under the pressure 0.332 MPa. The experimental data shows that the chlorine adsorption capacity influenced by temperature and pressure. Pore volume and aperture type are main factors attribute to the capacity difference. Activated carbon, carbon molecular sieves and carbon nanotubes are found to be potential candidates for adsorbing chlorine.

Key Words: Chlorine adsorption, Activated carbon, Carbon molecular sieves, Carbon nanotubes.

INTRODUCTION

Chlor-alkali industry is the backbone industry of inorganic chemical field. The output of chlor-alkali is more than 8000 million tons in the worldwide, approximately¹. Chlorine as the tail gas of chlor-alkali plant is damage to environment. There are plenty of corresponding methods to deal with chlorine plant offgas due to the source is different. These factors have to be taken into mind, component, quality of gas, dispose capacity and the productive technology. At present, the main dispose methods are water absorption, alkali absorption method, combustion absorption, solvent absorption, activated carbon or silica gel adsorption, membrane process², compression, freezing, *etc.* Combustion absorption method³ is widely used in plant which use water to adsorb hydrochloric synthesized by hydrogen and chlorine combustion, however, the production is inferior-quality hydrochloric acid which economic value is much less than the chlorine.

Pressure swing adsorption (PSA)^{4,5} separation and recovery of chlorine plant offgas with solid adsorbent such as silica and zeolite is a new method in recent years⁶. The adsorption-desorption property of adsorbent is critical. Although the type of porous material is a wide variety, the study of chlorine adsorbent is limited. These applications have provided an early

incentive for both theoretical⁷ and experimental^{8,9} studies on the adsorption of a range of gases (*e.g.*, Ar, Xe, Kr, N₂) on zeolite materials. It is significant and necessary to study the property of chlorine adsorbent in order to solve the problem of adsorption and separation of chlorine plant offgas, raise the economic value of chlorine plant offgas and reduce environmental pollution from chlor-alkali industry.

Activated carbon, carbon molecular sieves and carbon nanotubes as ordered porous carbon materials, have been applied well in gas storage and adsorption¹⁰. Siriwardane *et al.*¹¹ studied the volumetric adsorption of CO₂, N₂, or H₂ on molecular sieve 13X, molecular sieve 4A and activated carbon with pressure swing adsorption. Activated carbon shows higher CO₂ capacities than molecular sieves' under higher pressures (> 25 psi), significantly. Fujiwara *et al.*¹² finds that nitrogen and oxygen gases are adsorbed first inside of tubes and next in the interstitial channels in single-walled carbon nanotubes. These results indicate that the inside of nanotube has strong affinity for gas adsorption than the interstitial channels of bundles. We select activated carbon, carbon molecular sieves and carbon nanotubes as research object, they adsorption properties at different temperature and pressure and adsorption life are studied in this paper.

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EXPERIMENTAL

Activated carbon, carbon molecular sieves and carbon nanotubes used in experiment were industrial products. Activated carbon and carbon molecular sieves crushed and screened to 40-60 mesh. Carbon nanotubes powders were first compressed by a single punch tablet compression machine and then were broken into 40-60 mesh particles. Samples used in the experiment needed to be activated in a muffle furnace at 230 °C of 2.5 h.

Pressure composition temperature (P-C-T) chlorine-specific adsorption device was employed to test chlorine adsorption was shown in Fig. 1. The P_1 instructions source pressure of chlorine gas; P_2 , Precision pressure gauge for the range 0-1.6 MPa (gauge pressure); P_3 , vacuum gauge range -0.1-0 MPa (vacuum); D, dry filter tube within silica and calcium chloride; V_1 , the volume of standard size; V_2 , the volume of adsorption tube; F_1 - F_6 , copper valves; G, drying device filled by silica gel and NaA zeolite.

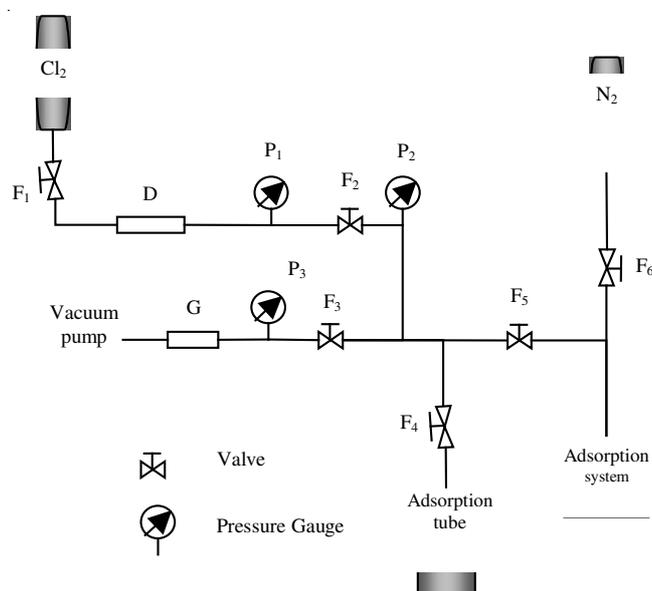


Fig. 1. Pressure composition temperature experimental setup

Weighted the samples first, accurately, put it into the reaction tube and then vacuumized the instrument for 3 h, continuously, while the temperature reached to the desired activation degree. In the process the vacuum was maintained as -0.095 MPa. The remaining chlorine absorbed by the potassium iodide solution, iodine generated by the reaction calibrated by sodium thiosulfate. According to the experimental data we calculated gas storage capacity and drew chlorine adsorption isotherms.

The crystallization framework structures and phase purity of the samples in Rigaku D/2500 X-ray diffractometer were measured by using copper K_{α} radiation where Cu target K_{α} as the X-ray source and scanning ranged from 5.0° to 45° under voltage 40 kV and current 100 mA. The skeleton structures of the samples were measured with Shimadzu FT-IR-8400 S infrared spectrometer which detected under the frequency 4500-350 cm^{-1} . Morphological data was acquired through scanning electron microscopy on JSM-6360LV manipulated at 10 kV.

RESULTS AND DISCUSSION

X-ray powder diffraction analysis of porous carbon samples before and after chlorine adsorption: XRD pattern of activated carbon before and after adsorption showed that the diffraction peaks of activated carbon existed and the carbon graphite crystallite's diffraction¹³ peaks at 26.5° could still be found after the adsorption, the amorphous carbon had not been damage as well. With the adsorption time increased the number of activated carbon graphite crystallites characteristic diffraction peak intensity weakened, however, the structure did not collapse. The decline of adsorption might be due to the heating activation process did not take the protection of nitrogen, which caused partial oxidation of activated carbon.

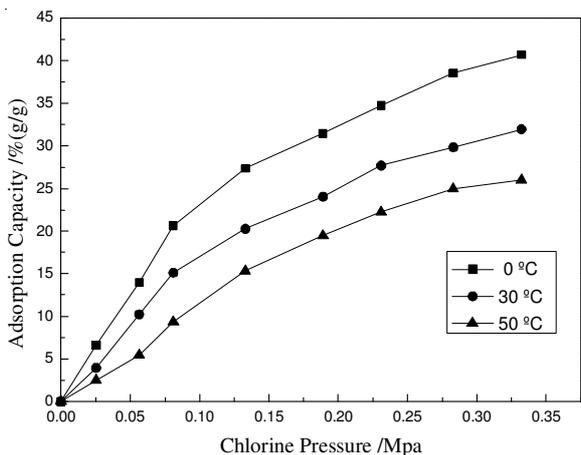
The XRD diffraction analysis of the carbon molecular sieve shows that the peak position and peak intensity matched with the standard pattern. There were three distinct peaks when the value of 2θ was between 20-25°, which were net carbon graphite plane (002), the value of 2θ at 45° existed diffraction peaks were (100) (001) diffraction peaks. After adsorption of chlorine, the peak intensity weakened especially in the value of 2θ is 45°. But the overall framework of carbon molecular sieve structure and the amorphous structure were not destroyed. As a result carbon molecular sieve could act as a chlorine adsorbent.

The XRD patterns of carbon nanotubes before and after adsorption of chlorine showed that the diffraction peaks occurred around 25° and 45°, clearly, indicated that the carbon nanotubes with a certain degree of crystallinity of graphite. The intensity of adsorption peak weakened after adsorption, but the micro-crystalline structure of graphite nanotubes and amorphous structure damage did not occur after adsorption.

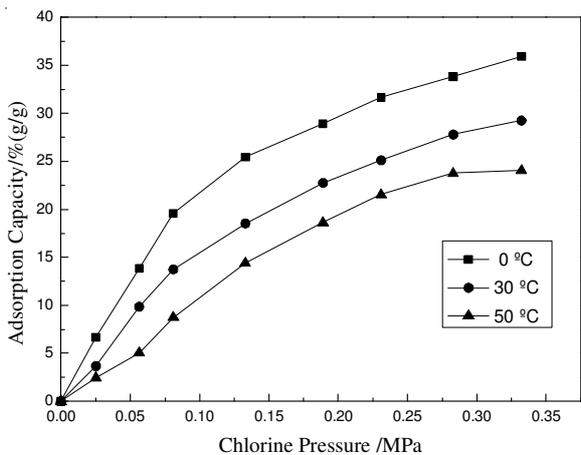
Infrared spectral analysis of three porous carbon samples before and after chlorine adsorption: Activated carbon, carbon molecular sieves, carbon nanotubes belonged to porous carbon materials in the infrared spectrum, had the same characteristic diffraction peaks. The data showed that the peak in the 3600-3100 cm^{-1} belonged to the carbon surface hydroxyl groups or stretching vibration by absorbed water, the peak at 2955 and 2885 cm^{-1} belonged to C-H bonds vibration for weak infrared absorption, the peak at 1680-1600 cm^{-1} belonged to unsaturated C=C bonds stretching vibration, the peak at 1200-1050 cm^{-1} belonged to the C-O-C bonds asymmetric stretching vibration, the strong absorption peak at 3439 cm^{-1} might be belonged to carbon surface water stretching vibration because the phenolic hydroxyl absorption peak at 1300-1100 cm^{-1} , which didn't appear on the infrared spectrum. The weak absorption peak at 2950 cm^{-1} and 2885 cm^{-1} belonged to the C-H bonds vibration and the weak absorption peak at 1631 cm^{-1} belonged to the unsaturated C=C bonds stretching vibration of carbon material. The absorption peak at 1092 cm^{-1} belonged to the absorption for the C-O-C. After adsorption of chlorine the characteristic diffraction peak still existed but the intensity decreased, the reason might be that, a small part of the chlorine atoms into the porous carbon material and combined a small part of the C=C unsaturated bonds and C-O-C bonds.

Chlorine adsorption properties of there porous carbon material under different temperature and pressure: The

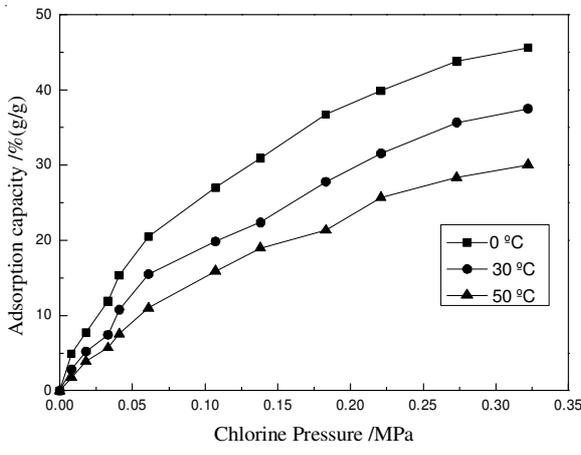
isotherm curves of the chlorine adsorption of activated carbon, carbon molecular sieves and carbon nanotubes at different temperatures were depicted in Fig. 2(a-c). These curves were similar to the Langmuir's adsorption and the isotherm curves were considered to conform to physisorption. The adsorption capacities increased with the pressure increased whereas decreased with temperature increased. Compared with the activated carbon and carbon molecular sieves, the chlorine adsorption capacity of carbon nanotubes were much strong and reached 37.51 % at 30 °C and 0.332 MPa.



(a) activated carbon



(b) carbon molecular sieves



(c) carbon nanotubes

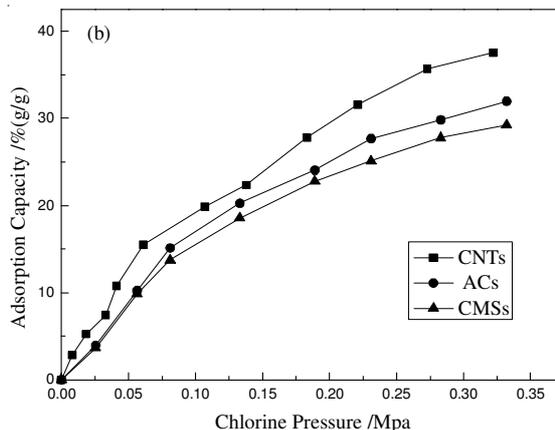
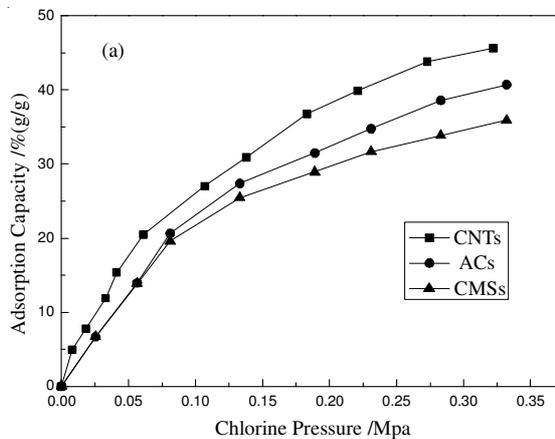
Fig. 2(a-c). Chlorine adsorption isotherm at 0 °C, 30 °C, 50 °C

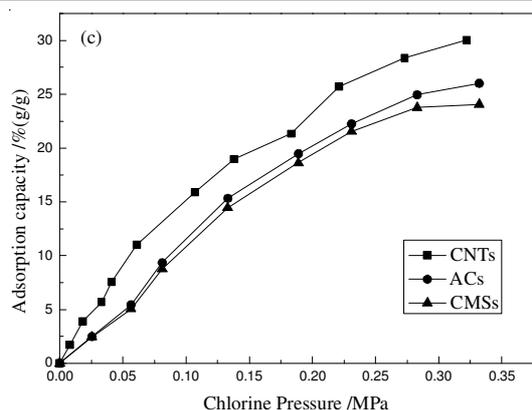
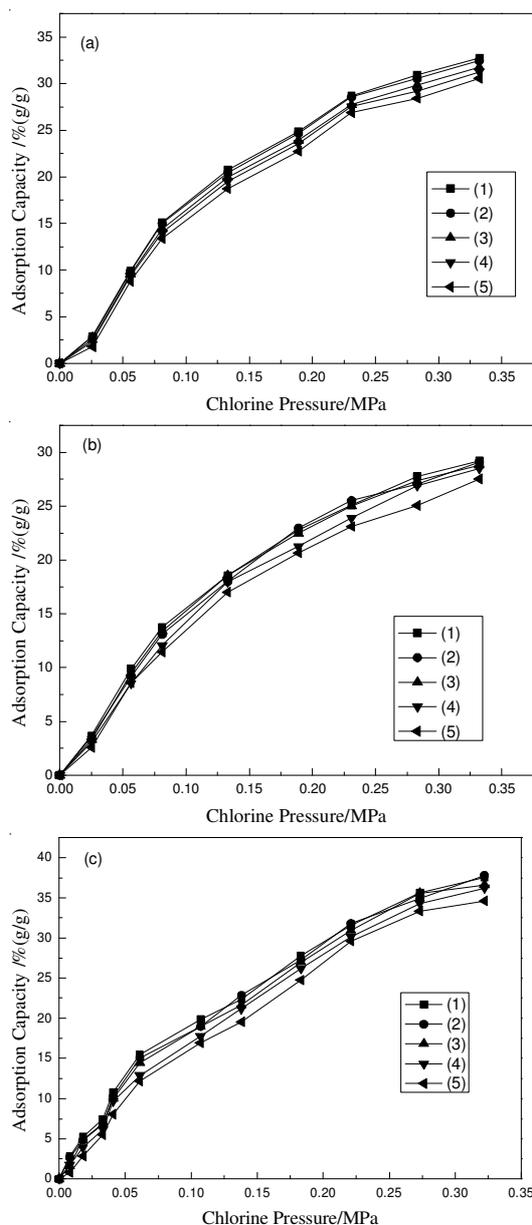
The SEM micrographs of activated carbon, carbon molecular sieve and carbon nanotubes showed that the particle sizes were irregular and the pore sizes were in a wide scale. That was because the samples used in experiment were industry grade. We could observe that there were no adsorption platforms in Fig. 2(a-c), which were conformed to adsorption theory type II adsorption curve.

Adsorption times effects on adsorption properties of three porous carbon materials: As we could see from Fig. 3(a-c), the adsorption capacities increased with the temperature decreased. The maximum adsorption capacity of three porous carbon material emerged at 0 °C. At room temperature they also had large adsorption capacity. In this paper we studied and compared the adsorption capacity of activated carbon, carbon molecular and carbon nanotubes at 30 °C for adsorption five times, respectively.

Adsorption isotherms in Fig. 4(a-c) conformed to the Langmuir's adsorption. The chlorine adsorption capacity of three samples decreased after five times adsorptions-desorption. The maximum adsorption capacity declined respectively from 32.75 to 32.57 %, 29.24 to 27.54 % and 37.51 to 34.63 %. The data showed that there were no obvious declines after five times adsorption-desorption. This means that the skeleton structures, before and after adsorption, were no significant change and the collapse of the skeleton did not occur.

Skeleton structure effect on the adsorption capacity of materials: The adsorption capacity of carbon nanotubes was larger than activated carbon and carbon molecular sieve at the different temperature in Fig. 4(a-c). As we could see from Table-1, compared with activated carbon, the pore size,



Fig. 3. Cl₂ Adsorption isotherms on carbon materials under 0 °CFig. 4. (a-c) Five times Cl₂ adsorption isotherms on carbon materials under 30 °C

pore volume and specific surface of carbon molecular sieves were much smaller, which were in contrary to carbon nanotubes. Those contributed to the adsorption capacity. However, because

of the length of carbon nanotubes was long, there was long time required for adsorption-desorption, so we usually took activated carbon as adsorption materials for gas masks, instead of using other two porous carbon material we discussed in this paper.

TABLE-1
PARAMETERS OF THREE SAMPLES

Samples	Pore aperture (nm)	Pore volume (m ³ /g)	BET(m ² /g)
ACs	2-50	300-400	900-1100
CMSs	1.5-2.2	150-250	800
CNTs	5-10	400-500	500

Conclusion

The adsorption isotherms of the activated carbon, carbon molecular sieves and carbon nanotubes at 0, 30 and 50 °C conform with Langmuir adsorption which belongs to physical adsorption. Adsorption capacity increases with temperature decreased but decreases with the pressure decreased.

Experimental data showed that the adsorption capacity of carbon materials vulnerable influenced by the pore volume and pore size. The adsorption properties of carbon nanotubes are better than activated carbon and the adsorption properties of activated carbon are better than carbon molecular sieves, which are due to carbon nanotubes with a large pore volume and pore size and the diameter of the dynamics of chlorine is 0.44 nm and micro-pore size of selected carbon material reach to the size that allows chlorine molecules diffuse into. Meanwhile, the molecular dynamics diameter of the best adsorption pore diameter of zeolite is 2-6 times^{14,15}. The adsorption capacity meets the requirements for chlorine adsorption.

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