Chemical Engineering Journal 148 (2009) 242–247

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effect of thermal oxidation of activated carbon surface on its adsorption towards dibenzothiophene

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ARTICLE INFO

Article history:
Received 7 May 2008
Received in revised form 7 August 2008
Accepted 19 August 2008

Keywords:
Activated carbon
Thermal oxidation
Oxygen-containing groups
Desulfurization

ABSTRACT

The effect of thermal oxidation of activated carbon (AC) on adsorption capacity of dibenzothiophene (DBT) was investigated. ACs were treated in air by thermal oxidation at different temperature 473, 573 and 673 K and thus modified ACs, AC_{473}, AC_{573} and AC_{673} were separately available. The oxygen functional groups on the surfaces of the ACs were determined separately by diffuse reflectance infrared Fourier transform spectroscopy and Boehm titration. The influence of the surface chemistry of the ACs on its adsorption towards DBT was discussed. The results showed that after the thermal oxidation of carbon surfaces, its total basicity decreased, while its total acidity increased. The higher the oxidation temperature was, the more the amounts of surface acidic oxygen-containing groups were, and thus the higher the amounts adsorbed of DBT on corresponding carbon were. For the original AC, AC_{473}, AC_{573} and AC_{673}, the breakthrough amount of the treat fuel with containing 320 mg S l^{-1} was 35.5, 45, 52.5 and 61 ml fuel g^{-1} A^{-1}, respectively, corresponding to the breakthrough capacity of 11.4, 14.5, 16.8 and 19.5 mg of sulfur per gram of adsorbent (mg S g^{-1} A^{-1}). The adsorption capacity of the AC_{473}, AC_{573} and AC_{673} for DBT increased separately by 27.2%, 47.4% and 70.2% compared to the original AC.

1. Introduction

Air pollution due to exhaust gas from commercial gasoline and diesel has been a major concern of the public because the sulfur compounds in gasoline and diesel are the main source of SO_x in the exhaust gas. For this reason, the stricter regulations have been decided for near future for sulfur content in fuels. Currently, a new standard has been set up by the Environmental Protection Agency of the United States and the European Commission to reduce the sulfur content to less than 10 ppmw by 2008 [1]. For both environment protection and market competition, China's government mandates sulfur level to less than 10 ppmw by 2010 from the current levels of less than 800 ppmw for gasoline and 2000 ppmw for diesel except in large cities like Beijing and Shanghai where the current limit is already 150 ppmw [2]. In addition, the diesel fuel is preferred for fuel-cell applications. However, for proton-exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs), the sulfur content in liquid hydrocarbon fuels needs to be reduced to <1 ppmw and <3–30 ppmw, respectively [2]. Hence a considerable effort is being made to remove the organic sulfur molecules from hydrocarbon based fuel to obtain sulfur free or ultra-low-sulfur fuel.

The major sulfur compounds existing in current commercial diesel are the alkyl dibenzothiophenes (DBTs) with one or two alkyl groups at 4-or/ and 6-positions, which have been considered to be the refractory sulfur compounds in the fuel due to the steric hindrance of the alkyl groups in traditional hydrodesulfurization (HDS) [1]. Consequently, it is difficult or very costly to reduce the sulfur in diesel fuel to less than 10 ppmw by using the existing HDS technology [1]. So, alternative technologies are of particular interest to obtain sulfur free fuels. One new approach for desulfurization is by selective adsorption of thiophenic sulfur on adsorbents. This method might be the most economical way for the removal of thiophenic sulfur. Song and Ma [3] and Song [4] explored a process which is called selective adsorption for removing sulfur (PSU-SARS) over various materials including metals, metal halides, metal oxides, metal sulfides, and modified zeolites. Among them, nicked-based adsorbents showed a much higher adsorptive capacity in comparison with that of others [5–7]. Yang et al. [8,9] have developed a variety of π-complexation-based sorbents obtained by ion exchanging zeolites with different metal cations, including Ag^+, Cu^+, Ni^{2+} and Zn^{2+}. These ion-exchanged materials were capable of producing fuels with a total sulfur concentration of less than 1 ppmw. In particular, the Cu(I)Y zeolite (vapor-phase ion exchange or VPIE) showed the highest selectivity and capacity for sulfur[10–12]. Activated carbons (ACs) were also used as adsorbent in desulfurization because of their very high surface areas and large pore volumes. Salem and coworkers compared the desulfurization

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doi:10.1016/j.cej.2008.08.018

performance on activated carbon (AC) and 13X zeolite [13,14], and reported that the AC had three times greater capacity for mercaptan and thiophene than 13X zeolite at high concentrations at 20 °C. Lee et al. investigated the removal of thiophenic sulfur with ten different commercially available ACs [15], and reported that coconut shell-based carbons activated by high-temperature steam were more effective at sulfur removal than coal-based carbons. Zhou et al. tested the adsorption desulfurization performance of carbon materials with different surface properties [16], and his results showed that sulfur-adsorption capacities and selectivities depended not only on textural structure but also on surface functional groups.

The objective of this work was to study the effect of thermal oxidation [17,18] of AC on its adsorption toward DBT. ACs were modified by thermal oxidation at different temperature to get different acidic oxygen-containing groups. Static equilibrium adsorption experiments were conducted to determine the isotherms of DBT on the original AC and modified ACs by thermal oxidation. The textural structures of the ACs were characterized. The surface oxygen-containing groups were further analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and Boehm titration separately. The influence of the surface chemistry of the ACs on its adsorption toward DBT would be discussed and reported here.

2. Experimental

2.1. Reagents

The adsorbate, DBT (98%), was purchased from Acros Organics, NJ, USA. AC, SY-6 (60–80 mesh), based on coconut shell was supplied by Zhaoyang Senyuan activated carbon Company, China. The model diesel fuel (MDF) which contains 320 mg sulfur per liter of fuel ($\mathrm{mg\,S\,l^{-1}}$) used in this work is a mixture of *n*-octane and DBT.

2.2. Surface modification of ACs by thermal oxidation

The ACs were washed several times by deionized water, and subsequently dried at 383 K in a vacuum for 24 h. Ten grams of the pretreated ACs were placed in a large crucible within a muffle furnace. The samples were separately treated in air by thermal oxidation for 12 h at temperature 473, 573 or 673 K, and the modified ACs were then labeled as AC_{473}, AC_{573} and AC_{673}, respectively. The original carbon was labeled as AC.

2.3. Nitrogen adsorption measurements

Nitrogen adsorption measurements were carried out at 77 K using an accelerated surface area and porosimeter system (ASAP 2010, Micromeritics), to determine the textural properties of all the ACs studied. BET surface area was calculated from adsorption isotherms using the standard Brunauer–Emmett–Teller (BET) equation. The *t*-plot method was used to calculate micropore volume. Pore size distributions (PSD) were determined using density functional theory (DFT) based on statistical mechanics [19].

2.4. DRIFTS

In order to obtain information concerning the surface functional groups of the ACs, DRIFTS was carried out using a FT-IR spectrometer equipped with a diffuse reflectance attachment (Vector 33, Bruker). KBr was used as background for each sample [20].

2.5. Boehm titration

The Boehm titration method can be used to determine a number of oxygen-containing groups on a sample surface. Thus, a 1 g sample of a given activated carbon was weighed carefully and placed into a vial containing 50 ml of a 0.05 mol/l solution of hydrochloric acid, sodium hydroxide, sodium carbonate and sodium bicarbonate, respectively. These vials were then sealed, stirred by shaking for 24 h then filtered. 5 ml of each filtrate with either excess base or acid was titrated with HCl or NaOH. The numbers of different acidic sites were then calculated assuming that NaOH neutralizes carboxylic, phenolic and lactonic groups, Na_2CO_3 neutralizes carboxylic and lactonic groups and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites could be calculated from the amount of HCl that reacted with the basic groups of the carbon surfaces [21].

2.6. Adsorption isotherm measurements [22]

The adsorption isotherms of DBT in MDF on the original AC, AC_{473}, AC_{573} and AC_{673} were determined at 303 K using the bottle-point method. Different amounts of ACs were weighed and put into bottles with 5 ml of MDF in which S content is $320\,\mathrm{mg\,S\,l^{-1}}$. The bottles were then covered with caps, and placed on a shaker for 24 h. Subsequently, the equilibrium concentration of DBT solution (C_i^*) was determined using Agilent liquid chromatograph with UV–visible detector. The mobile phase was 100% HPLC-grade methanol. The analyses were performed at 298 K at a flow rate of 1.0 ml/min. The wavelength of the UV detector was set to 220 nm. Then the equilibrium adsorption capacity q_i was calculated from a material balance equation:

$$q_i = \frac{V}{M_i}(C_0 - C_i^*) \tag{1}$$

where q_i is amount adsorbed in equilibrium with the concentration of solute in fluid phase ($\mathrm{mg\,S\,g^{-1}}$), C_0 is the initial concentration of solute in fluid phase ($\mathrm{mg\,S\,l^{-1}}$), C_i^* is the equilibrium concentration of solute in fluid phase ($\mathrm{mg\,S\,l^{-1}}$), V is the volume of solution (l), M_i is the weight of AC used (g).

2.7. Fixed-bed adsorption experiment [16]

Four AC samples, AC, AC_{473}, AC_{573} and AC_{673} were further tested in a fixed-bed flowing system. The fixed-bed adsorption experiments were performed at 298 K under ambient pressure. About 1.0 g of AC was packed in a stainless steel column having a bed dimension of 6 mm i.d. and 150 mm length, and the bed length of packed AC was about 92 mm. In the adsorptive desulfurization, the model fuel was sent into the adsorbent column by a HPLC pump, flowed up through the adsorbent bed at a rate of 0.5 ml/min. All the sorbent beds were washed with a sulfur free *n*-octane to remove any entrapped gas first. After allowing the liquid hydrocarbon head to disappear, the model fuel was allowed to contact the bed. The effluent from the top of the column was collected periodically for analysis until saturation was achieved.

3. Results and discussion

3.1. Textural properties

Fig. 1 shows the nitrogen adsorption isotherms for the AC, AC_{473}, AC_{573} and AC_{673}. Fig. 2 shows the DFT pore size distributions of the ACs. It indicates that the ACs had mainly micropores and mesopores. Table 1 lists the structure parameters of the ACs used in this work. The data in Table 1 indicated that the BET surface area and total pore volume of the ACs treated by thermal oxidation became slightly smaller in comparison with the original AC. The higher the temperature of thermal oxidation used for modification of the ACs,

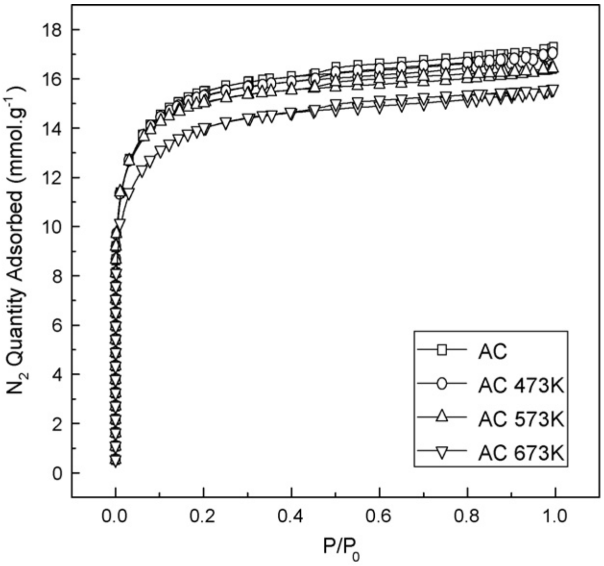

Fig. 1. N_2 adsorption–desorption isotherm of activated carbons.

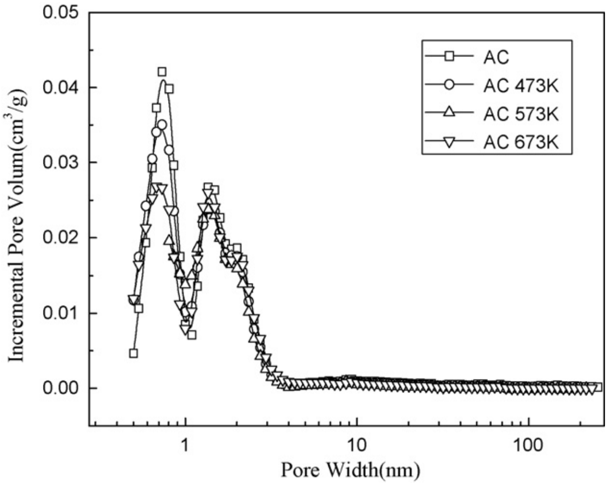

Fig. 2. DFT pore distribution.

the smaller their BET surface area and total pore volume became. It was also noticed that after thermal oxidation of the ACs, their micropore area decreased, while their mesopore area increased slightly due to collapse of pore walls. The changes in porosity for the ACs could be ascribed to the partial gasification of the samples because during the heat treatment the oxygen surface complexes were evolved as CO and CO_2 [23]. The BET and micropore area decreased with the thermal oxidation temperature because the higher temperature led to drastic reactions of the carbon surface with oxygen.

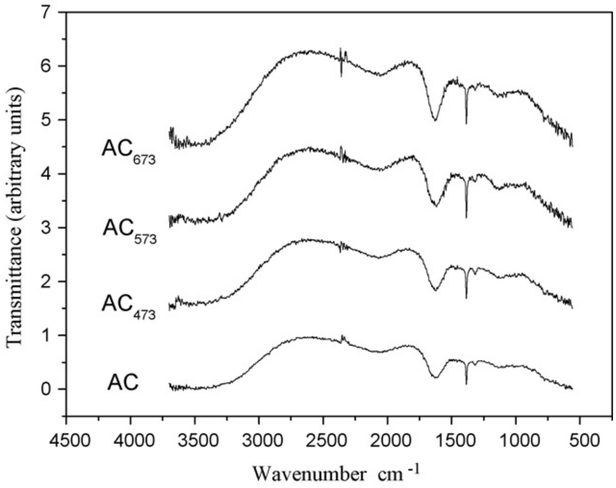

Fig. 3. Infrared ray diffuse reflection spectrum of activated carbons.

3.2. DRIFTS and Boehm titration analyses

The diffuse reflectance infrared Fourier transform spectroscopy method was used to determine the type of oxygen-containing groups on the ACs. Fig. 3 shows the DRIFTS spectra recorded for the original AC. There are four bands of interest: one broad band centered around at 2750 cm^{-1}, associated with carboxylic acids and phenolic groups, one at 1750 cm^{-1}, associated with C=O stretching in lactones and carboxylic anhydrides, one at 1600 cm^{-1}, associated with quinone, and one at 1250 cm^{-1} associated with C—O stretching in ethers, lactones, phenols and carboxylic anhydrides [24,25]. It indicated that there existed a mass of phenols, carboxylic anhydrides and a small quantity of carboxylic acids on the surfaces of the original AC. Fig. 3 also shows the DRIFTS spectra recorded for the ACs treated by thermal oxidation respectively at different heat temperatures. It can be seen that the surfaces of the modified ACs contained the same oxygen functional groups mainly including phenols, carboxylic anhydrides and carboxylic acids as the original AC did.

Table 2 lists the surface acidity strengths of AC, AC_{473}, AC_{573} and AC_{673} as obtained via the Boehm titration method. The data indicated that after the thermal oxidation of carbon surfaces, its total basicity decreased, while its total acidity increased due to the increase of acidic carboxylic, phenolic and lactone groups on the carbon surfaces. The amount of the surface acid groups on AC_{673} was the greatest whilst that on AC was the lowest, which suggests that the use of thermal oxidation can obviously increase the total acidic groups of the carbon surfaces, especially the carboxylic acids and phenolic acids, due to the formation of new oxygenated groups on the surface resulting from air in the furnace [23]. It was also noticed that the higher the temperature of thermal oxidation used to treat the ACs, the more the amount of the surface acid groups was while the lower the amount of the surface basic groups was.

Table 1
Porous structure parameters of the ACs used in this work

Activated carbon	BET surface ($m^2 g^{-1}$)	BET micropore surface ($m^2 g^{-1}$)	BET mesopore surface ($m^2 g^{-1}$)	Average pore diameter (nm)	Micropore volume ($cm^3 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)
Original AC	1187	780	407	1.99	0.357	0.594
AC_{473}	1171	746	425	2.01	0.344	0.587
AC_{573}	1144	715	429	1.99	0.335	0.567
AC_{673}	1077	630	447	1.99	0.289	0.538

At $P/P_0 = 0.98$.

Table 2
Surface groups on the ACs as measured by Boehm method

Samples	Total basicity (mmol g^{-1})	Total acidity (mmol g^{-1})	Carboxylic (mmol g^{-1})	Phenolic (mmol g^{-1})	Lactone (mmol g^{-1})
AC	0.2935	0.3846	0.0765	0.2123	0.0957
AC_{473}	0.2535	0.4584	0.1124	0.2405	0.1055
AC_{573}	0.2347	0.6923	0.2015	0.3546	0.1362
AC_{673}	0.2152	0.8468	0.2903	0.4088	0.1477

3.3. Effect of surface chemistry properties of the ACs on the adsorption capacity

Fig. 4 showed the adsorption isotherms of DBT on the ACs at 303 K. It can be seen from the figure that the isotherms of DBT on the ACs treated using thermal oxidation were higher than that on the original AC, of which the isotherm of DBT on AC_{673} was the highest, that on AC_{573} was the next higher, that on AC_{473} was in the third place and that on AC was the lowest. That is to say, the application of thermal oxidation to treat the carbon surfaces can obviously improve its adsorption towards DBT. The higher the temperature at which the carbon surfaces were oxidized, the more the amounts of acidic oxygen-containing groups were, and thus the higher the amount adsorbed of DBT on corresponding carbon was. The acidic oxygen-containing groups of the carbon surface played an important role in enhancing the adsorption of DBT. However, it should be mentioned that the thermal oxidation temperature was limited because the ACs were easily burned out once the temperature was higher than 673 K in this work.

In order to describe the DBT adsorption on these ACs clearly, the Langmuir equation was used to fit the isotherms. Langmuir derived the simple equation for the equilibrium adsorption isotherm as:

$$q_i = \frac{q_{\max} b C_i^*}{1 + b C_i^*} \tag{2}$$

where q_i is the amount adsorbed in equilibrium with the concentration of solute in fluid phase (mg g^{-1}), $q_{\max}$ is the maximum adsorption amount (mg/g), C_i^* is the equilibrium concentration of solute in fluid phase (mg l^{-1}), b is equilibrium constant of adsorption.

Fig. 4 also showed the Langmuir adsorption isotherms of DBT on the ACs at 303 K, which were denoted by solid lines. It showed that the Langmuir adsorption isotherms of DBT were in agreement with the experimental data. Table 3 shows the parameters of Langmuir equation as well as the correlation coefficients (R^2) for the linear regression of the data presented in Fig. 4. The linear correlation of the data was good because the correlation coefficients were up to 0.96. The $q_{\max}$ values of DBT on these ACs studied followed the order: AC < AC_{473} < AC_{573} < AC_{673}, implying that the ACs treated by thermal oxidation had much higher $q_{\max}$ value in comparison with the original activated carbon, and the higher the temperature at which the AC was oxidized was, the higher the $q_{\max}$ values of DBT on the corresponding ACs was, which could ascribe to the variation of surface chemistry of the ACs.

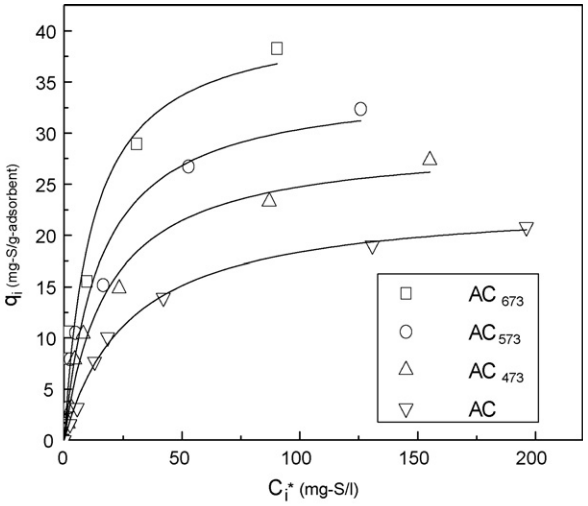

Fig. 4. Adsorption isotherms of DBT on different activated carbons at 303 K. Symbols are experimental data points; curves are fitted with Langmuir isotherm equation (solid line).

Table 4 lists the surface area of the ACs, the maximum amount adsorbed of DBT per unit surface area and acidity per unit surface area. The data in Table 4 indicated that the surface area of the ACs followed the order: AC > AC_{473} > AC_{573} > AC_{673}, while the acidity per unit surface area of the ACs followed the order: AC_{673} > AC_{573} > AC_{473} > AC. The maximum amount adsorbed of DBT on these ACs followed the order: AC_{673} > AC_{573} > AC_{473} > AC. The acidity per unit surface area of the ACs followed the same order of the maximum amount adsorbed of DBT on these ACs. It suggests that the acidity per unit surface area of the ACs played more important role in adsorption of DBT than its surface area did. That is to say, the density of the acidic oxygen-containing function groups on the carbon surface had a significant role in improving the adsorption capacity of the ACs for DBT. When the AC was treated by thermal oxidation, the acidic functional groups on its surface were increased, especially the carboxylic groups and phenolic acid groups, of which carboxylic acids belongs to Lewis acid and phenolic acids belongs to Bronsted acid. The carboxylic groups are electron-withdrawing groups [26], i.e. electron acceptors. On the other hand, the sulfur atom in DBT has two unpaired electrons and hence DBT can act as an electron donor. As a consequence of that, with the increase of acidic functional groups, more donor–acceptor complexes would be formed in which the strong acidic groups on the carbon surfaces would be the acceptor and DBT would be the donor [26]. This was the reason why the more the acidic functional groups on the carbon surfaces were, the higher the amounts adsorbed or $q_{\max}$ values of DBT on the corresponding ACs were.

3.4. Adsorption performance in fixed-beds packed with the ACs

Fig. 5 shows the breakthrough curves of MDF in fixed beds packed separately with the AC, AC_{473}, AC_{573} and AC_{673} at 298 K with a feed containing 320 mg S l^{-1} of DBT. In order to get “sulfur-free” diesel, the breakthrough (i.e., the break point) was defined as

Table 3
Parameters of Langmuir equation as well as the correlation coefficients (R^2)

Activated carbons	Temperature (K)	Langmuir		
		$q_{\max}$ (mg g^{-1})	b	R^2
AC	303	23.42	0.0363	0.9968
AC_{437}	303	29.25	0.0549	0.9802
AC_{573}	303	34.98	0.0657	0.9767
AC_{673}	303	41.53	0.0857	0.9611

Table 4
Effect of acidic groups and BET surface area and of ACs on its adsorption towards DBT at 303 K

Activated carbon	BET surface ($m^2\,g^{-1}$)	q_{max} ($mg\,g^{-1}$)	q_{max} per unit area ($\mu mol\,m^{-2}$)	Acidic per unit area ($\mu mol\,m^{-2}$)	Carboxylic per unit area ($\mu mol\,m^{-2}$)
AC	1187	23.42	0.617	0.324	0.065
AC_{473}	1171	29.25	0.781	0.391	0.096
AC_{573}	1144	34.98	0.955	0.605	0.176
AC_{673}	1077	41.53	1.205	0.786	0.269

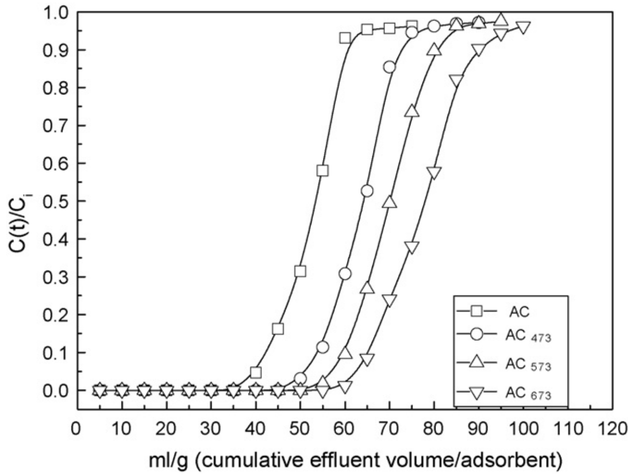

Fig. 5. The sulfur breakthrough curves for adsorption desulfurization of the MDF over the original AC, AC_{473}, AC_{573} and AC_{673} adsorbents at 298 K and flow rate 0.5 ml/min. the initial concentration of sulfur in the MDF (320 mg S l^{-1}).

the first point with detectable sulfur (<1 mg S l^{-1}). It can been seen from the figure that the cumulative effluent volume per adsorbent at breakthrough of DBT in the fixed beds packed with AC_{673} was the highest, that in the fixed beds packed with AC_{573} was the next higher, that in the fixed beds packed with AC_{473} was the third higher while that in the fixed beds packed with the original AC was the lowest. It could ascribe to the difference of the amounts adsorbed of the ACs for DBT. The higher the amounts adsorbed of the ACs for DBT, the higher the cumulative effluent volume per adsorbent at breakthrough of DBT in the fixed bed was. For the original AC, AC_{473}, AC_{573} and AC_{673}, the breakthrough amount of the treat fuel was 35.5, 45, 52.5 and 61 ml fuel g^{-1} A^{-1}, respectively, corresponding to the breakthrough capacity of 11.4, 14.5, 16.8 and 19.5 mg of sulfur per gram of adsorbent (mg S g^{-1} A^{-1}). The adsorption capacity of the AC_{473}, AC_{573} and AC_{673} for DBT increased separately by 27.2, 47.4 and 70.2% in comparison with the original AC.

4. Conclusions

The activated carbon surface has strong adsorption for DBT. After the thermal oxidation of carbon surfaces, its total basicity decreased, while its total acidity increased due to the increase of acidic carboxylic, phenolic and lactone groups on the carbon surfaces. The higher the temperature at which the carbon surfaces were oxidized, the more the amounts of its acidic oxygen-containing groups were, and thus the higher the amounts adsorbed of DBT on corresponding carbon were. The adsorption of DBT on ACs was found to obey the Langmuir isotherm. For the original AC, AC_{473}, AC_{573} and AC_{673}, the breakthrough amount of the treat fuel with containing 320 mg S l^{-1} was 35.5, 45, 52.5 and 61 ml fuel g^{-1} A^{-1}, respectively, corresponding to the breakthrough capacity of 11.4, 14.5, 16.8 and 19.5 mg of sulfur per gram of adsorbent (mg S g^{-1} A^{-1}). The adsorption capacity of the AC_{473}, AC_{573} and AC_{673} for DBT increased separately by 27.2, 47.4 and 70.2% compared to the original AC. The fact that the ACs modified by thermal oxidation have high fixed-bed adsorption performance indicates that they are promising adsorbents for deep desulfurization of diesel fuel.

Acknowledgments

The authors are very grateful to the Science Foundation of Guangdong Province (No. 8251064101000018), the National Science Foundation of China (No. 20806026) and the China Postdoctoral Science Foundation (No.20080430834) for financial support.

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