Study on Chlorine Adsorption Properties of Cu/AC, Ag/AC and Pd/AC

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Activated carbon (AC) is widely used for adsorbent and supporter of catalyst owing to its efficient adsorption capacity and large specific surface area. The objective of this study is to investigate chlorine adsorption properties of Cu/AC, Ag/AC and Pd/AC, which were prepared by impregnation method. The samples were characterized by X-ray diffraction and Fourier transform infrared spectroscopy techniques. The experimental data showed the loading of copper, silver and palladium could significantly improve the adsorption capacity of activated carbon for chlorine. The maximal adsorption of Cu/AC with 5 wt. % copper content could reach 32.73 % at 30 °C under 0.22 MPa. While the adsorption capacity of 9 wt. % Ag/AC and 9 wt. % Pd/AC are larger, of which the values were 33.46 and 34 %, respectively. Moreover, the structural framework of Cu/AC, Ag/AC and Pd/AC still existed and its adsorption ability remained stable after absorbing continuously for several times.

Keywords: Cu/AC, Ag/AC, Pd/AC, Chlorine, Adsorption.

INTRODUCTION

Activated carbon is a sort of carbon material with large specific surface area and ordered pores. As excellent adsorbents and catalysts, activated carbon plays an irreplaceable role in the fields of environment protection, food processing, metallurgy, pharmacy, chemical industry, which were all attributed to its high ordered structure, high mechanical and thermal strength and high surface area.

Using activated carbon to adsorb gases is an effective way to purify air, remove poisonous gases and recycle products. Dating back to World War-I, this material was embedded into the anti-gas masks to protect from a kind of toxicant gas-chlorine. Generally, in chlor-alkali industry, pressure swing adsorption[1] (PSA) separation method was applied to remove chlorine, which is an established commercial process for gas-separation in large quantity with low cost. Pressure swing adsorption is a technique that is capable of removing gas by applying pressure to make the gas adsorbed by the adsorbents and then desorbing below the adsorbing pressure. The advantages of pressure swing adsorption separation method are simple equipment, easy operation, economy and energy efficiency. Xue *et al.*[2] investigated chlorine adsorption properties of activated carbon with pressure-composition-temperature pressure swing adsorption device. They found that activated carbon performed certain adsorption ability for chlorine and the adsorbing capacity declined little after absorbing and desorbing continuously for several times.

The common activated carbon adsorbents currently used for gas adsorption show low efficiency and do not have the expected lifespan for certain gas. Sometimes it is necessary to modify them by loading relevant active composition so as to improve the adsorption capacity according to the various characteristics of different gases. Recently, the mixture of metal compounds containing copper, silver, zinc and molybdenum were loaded on activated carbon by impregnation method, which was named ASZM-TEDA. It was proved that the adsorption capacity of activated carbon for cyanogen chloride was significantly improved due to the loading of metals[3-6]. Li *et al.*[7] made chlorine adsorbents by impregnating activated carbon into certain soluble salt solution. The maximal adsorption capacity of their samples could reach 7-12 %. However, less attention has been received on the chlorine adsorption properties of activated carbon with metal loaded. In present experiment, copper, silver and palladium were loaded on activated carbon, respectively by impregnation method and their chlorine adsorption properties were investigated.

EXPERIMENTAL

Activated carbon (industrial grade) were screened to 40-60 mesh. The chlorine was also of industrial grade, with the purity of 99.99 %. Other reagents, such as CuCl, AgNO₃, PdCl₂, HNO₃, HCl, used in this study were of analytic grade.

The screened activated carbon were divided into three parts and each part contained 6 g. The first part was added

into a round-bottom flask filled with 2 mol/L hydrochloric acid solution at a rate of 2.5 rps at 120 °C. After stirring for 6 h, the suspension was filtrated, washed several times with deionized water to remove weak adsorbed metal ions on the AC surface and dried in oven at 110 °C for 12 h. It was marked with AC-HCl.

In second part, the activated carbon was dipped into a 5 mol/L nitric acid solution in another round-bottom flask. The activated carbon was stirred and dried under the same operating conditions as AC-HCl. The pre-prepared sample was marked with AC-HNO₃.

The last part was impregnated into a beaker with 1 mol/L sodium hydroxide for 12 h. Then it was washed into neutral and immersed into another beaker with 2 mol/L nitric acid solution. After 24 h, the sample was filtered and dried for 12 h at 110 °C. The modified activated carbon was marked with AC-NaOH/HNO₃.

The modified AC-HCl was impregnated into several beakers filled with the cuprous chloride solution of different concentrations for 6 h at room temperature, in a similar way, AC-HNO₃ into palladium chloride solution and AC-NaOH/HNO₃ into silver nitrate solution. After that the samples were dried in the oven at 120 °C overnight to remove the solvent and the moisture completely. The dried activated carbon were deoxidated under hydrogen atmosphere and the samples were kept in an airtight bottle for use. Then we obtained Cu/AC, Pd/AC and Ag/AC.

The pressure-composition-temperature (P-C-T) apparatus for chlorine adsorption is displayed in Fig. 1. The weighed samples were put into the adsorption tube, which should be heated up to 150 °C and vacuumized for 3 h continuously keeping the temperature constant. When the tube was cooled to room temperature, it was placed into a thermostatic container and the chlorine was filled into the system under certain temperature. The pressure value should be recorded when the pressure gage was constant, which meant the adsorption of activated
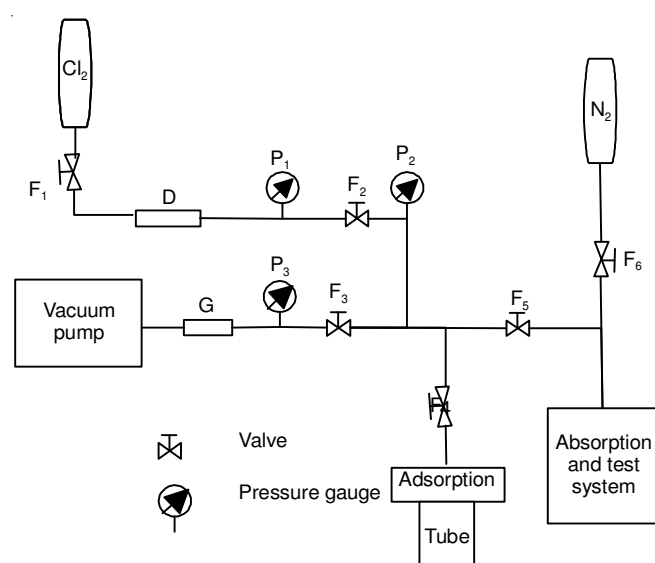
gradually reduced several times and the pressure value was recorded as the method described above. The released chlorine was measured with potassium iodide through titration. The chlorine storage volume of activated carbon was calculated under each balanced pressure according to the indication of the pressure gauge. The chlorine adsorption isotherm was drawn in accordance with pressure and adsorption capacity.

Detection method: Rigaku D/2500 X-Ray diffractometer was used to analyze the crystallization framework structures and phase purity of the samples. The surface functional groups and chemical bonds of the samples were measured by Shimadzu FT-IR-8400S infrared spectrometer.

RESULTS AND DISCUSSION

The chlorine adsorption isotherms under the different pressure on AC, 5 % Cu/AC, 5 % Ag/AC and 5 % Pd/AC were displayed in Fig. 2. This test was conducted at 30 °C. According to the Figure, four adsorption curves were consistent with Langmuir's adsorption isotherms and the adsorption type conformed to physisorption. Apparently, the adsorption capacity of activated carbon for chlorine was improved owing to the loading of copper, silver and palladium. Compared with the 29.47 % adsorption capacity on AC, 5 % Cu/AC, 9 % Ag/ AC and 9 % Pd/AC could reach a maximal capacity of 32.73, 31.65 and 32.55 %, respectively under 0.28 MPa. This phenomenon might be caused by two reasons. The metal particles inside the pores and on the surface of activated carbon could gather chlorine, making it hard to escape from the adsorbents[8,9]. This gathering effect expanded the chlorine storage volume of activated carbon, which led to the increasing of adsorption capacity. While the other reason might result from the modifying process of activated carbon before impregnation, nevertheless, the adding of acid and alkali removed the impurities inside the pores and increased the specific surface area of activated carbon.
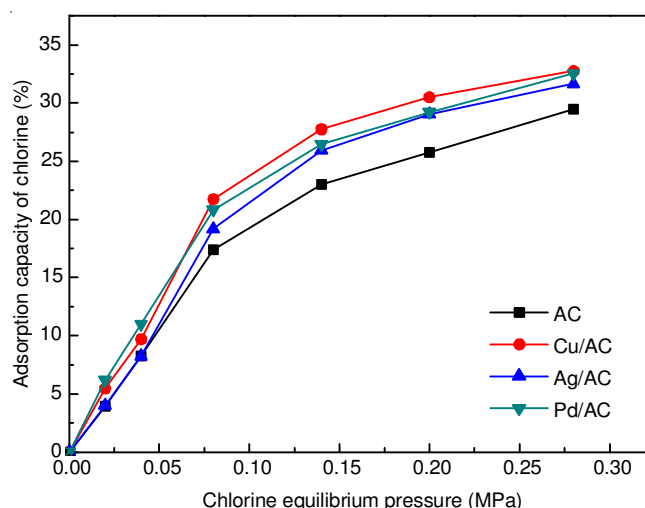

Fig. 1.   P-C-T Apparatus. P_1:source pressure of the chlorine gas (0-1.6 MPa); P_2:gauge pressure (0-1.6 MPa); P_3:vacuum gauge range (-0.1-0.3 MPa); D:dry filter tube (silica gel, anhydrous calcium chloride); F_1-F_7:copper valves; G:drying device (silica gel and NaA zeolite)

Fig. 2.   Chlorine adsorption performance curves of 5 % Cu/AC, Ag/AC and Pd/AC at 30 °C

Effects of metal loading percentage on the adsorption capacity: Fig. 3 indicated the chlorine adsorption curves of Cu/AC, Ag/AC and Pd/AC with different metal percentage composition at 30 °C and under 0.28 MPa. The adsorption
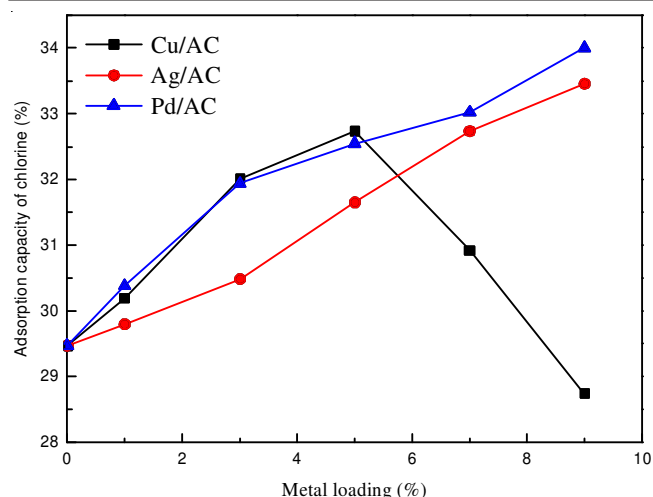
Fig. 3. Chlorine adsorption curves of Cu/AC, Ag/AC and Pd/AC in different mass fraction at 30 °C

Fig. 4. Chlorine adsorption curves of 5 % Cu/AC for chlorine adsorption five times repeatedly at 30 °C

capacity of Cu/AC was improved along with the increasing of metal loading content from 1 to 5 %, while the adsorbing curve of Cu/AC declined with the content from 5 to 9 %, which meant Cu/AC with 5 % copper content had the maximum adsorption capacity of 32.73 %. However, unlike Cu/AC, the chlorine storage volume of Ag/AC and Pd/AC grew continuously with the content from 1 to 9 %. And 9 % Ag/AC and 9 % Pd/AC had the adsorption capacity of 33.46 and 34 %, respectively. It could be inferred from these curves that 33.46 and 34 % were not the maximum adsorption percentage of Ag/AC and Pd/AC in theory. The adsorption capacity of these two modified activated carbon would still have a trend of growth until the metal content reached a certain value, then it declined as metal content increased. This trend could be explained as that, with the increasing of loading percentage, the gathering effect of metal particles enhanced. However, when the metal particles were overloaded to fill up the pore channels, they would block up the pore, resulting in a decreasing of adsorbability.

According to the difference among the three adsorption curves above, it could be speculated that two factors might cause the change in the adsorbability of metal-loaded activated carbon. One was the different gathering ability of metal particles on the surface and inside the pore channels of activated carbon. The other was the density of metal. For instance, as the density of palladium was greater than that of copper, the same mass of copper and palladium were loaded on activated carbon, copper would occupy larger pore volume. So Pd/AC had a larger adsorption capacity than Cu/AC.

Effects of repeatedly cyclic adsorption on the chlorine adsorption properties: The chlorine adsorption capacity of 5 % Cu/AC, 9 % Ag/AC and 9 % Pd/AC at 30 °C were shown in Figs. 4-6. These figures represented the adsorption isotherms of three samples of chlorine adsorption for 1, 2, 3, 4 and 5 times. According to the curves, the maximum adsorption capacity of Cu/AC, Ag/AC and Pd/AC declined respectively from 32.73 to 29.83 %, 33.46 to 30.92 % and 34 to 32.01 %. The results showed that there were no obvious declines in adsorption capacity of these three samples, which meant that the skeleton structures were not damaged and the metal particles outflowed little after a 5 time adsorption. Repeatedly
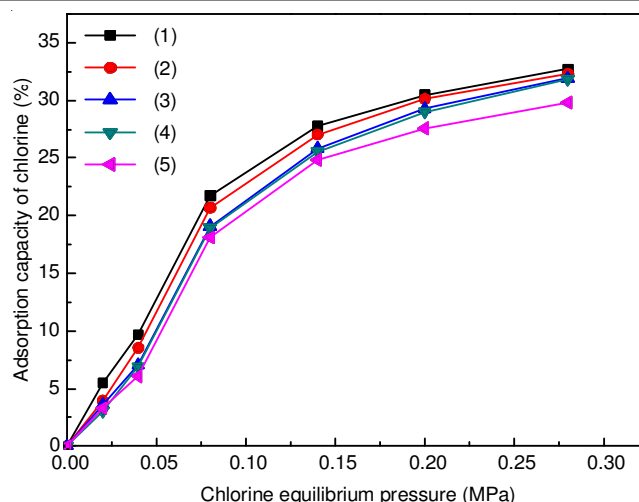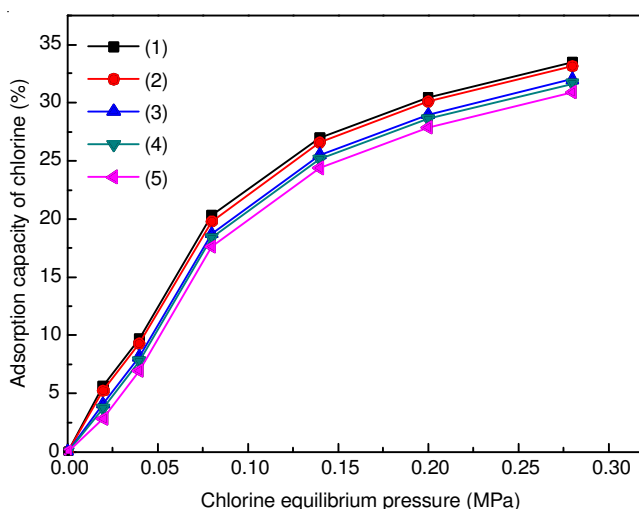

Fig. 5. Chlorine adsorption curves of 9 % Ag/AC for chlorine adsorption five times repeatedly at 30 °C
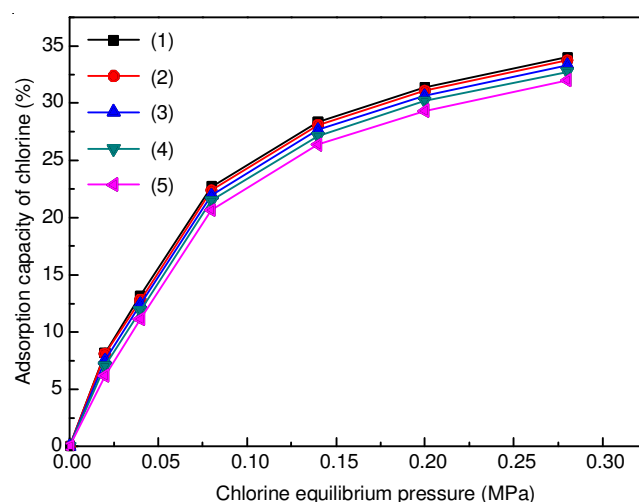

Fig. 6. Chlorine adsorption curves of 9 % Pd/AC for chlorine adsorption five times repeatedly at 30 °C

cyclic adsorption had little impact on the chlorine adsorption properties. As a result, these three modified activated carbon could be repeatedly used as chlorine adsorption.

Infrared spectral characterization of the three samples before and after loading metal: The infrared spectra of AC, 5 % Cu/AC, 5 % Ag/AC and 5 % Pd/AC were displayed in Figs. 7-9. From these spectra, the absorption peak between 3600 and 3300 cm^{-1} were induced by the phenolic hydroxyl group on the surface of carbon materials. The characteristic adsorbing peaks, caused by stretching vibration of the unsaturated C=C bonds, were between 1700 and 1500 cm^{-1}. The peaks found at 1200-1000 cm^{-1} were due to the asymmetric stretching vibration of C-O-C bonds[10,11]. The characteristic adsorbing peaks of activated carbon still existed after the loading of metal, but the peak intensity decreased, which can be explained by partly damage of unsaturated C=C bonds and C-O-C bonds during the acid and alkali treatment. As a whole, the framework of activated carbon remained stable. In other words, the modifying process did not lead to a large area of collapse inside activated carbon.

X-ray diffraction analysis of three samples before and after a 5 time adsorption: The phase and crystallization structures of the samples were measured by XRD. Figs.10-12,
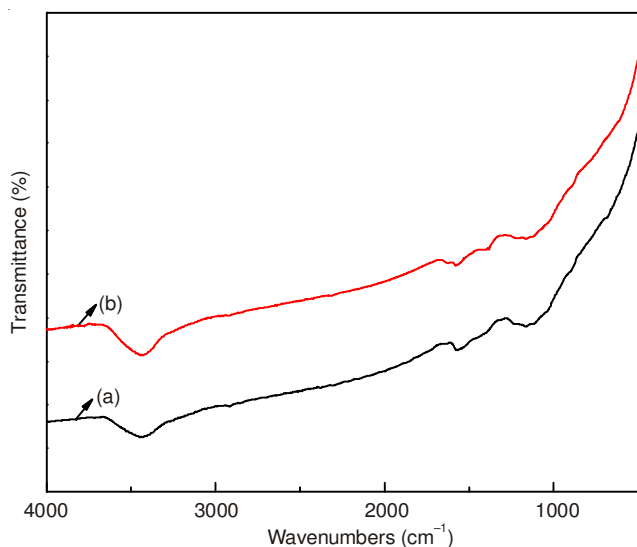

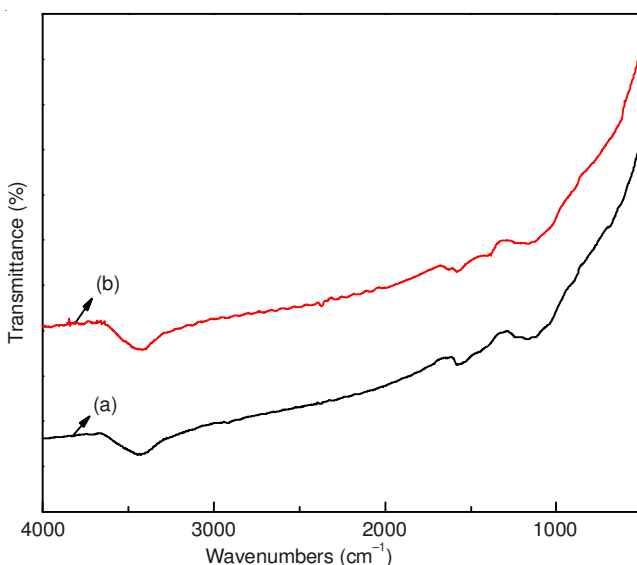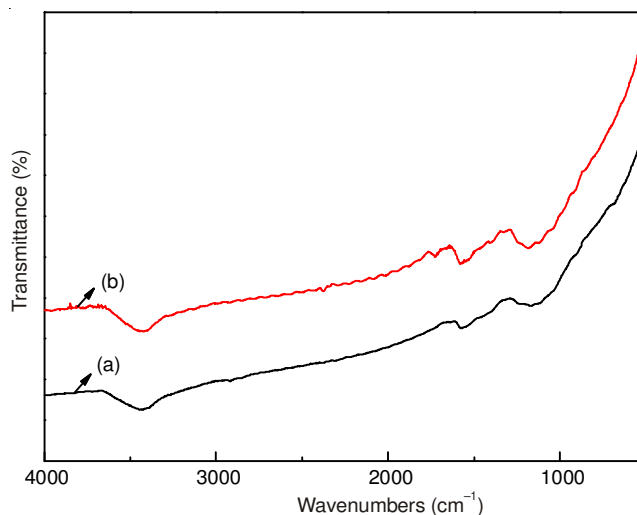Fig. 9. (a) FTIR spectra of AC (b) FTIR spectra of 9 % Pd/AC

respectively showed the XRD patterns of Cu/AC, Ag/AC and Pd/AC before and after adsorbing for 5 times. There were obvious characteristic diffraction peaks at 43.3º and 50.4º in Fig.10, at 38.0º, 44.2º and 64.3º in Fig. 11 and at 40º, 46.5º and 68º in Fig. 12. All of which corresponded to the location of standard XRD spectrum of copper, silver and palladium. Compared with the original samples, the three types of activated carbon had relatively weaker diffraction peaks after a 5 time adsorption. Overall, little decreasing was observed on the peak intensity of Cu/AC and Ag/AC. But it became visible that the peak intensity of Pd/AC declined obviously after cyclic adsorption. The spectra implied that Pd/AC would not have a long lifespan because part of palladium particles outflowed during the adsorbing progress. Further improvement is needed to expand the lifespan of Pd/AC. So Cu/AC and Ag/AC were the expected adsorbents.
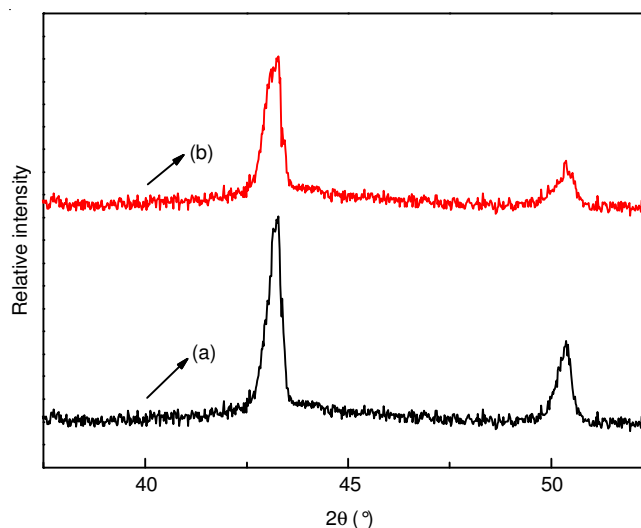

Fig. 7. (a) FTIR spectra of AC (b) FTIR spectra of 5 % Cu/AC

Fig. 10. (a) XRD patterns of 5 % Cu/AC (b) XRD patterns of 5 % Cu/AC after chlorine adsorption five times repeatedly

Conclusions

• The adsorption capacity of Cu/AC, Ag/AC and Pd/AC were larger than that of original activated carbon. The maximum chlorine storage volume reached 32.73, 33.46 and 34 %

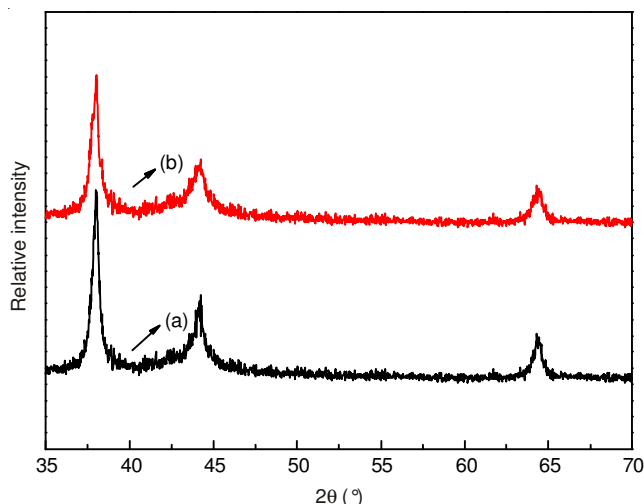Fig. 8. (a) FTIR spectra of AC (b) FTIR spectra of 9 % Ag/AC

Fig. 11. (a) XRD patterns of 9 % Ag/AC (b) XRD patterns of 9 % Ag/AC after chlorine adsorption five times repeatedly
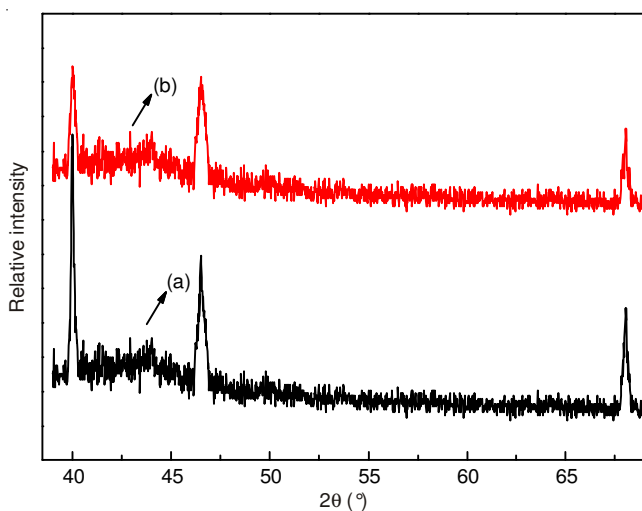

Fig. 12. (a) XRD patterns of 9 % Pd/AC (b) XRD patterns of 9 % Pd/AC after chlorine adsorption 5 times repeatedly

with 5 % Cu, 9 % Ag, 9 % Pd loaded, respectively. FT-IR showed that framework of modified activated carbon remained stable and the modifying process lead to little area of collapse inside activated carbon.

• There was no obvious decline in adsorption capacity of the three samples after a 5 time adsorption. The XRD patterns illustrated the peak intensity of Cu/AC and Ag/AC decreased slightly after absorbing for 5 times, however, the intensity of Pd/AC declined obviously. This was because part of palladium particles outflowed during the adsorbing progress.

REFERENCES

1. K.T. Chue, J.N. Kim, Y.J. Yoo, S.H. Cho and R.T. Yang, *Ind. Eng. Chem. Res*., **34**, 591 (1995).
2. J.W. Xue, X.G. Wen, H.L. Zhao, F.X. Li and Z.P. Lv, *Asian J. Chem*., **24**, 5481 (2012).
3. R.N. Nickolov and D.R. Mehandjiev, *J. Colloid Interf. Sci*., **273**, 87 (2004).
4. R. Szmigielski, S. Zietek, A. Swiatkowski, D. Palijczuk and M. Kielczewski, *J. Hazard. Mater*., **163**, 471 (2009).
5. D.T. Doughty and W.J. Knebel, Chromium-Free Impregnated Activated Universal Respirator Carbon for Adsorption of Toxic Gases and/or Vapors in Industrial Applications, US Patent 5492882 (1996).
6. D.T. Doughty and J.D. Groose, Chromium-Free Impregnated Activated Carbon for Adsorption of Toxic Gases and/or Vapors, US Patent 5063196 (1991).
7. Y.S. Li, X.X. Xia, X.H. Li, Q. Xin and C.H. Liang, *Chem. Eng. (China)*, **144**, 54 (2007).
8. E. Kim, J. Lee, J.K. Jeon, Y. Lee, S. Lee and J. Kim, *J. Korean Phys. Soc*., **52**, 892 (2008).
9. S. Wethekam, D. Valdes and R.C. Monreal, *Phys. Rev. B*, **78**, 075423 (2008).
10. J.G. Jia and C.Y. Xiao, *Chem. Def. Ships*, **4**, 23 (2007).
11. J.G. Jia and L.C. Zhu, *Carbon. Technol. (China)*, **6**, 11 (2009).