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Physicochemical studies of adsorptive denitrogenation by oxidized activated carbons

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ABSTRACT

A commercially available activated carbon was oxidized by concentrated sulfuric acid, saturated ammonium persulfate solution and mixed sulfuric acid and ammonium persulfate, respectively. The original carbon and the modified carbons were evaluated by batch adsorption using model diesel fuels. The pore structure and surface chemistry of adsorbents were characterized with N₂ adsorption/desorption, Fourier transform infrared spectroscopy (FTIR) and Boehm's titration. Both physical and chemical aspects of the selectively adsorptive denitrogenation of oxidized activated carbons were investigated. Appropriate oxidation can promote the carbon's ability to adsorb nitrogen-containing compounds. The effect of the density of acidic oxygen functional groups on the adsorption of nitrogen-containing compounds was demonstrated by the regression method and quantum chemistry calculations. The capacities due to physisorption were also estimated. The behaviors of N-containing compounds in a competitive adsorption system were dependent on the molecular size and the properties of adsorbates.

Keywords: Adsorptive denitrogenation, Activated carbon, Oxidative modification, Competitive adsorption, Selectivity

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1 Introduction

Hydrodenitrogenation (HDN) reactions commonly take place along with hydrodesulfurization (HDS) reactions in a hydrotreater. Nitrogen-containing compounds competitively adsorb with sulfur-containing compounds on the active sites of catalysts. Therefore, HDN can significantly lower the HDS efficiency of catalysts. As a gas product of HDN, NH_3 , is also poisonous to the hydrotreating catalyst^{1,2}. Thus, elimination of nitrogen-containing compounds from hydrocarbon feeds before the hydrotreatment process can be beneficial to the hydrotreating process and other downstream processes.

A few approaches have been studied to remove nitrogen-containing compounds from liquid hydrocarbons, among which adsorptive removal of nitrogen compounds is attractive. The adsorption process can be conducted under ambient conditions and does not need hydrogen gas. Development of an efficient adsorbent material that has excellent adsorptive capacity, selectivity and regenerability³⁻⁶ is the key to successful adsorptive removal of nitrogen compounds. Carbon-based adsorbents are promising due to their large surface area, modifiable physical structure and surface properties, and wide availability^{3,5,7}.

The adsorption behavior of carbon materials is highly associated with their pore structure and surface chemical characteristics. Previous studies showed that surface oxygen content of carbons was more important than micropore volume in estimating nitrogen adsorption capacity^{8,9}. Higher density of oxygen functional groups can lead to higher adsorption capacity of nitrogen-containing compounds. The type of oxygen-functional groups is closely correlated with the adsorption selectivity of different compounds. Acidic functional groups (e.g. carboxyl and carboxylic anhydride) favor adsorbing basic nitrogen compounds such as quinoline. On the other hand, basic constituents, such as carbonyl and quinoline groups, tend to attract neutral nitrogen compounds such as indole¹⁰.

An oxidative treatment has been used to modify the physical and chemical nature of activated carbon (AC) to improve its adsorption performance. Yu et al.¹¹ treated the activated carbon using 65 wt% HNO_3 at different temperatures. They observed that the oxygen-containing functional

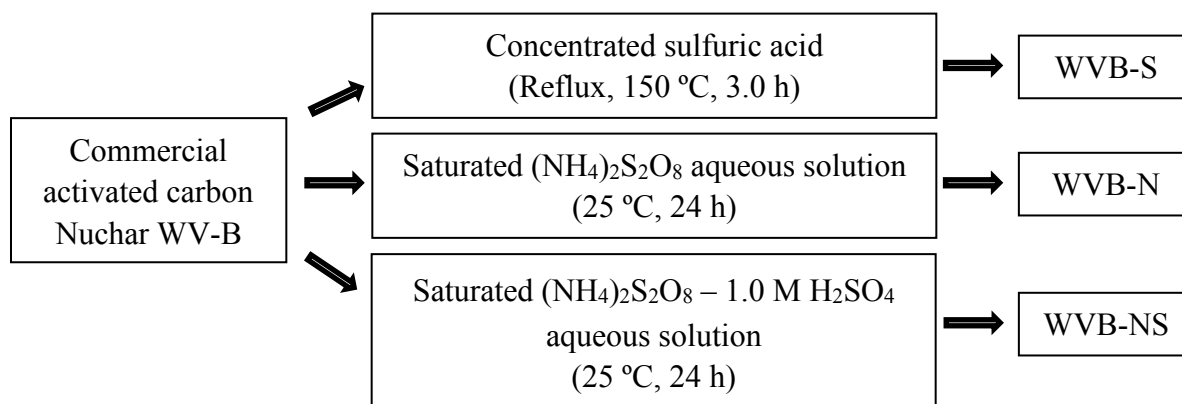
groups on the surface of AC samples increases as the treatment temperature increases. Strelko Jr. et al.¹² reported that oxidation of carbons with hot air resulted in a great proportion of relatively weak acidic oxygen functional groups (phenolic), whereas the nitric acid modification primarily introduced carboxylic groups to the carbon surface. Jiang et al.¹³ suggested that the treatment of concentrated H₂SO₄ led to an increase in both mesopores and acidic oxygen functional groups of carboxyls and phenols. Saha's group¹⁴ washed a coal-based activated carbon with nitric acid and found an enhancement in weakly acidic functional groups accompanied with a significant loss in microporosity. Concentrated solution of (NH₄)₂S₂O₈ was also adopted to oxidize AC¹⁵. Oxidation process can remarkably increase oxygen functional groups to the carbon surface but cause different levels of detriment to the physical structure of carbon at the same time. Thus, an optimal oxidation process is needed to be studied. Li et al. reported the roles of different oxygen functional groups in the adsorption of single N compound (indole or quinoline)¹⁶. Han et al. examined the influence of individual oxygen groups on the denitrogenation of a light cycled oil¹⁷, in which so many heteroaromatic N compounds are contained in feed that they can only be studied by dividing them into groups according to the ring number. In this work, a commercial activated carbon was oxidized using concentrated H₂SO₄, saturated (NH₄)₂S₂O₈ solution, and a mixture of H₂SO₄ and (NH₄)₂S₂O₈. Representative model diesel fuels were prepared using typical N compounds. The factors that affect the adsorptive selectivity of carbons were investigated in detail in terms of the structure and properties of adsorbates.

2 Experimental

2.1 Activated carbon

Carbon WV-B purchased from Westvaco is a wood-based carbon activated by H₃PO₄. The moisture in the carbon sample was removed prior to use and the dried carbon was denoted as WVB. To increase the surface heterogeneity, the carbon was modified using oxidizing agents in three different approaches. The process of oxidative treatment is shown in Scheme 1. (1) 30 mL of concentrated H₂SO₄ (98 wt%) was added to 6 g carbon and kept at 150 °C for 3 hours with

stirring. Then the slurry was filtered, washed by distilled water and then treated in a 120 °C oven for 24 hours. The resultant carbon was denoted as WVB-S. (2) 5 g carbon was mixed with 100 mL of saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution at room temperature for 24 hours, followed by filtration, washing and drying. The sample was designated WVB-N. (3) Saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ aqueous solution mixed with 1M H_2SO_4 was used as the oxidant. The procedures were the same as those in approach 2. The oxidized product was denoted WVB-NS.



Scheme 1 The oxidative treatment process of activated carbons

2.2 Adsorption

Heterocyclic nitrogen removal (denitrogenation) was carried out by adsorption experiments using model diesel fuels. Model fuel MF#1 contained one nitrogen compound while MF#2 contained three nitrogen compounds. MF#3 contained neutral nitrogen and aromatic compounds. The compositions of MF#1, MF#2 and MF#3 are shown in Table 1, Table 2 and Table 3, respectively. Quinoline belongs to basic nitrogen and both indole and carbazole are neutral nitrogen.

Table 1 The composition of model fuel MF#1

Chemicals	Concentration		Molar concentration
	wt%	ppmw N	($\mu\text{mol/g}$)
N compound ^a		333.3	23.8
Ethyl acetate	25		

Dodecane	Balanced
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^a The N compound is one of quinoline, indole and carbazole

Table 2 The composition of model fuel MF#2

Chemicals	Concentration		Molar concentration ($\mu\text{mol/g}$)
	wt%	ppmw N	
Quinoline	0.31	333.3	23.8
Indole	0.28	333.3	23.8
Carbazole	0.42	333.3	23.8
Ethyl acetate	25		
Dodecane	73.99		

Table 3 The composition of model fuel MF#3

Chemicals	Concentration		Molar concentration ($\mu\text{mol/g}$)
	wt%	ppmw N	
Indole	0.28	333.3	23.8
Carbazole	0.42	333.3	23.8
Naphtalene	0.31		23.8
1-Methylnaphalene	40		
Ethyl acetate	10		
Dodecane	48.99		

The batch adsorption was conducted in capped vials with a sorbent-to-oil mass ratio of 1:50. The mixture was vigorously stirred at ambient temperature and atmospheric pressure for 24h. The breakthrough of the adsorption were examined using a packed column. MF#3 was used as the feed. The glass tubing column was packed with 0.5 gram activated carbon diluted by glass beads of sizes ranging from 20 to 40 meshes. The two ends of the column were blocked with glass wool fibers. The liquid flow rate was set at 0.1 mL/min and sampling was taken place every 15-20 min. A Varian GC450 gas chromatograph was employed to analyze the liquid products with

1,2,3,4-tetrahydronaphthalene serving as an internal standard. All chemicals used in this work were purchased from Sigma-Aldrich and used as received.

2.3 Characterization of adsorbents

2.3.1 N₂ adsorption/desorption

The sorbent materials were examined on a BELSORP-max (Belsorp Japan) at 77 K. The surface area (S_{BET}) of carbon was calculated using the multipoint Brunauer-Emmett-Teller (BET) method. The total pore volume was estimated by the N₂ adsorption capacity at P/P_0 of 0.995. The t-plot model was used to measure the micropore volume. The pore size distribution and mean pore size were determined using the DFT method. Moreover, percentage of micropore and mesopore was calculated from micropore and mesopore volume measured according to DFT method.

2.3.2 Boehm's titration

The quantities of oxygen functional groups were determined using Boehm's titration¹⁸. 0.05 N NaOH, Na₂CO₃ and NaHCO₃ solutions were used in the titration. Before titration, the carbon samples were stirred with excess bases until equilibrium. The amounts of acidic groups were determined by back titration. The weak acidic phenolic groups were quantified by the difference between NaOH and Na₂CO₃ consumed in the titration. The consumption difference between Na₂CO₃ and NaHCO₃ indicated the quantity of lactonic groups. NaHCO₃ neutralized carboxylic groups (also in the form of their cyclic anhydrides) only. The total quantity of basic groups was equal to the amount of consumed 0.05 N HCl.

2.3.3 Fourier transform infrared (FTIR) spectroscopy analysis

A Nicolet 6700 FTIR spectrometer was used to study the chemical bonds carried by the carbon adsorbents. Carbon samples were ground to fine powders before testing. The dried sample was mixed with KBr at a mass ratio of 1:400 and a wafer was cast for the IR analysis. The FTIR spectra were background subtracted.

2.3.4 Calculation details

The calculation method was based on the cluster model using the Dmol³ program implemented within the Accelrys Inc. Materials Studio¹⁹. The exchange-correlation approximation (GGA) parameterized by Perdew, Burke and Ernzerhof was adopted²⁰. Atomic orbitals were represented by a double-numeric quality basis set with d-polarization functions (DNP). All the calculations were all-electron ones and performed with the Extra-Fine mesh. A self-consistent field procedure was done with a convergence criterion of 10^{-6} a.u. Convergence tolerances of the energy, maximum force and maximum displacement applied during geometry optimization were 1.0×10^{-5} Ha, 2.0×10^{-3} Ha/Å and 5.0×10^{-3} Å, respectively.

3 Results and discussion

3.1 Physical properties of modified carbons

The nitrogen adsorption-desorption isotherms of WVB and the oxidized carbons are illustrated in Figure 1. All the samples show the type I isotherm²¹, which means that the adsorption mainly takes place in micropores. A hysteresis loop can be seen at high pressures on the isotherms of WVB and WVB-S, suggesting the presence of mesopores in these carbons. On the other hand, the hysteresis loop almost disappears for WVB-N and WVB-NS. Figure 2 shows the pore size distribution of carbon samples. Both micropores and mesopores are dramatically reduced when WVB was treated with saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or the mixture of oxidizing solutions. The possible reason is that the pores in these two adsorbents are collapsed after the strong oxidation. The texture parameters of the carbon adsorbents calculated from the nitrogen adsorption-desorption isotherms are shown in Table 4. The surface area and pore volumes of carbon sorbents show a similar trend, which is in the descending order of $\text{WVB} > \text{WVB-S} > \text{WVB-N} > \text{WVB-NS}$. Concentrated H_2SO_4 oxidation keeps 87% of total pore volume, while only 1/3 and 1/10 pores are left after the oxidation by saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the mixed solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and H_2SO_4 , respectively.

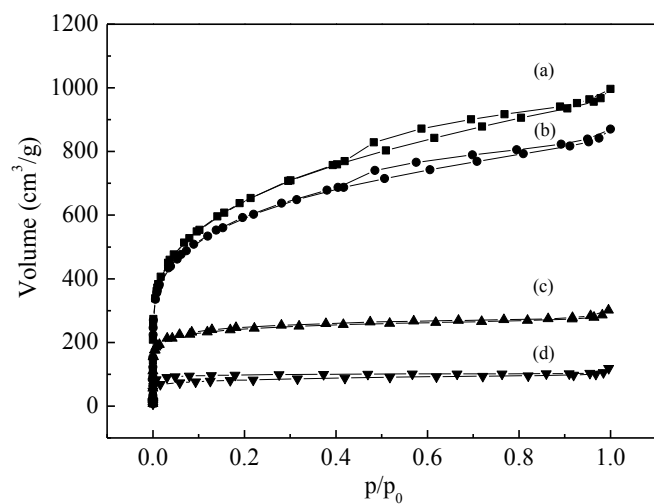


Figure 1 Isotherms of different activated carbons
 (a) WVB, (b) WVB-S, (c) WVB-N, (d) WVB-NS
 (Adsorbate: nitrogen, temperature: 77K)

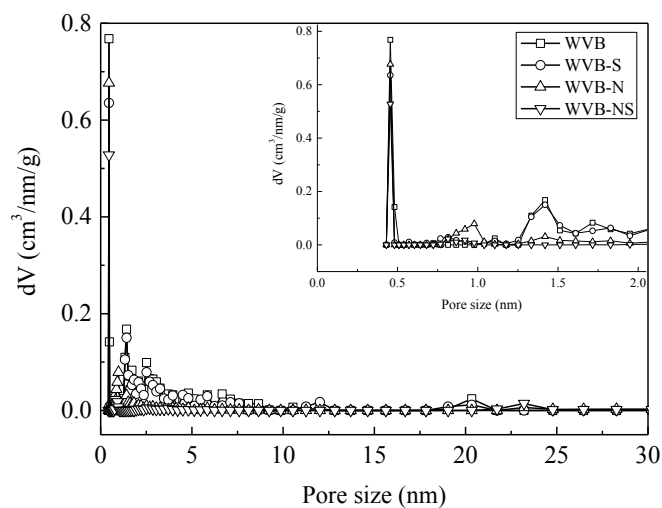


Figure 2 Pore size distribution of the WV-B series activated carbons

Table 4 Structural parameters calculated from nitrogen adsorption/desorption isotherms

Sample	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	$V_{micro-DFT}$ (cm^3/g)	$V_{meso-DFT}$ (cm^3/g)	Percentage of micropore (%)	Percentage of mesopore (%)	Pore size (nm)
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WVB	2330.6	1.520	1.363	0.699	0.641	52.2	47.8	0.64
WVB-S	2145.5	1.328	1.193	0.701	0.486	59.1	40.9	0.64
WVB-N	877.3	0.456	0.401	0.592	0.075	88.8	11.2	0.61
WVB-NS	386.7	0.173	0.142	0.241	0.000	100.0	0.0	0.60

3.2 Modification of carbon surface chemistry

Figure 3 shows the FTIR spectra of WVB series carbons. The peak at 3400 cm^{-1} is assigned to the stretching vibrations of hydroxyl groups²². The asymmetry of this peak for carbons WVB-N and WVB-NS at lower wave numbers indicates the presence of stronger hydrogen bonds than carbons WVB and WVB-S. The peak centered at 1720 cm^{-1} indicates the presence of C=O bonds in carboxylic and lactone²²⁻²⁵. Again, significant increase in relative intensity of the peaks can be observed for carbons WVB-N and WVB-NS. Carbonyl groups present a vibration at 1620 cm^{-1} ^{26, 27}. A new peak at 1400 cm^{-1} for WVB-N and WVB-NS is attributed to the symmetric stretching vibrations of COO^- ²⁶. The peak at around 1200 cm^{-1} characterizes the C-O stretching and O-H bending modes in ether, lactone and carboxyl structures²². The peak observed at 1080 cm^{-1} indicates the presence of phenols on the carbon surface²⁸. It appears that carbons WVB-N and WVB-NS have a noticeable increase in oxygen functional groups compared to carbons WVB and WVB-S.

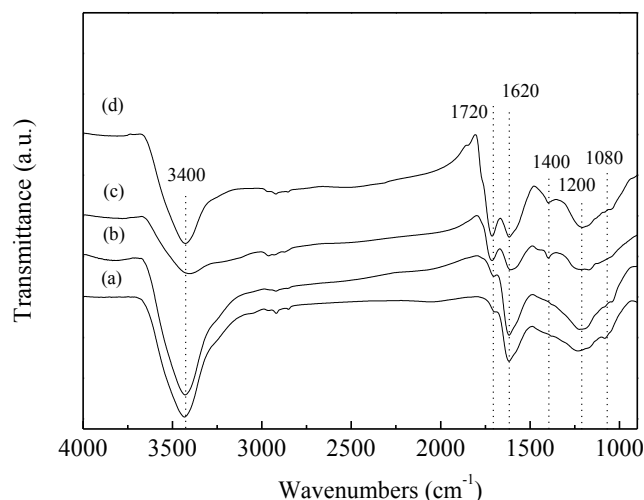


Figure 3 FTIR spectra of different activated carbons
 (a) WVB, (b) WVB-S, (c) WVB-N, (d) WVB-NS

The surface oxygen functional groups are quantitatively evaluated using Boehm's method¹⁸. The results are given in Table 5. The numbers of phenolic groups, lactonic groups, carboxylic groups and total acidic oxygen groups are all increased in the order of WVB < WVB-S < WVB-N < WVB-NS, which verifies the FTIR results. Oxidation of the original activated carbon by saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the mixture of sulfuric acid and saturated $(\text{NH}_4)_2\text{S}_2\text{O}_8$ can dramatically increase the acidic groups, especially the phenolic groups and carboxylic groups, on activated carbons. WVB-NS has approximately four times as many total acidic groups as original WVB. On the other hand, the basic functional groups have been neutralized during oxidation.

Table 5 Amount of surface groups from Boehm's titration

Sample	Surface acidic groups				Surface basic groups (mmol/g)
	Phenolic (mmol/g)	Lactonic (mmol/g)	Carboxylic (mmol/g)	Total (mmol/g)	
WVB	0.297	0.422	1.112	1.83	1.569
WVB-S	0.954	0.689	1.933	3.576	0.242

WVB-N	1.787	0.78	3.697	6.264	0
WVB-NS	1.617	1.015	4.39	7.022	0

3.3 Adsorption performance of activated carbons

Figure 4 shows the adsorption results with model fuel MF#1, which contains a single nitrogen compound. Using carbon WVB as the adsorbent, the adsorptive capacities for quinoline, indole and carbazole are 0.72 mmol-N/g, 0.52 mmol-N/g and 0.82 mmol-N/g, respectively. After being oxidized by concentrated H₂SO₄, carbon WVB-S has a noticeable increase in the adsorption capacity for the three nitrogen-containing compounds, especially for quinoline and indole. Carbons WVB-N and WVB-NS show an increase in adsorption capacity for quinoline and indole but a decrease for carbazole, compared to carbon WVB.

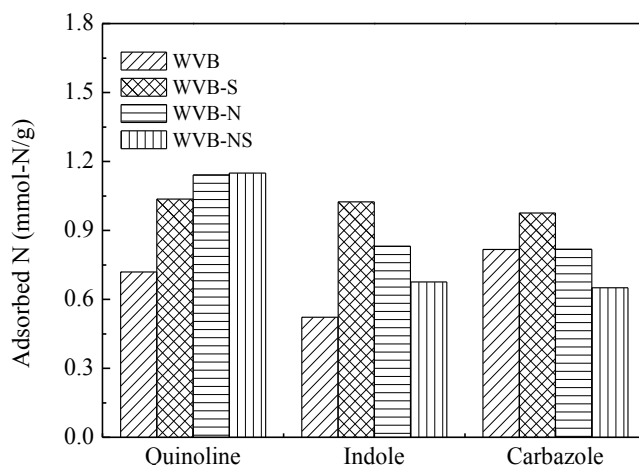


Figure 4 Adsorption capacities of activated carbons for single nitrogen containing compound

The total N concentration of model fuel MF#2 is three times that of model fuel MF#1, but the N concentration of each nitrogen-containing compound remains the same, which is 23.8 μmol/g. When MF#2 is used as the feed, the adsorption of total N for every carbon adsorbent is enhanced (compare Figure 5 with Figure 4). However, a reduced adsorption capacity for individual nitrogen-containing compound is observed. The batch adsorption capacities of nitrogen

compounds over modified activated carbons obtained in this work were compared in Table 6 with the previously reported results achieved using metal organic frameworks (MOFs), aluminosilicate (MSU-S) and activated carbon (AC) ²⁹⁻³³. The published adsorption capacities were expressed in the form of mg-N/g_{adsorbent} for the amount adsorbed. Carbon WVB-S exhibits excellent equilibrium adsorption capacities for all three nitrogen compounds, showing higher better results than those obtained using aluminosilicate (MSU-S), unmodified MOF and AC ^{29, 31-33}. Amino-functionalized MOF adsorbent shows higher adsorption capacity for indole and quinoline than the present work but the adsorption of carbazole, a hardly-adsorbed nitrogen compound, was not reported ³⁰.

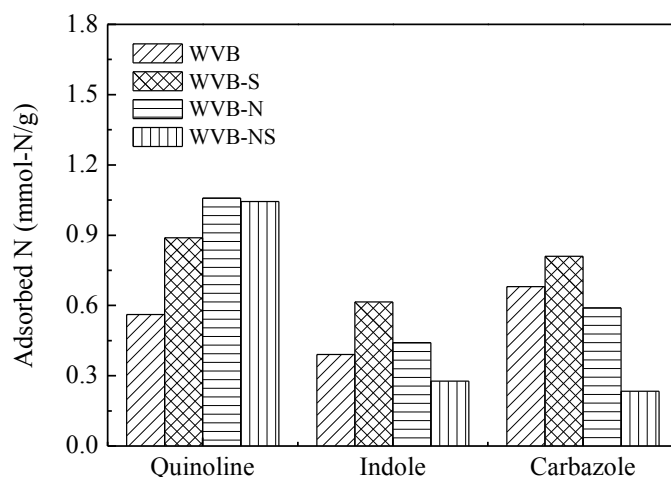


Figure 5 Adsorption capacities of activated carbons for triple nitrogen-containing compounds

Table 6 Comparison of the amounts adsorbed for nitrogen compounds on various adsorbents

Adsorbent	Surface area [m ² /g]	Capacity [mg-N/g _{ad.}]				Ref.
		Indole	Quinoline	Carbazole	Total N*	
MOF: MIL-101(Cr)	2789	8.59	14.28	---	---	29
Modified MOF: MIL-101(Cr)-NH ₂	1984	24	20	---	---	30
AC: Ni-GAC	553.2	---	13.3	---	---	31
WVB-S	2146	14.34	14.50	13.66	---	this work ^a

MOF: MIL-101(Cr)	2789	5.93	3.80	5.61	15.34	29
MSU-S: NiO/HPW-MSU-S	351.3	---	---	---	6.26	32
MSU-S: Fe ₂ O ₃ -MSU-S	400	---	5.59	2.06	7.65	33
WVB-S	2146	8.61	12.45	11.34	32.40	this work ^b

* Capacity for multiple nitrogen-containing model fuel

^a Adsorption in single nitrogen-containing model fuel

^b Adsorption in multiple nitrogen-containing model fuel

The nitrogen selectivity is expressed in Eq. 1:

$$\text{Selectivity for } N_i (\%) = \frac{\text{Capacity for } N_i}{\text{Capacity for } N_{\text{Total}}} \times 100 \quad (\text{Eq. 1})$$

where N_i and N_{Total} represent one specific nitrogen-containing compound and total nitrogen-containing compounds, respectively. The selectivity results are listed in Table 7. It is seen that the original carbon WVB favors the adsorption of carbazole, a large neutral nitrogen-containing molecule. The adsorptive selectivity for carbazole is at least 20% higher than those for the other two nitrogen-containing compounds. Higher selectivity for quinoline, a basic nitrogen-containing compound, is observed for the oxidized carbon samples, in the order of WVB-S < WVB-N < WVB-NS. The selectivity for carbazole, however, shows the opposite trend. WVB-S has a higher indole selectivity than WVB, while the selectivities for indole on the saturated (NH₄)₂S₂O₈ solution treated carbon and the mixed oxidants treated carbon are lower than that of the original carbon. The introduced oxygen functional groups improve the adsorption of basic nitrogen containing compounds. The carbon sample with the most surface acidic groups, WVB-NS, has its quinoline selectivity 3.8 and 4.5 times, respectively, those for indole and carbazole.

Table 7 Selectivity of carbon samples for different nitrogen-containing compounds

Sample	Selectivity (%)		
	Quinoline	Indole	Carbazole
WVB	34.4	24.0	41.7

WVB-S	38.4	26.6	35.0
WVB-N	50.7	21.1	28.2
WVB-NS	67.1	17.8	15.0

The competitive adsorption between neutral nitrogen and aromatic compounds on activated carbons WVB and WVB-S was further studied. The breakthrough curves of model fuel MF#3 are shown in Fig. 6. For the original carbon, WVB, the breakthrough of adsorbates increases in the order of naphthalene < indole < carbazole, as shown in Figure 6a. The modified carbon, WVB-S, adsorbs less naphthalene than the unmodified carbon, demonstrating a better selectivity on Nitrogen-containing compounds (Figure 6b). The adsorption of carbazole over WVB-S breakthroughs at a similar time to that of WVB, but the saturation of carbazole was reached via a longer time on WVB-S than WVB. Modification by concentrated H₂SO₄ increases the percentage of micropores in WVB-S (as shown in Table 4). On the other hand, carbazole is a large molecule and is mainly adsorbed via physisorption^{34, 35}. Mass transfer of carbazole within micropores plays an important role in the adsorption process. Figure 6 and Table 8 show that both the adsorption capacity of indole and the breakthrough time on WVB-S are tripled. Modification by concentrated H₂SO₄ doubles acidic oxygen functional groups and significantly reduces the amount of basic functional groups (Table 5). Indole is a basic nitrogen-containing compound and the acid-base and H bond interactions dominate the adsorption of Indole. Thus the available chemical adsorption sites of adsorbent determine the adsorption capacity. However, Fig. 6b shows the final saturation of indole was not reached on the WVB-S during the limited experimental time. As acidic functional groups are gradually occupied, indole molecules start to confront the repulsive forces of basic functional groups. Additionally, diffusion of indole gets slower in the narrow micropores. Thus, adsorption of indole faces both mass transfer and chemical adsorption limits as adsorption proceeds.

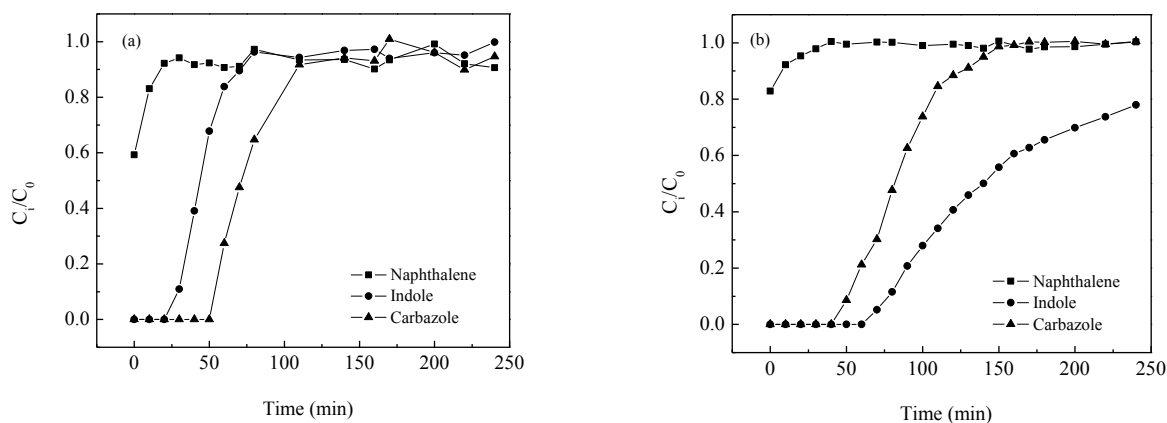


Fig. 6 The nitrogen compounds and naphthalene breakthrough curves of model fuel MF#3 on activated carbons (a) WVB and (b) WVB-S

Table 8 Adsorption capacity and selectivity in model fuel MF#3

Sample	Capacity [mmol/g _{ad.}]				Ratio of Naphthalene
	Naphthalene	Indole	Carbazole	Total N	%
WVB	0.075	0.22	0.34	0.56	11.81
WVB-S	0.015	0.63	0.35	0.98	1.51

3.4 Adsorptive denitrogenation mechanism

The results of Han et al. suggested that micropores may play an important role in adsorptive denitrogenation²⁸. However, not all the micropores are useful in adsorption. Considering the critical diameters of the three N compounds³⁶, which are 7.1, 6.7 and 9.0 Å for quinolone, indole and carbazole, respectively, the micropores that are available in adsorption can be estimated based on the pore size distribution curves. The results are summarized in Table 9. As indicated in the inset of Figure 2, WVB and WVB-S have a large proportion of large micropores. Therefore, even though carbazole is bigger than quinoline and indole, not much difference is observed between the number of micropores for carbazole adsorption and those for quinoline and indole adsorption for these two carbons. However, for the other carbon samples, the restriction of adsorbate size is significant. 57.8% of micropores in WVB-N can be used for quinoline and

indole adsorption, while 48.5% of micropores are available for carbazole to be adsorbed in. In the case of WVB-NS, the numbers are even lower. Only 1/5 of the micropores can accommodate quinoline and indole, and the available micropores for carbazole adsorption are less than 10%. Strong oxidation collapsed the pores in carbons and reduced the adsorption of N compounds, especially for big molecules.

Table 9 Available micropores for the adsorption of nitrogen-containing compounds

Sample	Available micropores for adsorption (%)		
	Quinoline	Indole	Carbazole
WVB	74.8	74.9	74.6
WVB-S	77.2	77.5	72.4
WVB-N	57.8	57.8	48.5
WVB-NS	20.4	20.4	8.9

One may note that the results in Table 9 cannot explain the adsorption performance (Figure 4). The role of surface chemistry needs to be identified. The density of acidic O groups is calculated using Eq. 2. The adsorptive capacity per unit surface area of carbons is plotted against the corresponding density of individual and total acidic oxygen functional groups. The plots are shown in Figures 7 and 8. For the nitrogen compounds in MF#1, good linear correlations are observed between N adsorption and the density of acidic O groups, with correlation factor R^2 values no lower than 0.94 (Figure 7). These results clearly indicate the key role of surface acidic groups in nitrogen adsorption. The influence of oxygen groups on N adsorption is in the order of Lactonic groups > Phenolic groups > Carboxylic groups. In addition, the steepest lines for quinoline indicate its greatest affinity to acidic oxygen groups among the three nitrogen-containing compounds. The affinity of indole is slightly greater compared to that of carbazole. In triple nitrogen adsorption (MF#2), good linear relationships exist between quinoline adsorption and the density of acidic oxygen groups, as seen in Figure 8 a. The slopes of fitting lines are a little smaller than those in the case of single nitrogen adsorption. Linear relationships can be observed between indole adsorption and oxygen density (Figure 8b). However, both R^2 values

and slopes of fitting lines are lower than those in Figure 7b. Carbazole adsorption, on the other hand, shows no linear relationships with the density of acidic oxygen groups (Figure 8c). These results indicate that the adsorption of quinoline is rarely affected by the competitive adsorption from indole and carbazole, and the effect of oxygen groups are not as dominant as that in MF#1 adsorption for indole. Oxygen density barely influences carbazole adsorption in a competitive adsorption. In the three model nitrogen-containing compounds, quinoline shows a basic property with the pKa value of 4.85, whereas indole and carbazole are neutral. Acid-base interaction is considered to dominate the adsorption of quinoline, while the adsorption of indole and carbazole may be governed by the H bond interaction³⁶. According to Reilly et al.³⁷, the acid-base interaction is stronger than the H bond interaction. Thus, quinoline is more favored in the competitive adsorption compared to indole and carbazole.

Density of acidic O groups

$$= \frac{\text{Amount of surface acidic groups from Boehm's titration}}{\text{Surface area of carbon}} \times 1000 \text{ (Eq. 2)}$$

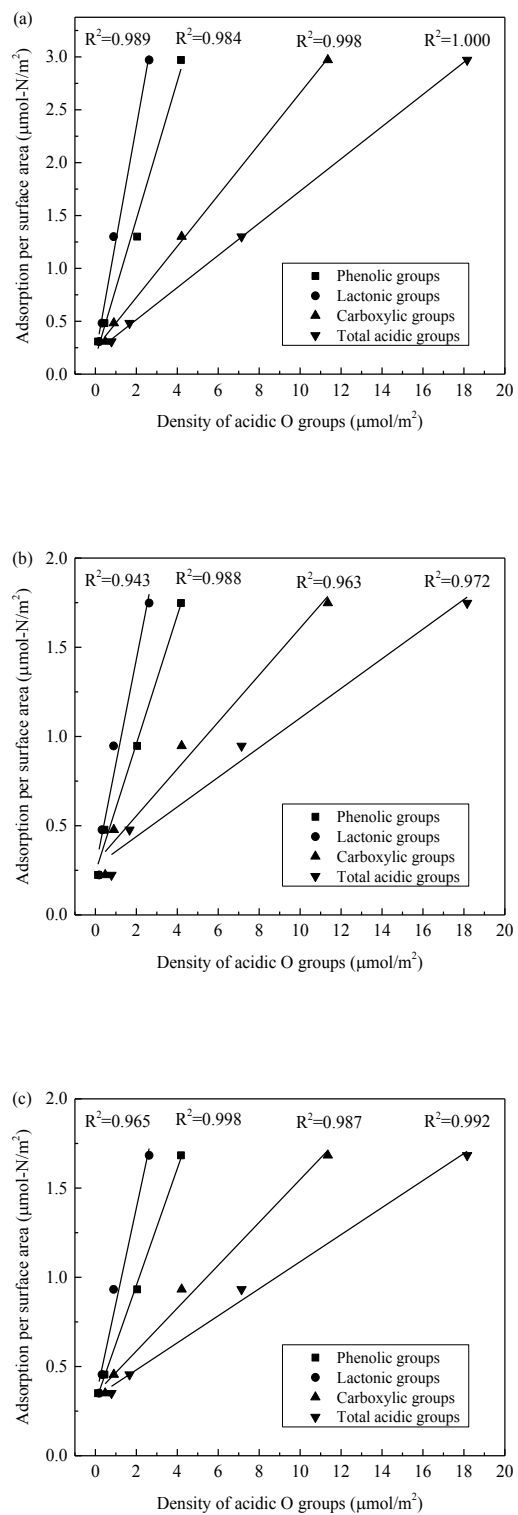


Figure 7 Capacity per unit surface area for nitrogen compounds in MF#1 as a function of the oxygen density on carbon surface (a) Quinoline (b) Indole (c) Carbazole

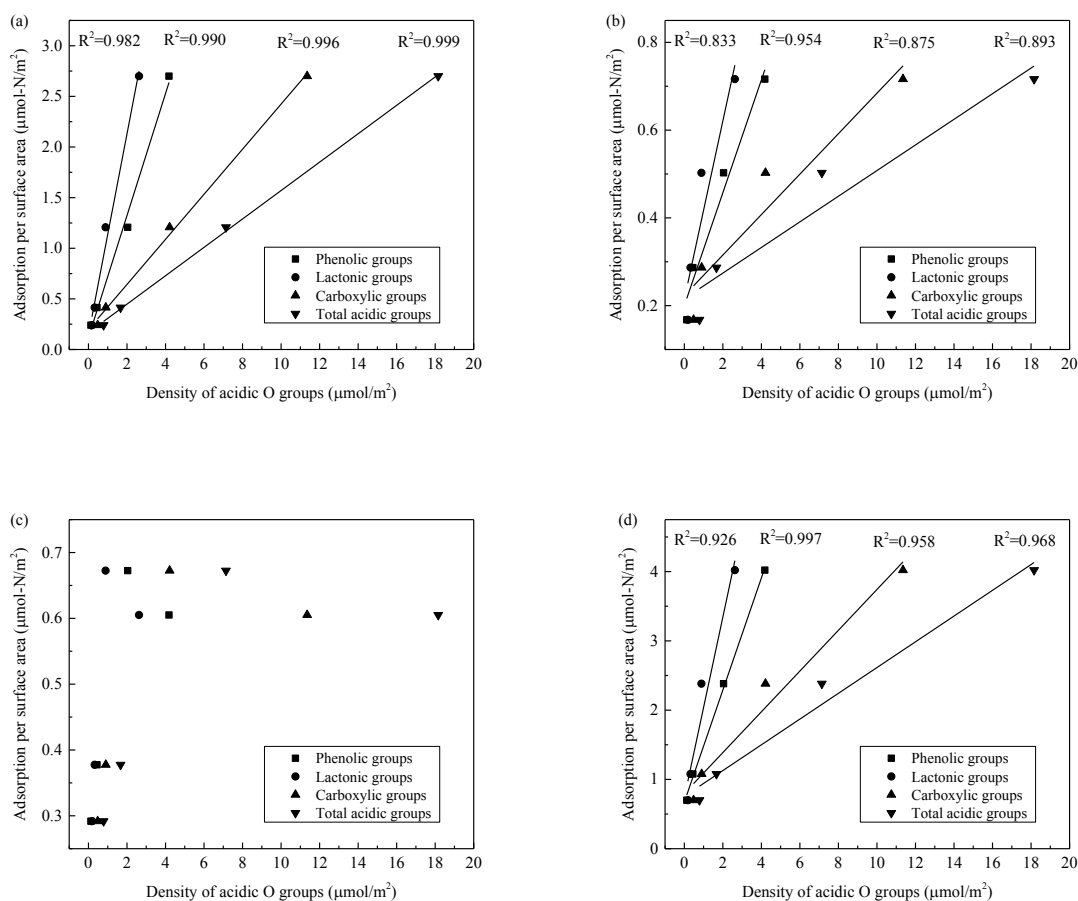


Figure 8 Capacity per unit surface area for nitrogen compounds in MF#2 as a function of the oxygen density on carbon surface (a) Quinoline (b) Indole (c) Carbazole (d) Total N

Quantum chemistry calculations were performed to determine the electronic properties of the three nitrogen-containing compounds. The energy of the highest occupied molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}) and the band gap energy (E_{gap}) which is the difference between E_{HOMO} and E_{LUMO} are shown in Table 10. The E_{gap} is associated with the energy required to remove an electron from its original orbit to an unoccupied orbit³⁸. In other words, lower E_{gap} value indicates higher affinity of adsorbate molecules to oxygen functional groups. The E_{gap} values of the three adsorbates increase in the order of quinoline < indole < carbazole, meaning that the adsorption affinity follows the

sequence of quinoline > indole > carbazole, which is in accordance with the effect of acidic oxygen groups.

Table 10 HOMO and LUMO orbital energy and band gap of different adsorbates

N-containing compound	E_{HOMO} (ev)	E_{LUMO} (ev)	E_{gap} (ev)
Quinoline	-5.384	-2.888	2.496
Indole	-4.627	-1.7	2.927
Carbazole	-4.81	-1.401	3.409

Nitrogen-containing compounds may be adsorbed on two different types of sites: type I - the adsorptive sites derived from the surface functional groups and type II - the sites due to pure physical adsorption. The intercepts of the fitting lines represent the adsorptive capacities per unit area without the influence of oxygen functional groups; adsorption is caused entirely by physisorption. The data are shown in Table 11. Quinoline has the smallest intercept among the three nitrogen compounds, suggesting that the adsorption of quinoline is the least influenced by the surface area of adsorbent. Carbazole adsorption is the most sensitive to carbon's surface area. When comparing the results of MF#1 and MF#2, the physisorption capacities of quinoline and indole decrease in a competitive system, while that of carbazole increases. The distinct behavior of carbazole from those of quinoline and indole may result from the bigger molecule size of carbazole and the interparticle interactions. However, the total N physisorption capacity in MF#2 is smaller than the addition of total N capacity due to physisorption in MF#1, which can be attributed to the steric hindrance.

Table 11 Adsorption of N-containing compounds due to physisorption

Model fuel	Physisorption capacity ($\mu\text{mol}/\text{m}^2$)			
	Quinoline	Indole	Carbazole	Sum
MF#1	0.210	0.273	0.329	0.812

MF#2

0.167

0.216

0.373

0.756

From the above discussion, it is evident that the adsorption of nitrogen-containing compounds is closely associated with the quantity of acidic groups and the textural structure of adsorbents. In addition, the affinity of adsorptive sites for different nitrogen compounds is of great importance. The acidic groups introduced by oxidation obviously improve the adsorption of basic nitrogen, while physisorption makes a greater contribution to the adsorption of big molecules.

4 Conclusions

The oxidative modification to activated carbon can introduce acidic oxygen groups to carbon surface but decrease its surface area and pore volume, which lead to two contradictory effects. Concentrated H₂SO₄ oxidation slightly changed the porous structure of WVB, and moderately increased the number of oxygen groups. The saturated (NH₄)₂S₂O₈ or mixture of saturated (NH₄)₂S₂O₈ and H₂SO₄, however, significantly damaged the pore structure of WVB, even though they produced numerous oxygen groups. WVB-S, the weakly oxidized carbon, has noticeably increased capacities for quinoline and indole. Severely oxidized carbons show an increased adsorption capacity for quinoline and indole but a diminished capacity for carbazole.

The adsorption of nitrogen compounds is governed by the density of acidic oxygen groups, with the influence of individual oxygen groups decreasing in the order of Lactonic groups > Phenolic groups > Carboxylic groups. Both the electronic properties and the molecular size of N-containing compounds dominate their adsorption selectivity in a competitive adsorption system.

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