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Surface properties of chemically modified activated carbons for adsorption rate of Cr (VI)

Naiqin Zhao[a,*], Na Wei[a], Jiajun Li[a], Zhijun Qiao[a], Jing Cui[a], Fei He[b]

[a] *School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China*
[b] *State Key laboratory of C1 Chemical technology of Tianjin University, Tainjin 300072, China*

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Abstract

The commercially available activated carbon (AC) was oxidized with different oxidizing agents such as HNO_3, H_2O_2 and $Fe(NO_3)_3$ and then followed by heat treatment at different temperatures in order to introduce more surface oxygen complexes. The effects of the oxidizing agent treatment on the surface chemical nature were characterized by ultimate Boehm titration and X-ray photoelectron spectrometer (XPS). The application of the chemically modified ACs in wastewater containing Cr (VI) was tested. Effects of surface oxygen groups of AC on Cr (VI) adsorption were investigated. The results showed that the adsorption of Cr (VI) ion was more effective for the chemically treated ACs. The extent of adsorption and reduction of ACs to Cr (VI) depends on the adsorption time, the pH value and the quality of AC in the Cr (VI) solution.

Keywords: Activated carbon; X-ray photoelectron spectroscopy; Surface properties; Adsorption properties

1. Introduction

Activated carbons (ACs) can be made from various raw materials that have a high carbonaceous content, including wood, coal, petroleum coke, sawdust, and coconut shell [1–3]. They can be activated by thermal decomposition in a high-temperature oxidation or a lower temperature chemical dehydration reaction process to come into being ACs.

ACs have been widely used in wastewater treatments to remove organic or inorganic pollutants because of their huge specific surface area, high adsorption amount and rate, and special surface chemical properties [4,5]. These physical and chemical natures of AC depend on its pore distribution and surface oxygen groups. The former can be controlled during the activation process such as activation time, activation agent and temperature and so on. However, the latter also can be made or changed by means of oxygen agent treatment, the chemical aqueous solution and thermal treatment in order to adjust the quality of surface functional groups on carbons such as carboxyl, phenol and lactone [6–9]. These groups can improve the adsorption capacity and selectivity on a certain adsorbate in the gaseous or liquid phase [10,11].

Chromium compounds are widely used in industry such as electroplating, metal finishing, leather tanning, pigments, etc. However, the effluent of chromium is a big environmental problem, since chromium is recognized as being harmful to human health [12,13]. Adsorption is one of the effective techniques for chromium removal from wastewater. Many researchers have suggested that activated carbons could be used for the removal of hexavalent chromium in the wastewater solution [14–18]. They have certificated that the pH and chromium concentration of solution affect the adsorption quality and remove rate of Cr (VI).

In this work, activated carbons were modified by chemical surface treatments with HNO_3, H_2O_2 and $Fe(NO_3)_3$ in orders to obtain modified ACs including different surface properties. The analyses were carried out by Boehm titration and X-ray photoelectron spectra (XPS). The objective of this work is to analyze the relationship between the chemical modification of activated carbon with wet oxygen agents and the removal rate of Cr (VI).

2. Experimental

2.1. Sample preparation

The commercial ACs with BET surface area 770.4 m^2/g, manufactured through carbonization and then steam activation at

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[*] Corresponding author. Tel.: +86 22 87401601; fax: +86 22 27404724.
E-mail address: nqzhao@tju.edu.cn (N. Zhao).

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Table 1
Chemical surface treatment conditions

Sample	Concentration of oxygen agent	Heat treatment condition
NAC1	3.2 mol/L	300 °C air ambience
NAC2	4.1 mol/L	
NAC3	5.4 mol/L	
NAC4	8.4 mol/L	
NAC5	13.2 mol/L	
HAC1	3%	500 °C nitrogen ambience
HAC2	6%	
HAC3	9%	
HAC4	12%	
HAC5	15%	
FAC1	5%	800 °C nitrogen ambience
FAC2	10%	
FAC3	15%	
FAC4	20%	

about 1123 K using coal particles as raw material. The activated carbons were oxidized with different concentration solutions such as HNO_3, H_2O_2 and $Fe(NO_3)_3$ at 373 K for 1 h and then were washed in the distilled water until the pH approached 7 and dried at 393 K for about 2 h. The oxidized ACs was obtained. The samples oxidized by HNO_3, H_2O_2 and $Fe(NO_3)_3$ were indicated as NACn, HACn, and FACn, respectively. Here the *n* represents the experimental list number. Then, the oxidized samples were heat-treated in different temperatures and conditions in order to improve their ion exchange capacity. The heat-treated samples were indicated as NACn′, HACn′, and FACn′. The specific treatment parameters were described in Table 1.

2.2. Methods

2.2.1. Boehm titration

The surface functional groups with oxygen were determined according to Boehm titration [19,20]. One gram of carbon sample was placed in 50 ml of the following solution: sodium hydroxide (0.1 mol/L), sodium carbonate (0.05 mol/L), sodium bicarbonate (0.1 mol/L). The bottles were sealed and shaken for 24 h, the mixture was filtered subsequently. The excess base was titrated with 0.1 mol/L HCl. The value of acidic sites was determined under the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups; that Na_2CO_3 neutralizes carboxylic and lactonic groups; and that $NaHCO_3$ neutralizes only carboxylic groups. At the same time, 0.1 mol/L NaOH solution was titrated with 0.1 mol/L HCl as the blank experiment. The mass of surface acid functional groups (SAFG) was calculated by following equation:

$$\text{Mass of SAFG} = \frac{0.1 \times f \times (T_\text{b} - T) \times 50/20}{w}\ (\text{mmol/g})$$

where T_b (ml) is the titration mass of 0.1 mol/L HCl for the blank experiment, T (ml) the mass of 0.1 mol/L HCl consumed in different filtrated solution, w(g) the mass of activated carbon that is equal to 1 g in this experiment, and f is the constant.

2.2.2. XPS

X-ray photoelectron spectra was carried out using a Perkin-Elmer PHI1600 ESCA system. The spectrophotometer was ASTM Calibrated and operated under vacuum (2.66×10^{-6} Pa). As the primary excitation source, non-monochromatic Mg Kα (300 W) radiation was used at an analysis area 0.8 mm^2 on the sample surface. Survey seams in the range of 1–1100 eV were recorded at a pass energy of 185.85 eV with a step size of 0.8 eV.

All binding energies (BE) were corrected for charging of the samples by calibration on the graphitic carbon C 1s peak at BE 284.50 eV. The spectra of C 1s and O 1s were analyzed by curve fitting into two and three peaks, respectively (in all cases Gauss-Lorentz curves were used), in order to obtain a good fit of the spectra. The BEs resulting from these analyses were interpreted for establishing a set of fixed bindings energies connected to specific surface groups.

2.3. Adsorption of Cr (VI) experiment

The adsorption of Cr (VI) from the dilute aqueous solution was operated as follows: (1) take a series of 100 ml glass flasks, containing from 0.025 to 0.15 g activated carbon and 25 ml solutions of sodium chromate ($Na_2CrO_4 \cdot 4H_2O$), respectively; (2) the initial pH value of the mixed solution was adjusted with 1 N HCl to about from 1 to 9 with the step 2; (3) the bottles were sealed and then shaken on a time sequence (0.5, 1, 1.5, 2, 2.5, and 3 h) at 25 °C at a frequency of 80 strokes/min using a shaking bath; (4) at the end of the reaction period, each reaction mixture was filtered to separate the solutions and ACs, the adsorbed amount of Cr (VI) was tested using the pink color complex developed between diphenyl carbohydrize and chromium ions in an acidified solution with a spectrophotometer (722s, Shanghai, China) at an absorbance of 540 nm.

3. Results and discussion

3.1. Surface properties

The amount of the surface functional groups of the oxidized samples and corresponding heat-treated samples were shown in Table 2. The results were calculated by dividing the number of groups obtained from the titration experiments. It can be seen that the amount of carboxylic group of the oxidized samples with HNO_3 in high concentration of oxygen agent increases comparing with the untreated AC. But the other oxidized treatment methods, H_2O_2 and $Fe(NO_3)_3$, made the amount of carboxylic on the surface of oxidized samples decrease obviously. Taking one with another, the oxidation process with both H_2O_2 and $Fe(NO_3)_3$ results in the increase of the amount of lactone. The amount of the phenol of the samples oxidized with HNO_3 increased more than those of samples oxidized with H_2O_2, whereas the reduction of the phenolic of the samples oxidized with $Fe(NO_3)_3$ is noticed.

The results show that different oxidation methods have the different effects to the amount of the acidic sites on the activated carbon surfaces. The most severe effect of oxidation is observed on sample NAC2 obtaining the total number of acidic functional

Table 2
Results of Boehm titration (mmol/g)

Sample	Carboxylic	Lactonic	Phenolic
AC	2.125	0.0625	6.187
NAC1	0.375	1.750	5.875
NAC2	1.750	1.000	8.750
NAC3	2.625	0.063	5.938
NAC4	2.625	0.125	6.375
NAC5	2.375	0.000	6.500
HAC1	0.500	1.375	5.625
HAC2	0.125	2.000	6.875
HAC3	0.625	1.562	5.187
HAC4	0.625	1.437	6.437
HAC5	0.750	1.375	7.875
FAC1	1.250	0.937	6.062
FAC2	0.125	1.937	5.312
FAC3	0.250	1.875	5.875
FAC4	0.375	1.812	6.187
NAC1′	0.240	−3.302	17.552
NAC2′	0.000	−2.750	17.000
NAC3′	−0.625	−1.875	14.875
NAC4′	−0.500	3.375	11.625
NAC5′	0.000	2.437	6.562
HAC1′	0.625	1.825	6.937
HAC2′	0.125	2.312	9.812
HAC3′	0.750	1.750	7.625
HAC4′	0.625	1.750	9.250
HAC5′	1.250	0.937	12.187
FAC1′	−1.125	3.437	6.187
FAC2′	−1.625	3.625	8.000
FAC3′	−2.750	4.812	7.813
FAC4′	−2.250	4.438	7.563

groups of 8.75 mmol/g. As for HAC5, oxidation with 15% H_2O_2 introduces a large number of lactonic and phenolic groups. The number of the total acidic sites of the samples oxidized with 20% $Fe(NO_3)_3$ is the highest in the samples with the same method. Compared with both H_2O_2 and $Fe(NO_3)_3$ as the oxygen agent, the oxidation effect of HNO_3 is stronger.

Many researchers verified that a little reduction of acidic sites through heat treatment would improve the property of ion exchange of activated carbon [21]. To some extent, the acidic sites on the surface of the oxidized activated carbons changed greatly after heat treatment at different temperatures and other conditions. The amount of phenolic groups on the oxidized samples oxidized with HNO_3 has increased in a great deal except NAC5′. Apart from NAC4′ and NAC5′, the amount of carboxylic and lactonic on the heat-treated sample surface significantly decreased. Whereas, the amount of all kinds of acidic groups on the surface of HACn′ increased obviously after heat-treatment. It is evident that the amplitude of the amount of phenolic groups on HACn′ is not as more as those of NACn′. The amount of the Carboxylic in samples FACn′ decreased greatly, while the amount of lactone and phenol has been caused a great increase due to heat-treating at high temperature. From Table 1, the amount of lactonic sites increased with the higher temperature during heat treatment. However, low heat treatment temperature might be in advantage to increase the amount of phenol on the ACs surface.

Table 3
XPS analysis of functional groups

Sample	Disassembled peaks	1	2	3	4
		C–C	C–OH	C=O	COOH
Raw material	BE (eV)	284.56	286.59	288.69	290.69
AC	Relative content %	61.10	29.51	5.87	3.52
NAC2′	BE (eV)	284.60	286.61	288.48	290.64
	Relative content %	52.16	35.71	7.24	4.89
HAC5′	BE (eV)	284.60	286.38	287.79	290.35
	Relative content %	46.39	36.87	10.97	5.77
FAC2′	BE (eV)	284.64	286.16	288.56	290.89
	Relative content %	66.42	21.88	6.40	5.31

3.2. XPS analysis

XPS has been shown to be a useful tool for analyzing the surface groups of activated carbons [22]. It allows for semi-quantitative analysis of functional groups by examining the shift in binding energies and thus the local chemical state. The binding energy increases when more electron density is withdrawn from the electron shell; thus not only the number of bonds to other atoms is essential but their electro negativity. XPS can provide valuable information by examining the C 1s core region. However, there are substantial amounts of primary carbon present so the chemically shifted carbon must first be distinguished from the primary carbon and then associated with specific surface groups. This technique also allows for elemental analysis of carbon, oxygen and other elements [23].

From the previous techniques it was apparent that there is the highest total number of the acidic sites in every treatment method. Therefore, XPS was chosen to test oxygen groups on the surface. After the disassembled peaks treatment, we can obtain the representative XPS C 1s that are shown in Fig. 1. According to the area of each simulating curve, the percentage of each functional group was calculated and listed in Table 3.

The C 1s core level signals also showed different behavior in the chemical modified and heat-treated modified samples (Fig. 1B). After fitting, the peaks could be attributed to C–C, C–O, C=O, and O–CO bonds. From the data in Table 3, we can observe that O–CO contribution of the heat-treated samples is higher than that of the raw material. The presence of C–OH, C=O, and O–CO bonds is especially remarkable for the sample HAC5′ heat-treatment at 500 °C with N_2 ambience protection (Fig. 1C). On the other hand, sample FAC2′ which was oxidized with $Fe(NO_3)_3$ and heat-treated at 800 °C, does not promote the production of C–OH (Fig. 1D). It indicates that the C–OH group may be separated at higher temperature.

Compared to the former wet measure method—Boehm titration, the results of XPS are consistent. It indicates that Boehm titration as a method for analyzing the functional groups is essentially accurate and inexpensive. But the titration method cannot quantify the low content of O–CO group between groups and the basic solution. Whereas the dry method XPS can easily detect the small amount of site.

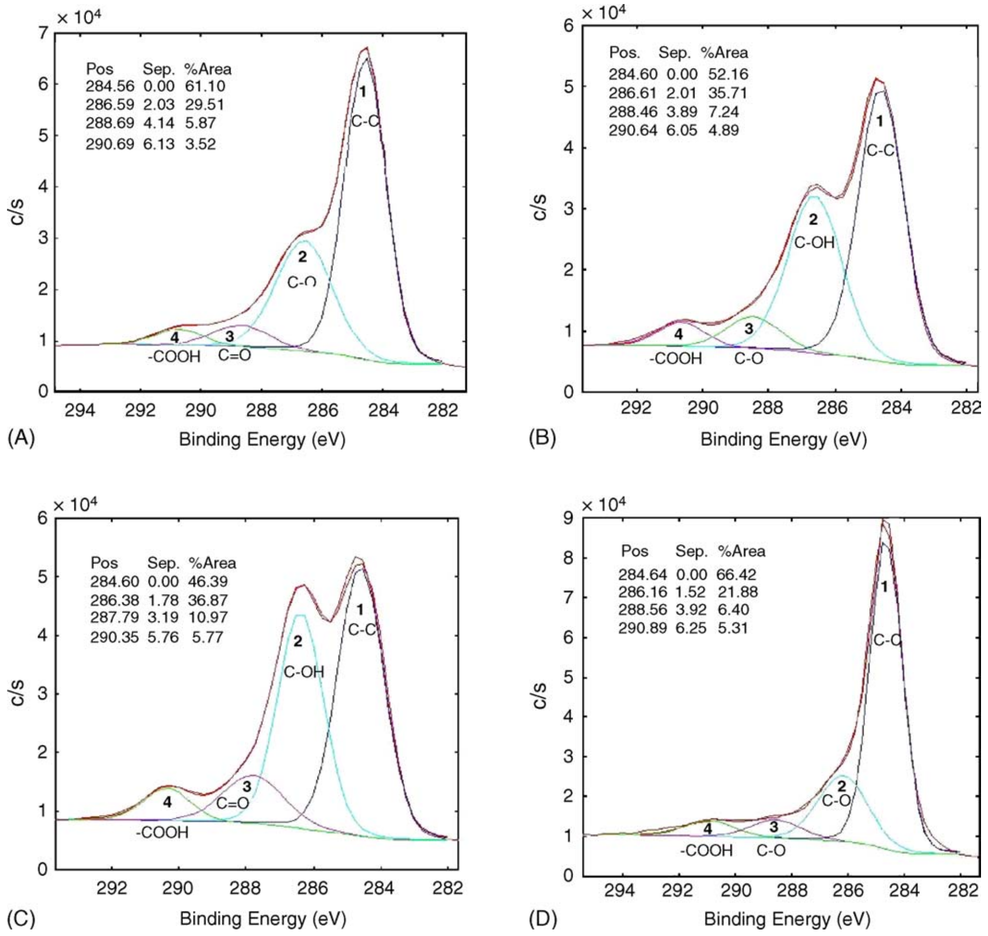

Fig. 1. C 1s peak patterns of ACs and modified ACs by curve fitting method. (A) Raw ACs; (B) NAC2′; (C) HAC5′; (D) FAC2′.

3.3. Adsorption of Cr (VI) in aqueous

3.3.1. Effect of pH

The pH of the system determines the adsorption capacity due to its influence on the surface roperties of the ACs and different ionic forms of the chromium solutions. Change of the adsorption capacity of Cr (VI) on FAC2′ ACs with pH is shown in Fig. 2. It is noticed that the adsorbed amount keeps a high level when the pH is less than 5, then it decreases distinctly in the range of pH 5–9. This indicates that the solution pH affects the Cr (VI) adsorption greatly. At pH 1.0, the chromium ions exist in the form of H_2CrO_4, while in the pH range of 1.0–5.0 different form of chromium ions such as $Cr_2O_7^{-}$, $HCrO_4^{-}$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$ coexist of which $HCrO_4^{-}$ predominates. As pH increases this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$. Chromium exists in different oxidation states and the stability of these forms depends upon the pH of the system [24,25]. The equilibrium that exists between different ionic species of chromium is as follows:

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \quad (1)$$

$$HCrO_4^{2-} \leftrightarrow H^+ + CrO_4^{2-} \quad (2)$$

$$2HCrO_4^- \leftrightarrow Cr_2O_7^{2-} + H_2O \quad (3)$$

From Fig. 2, it was observed that the maximum adsorption occurred at pH 3.0. Maximum adsorption at acidic pH indicates that the low pH leads to an increase in H^+ ions on the carbon surface and it results in significantly strong electrostatic attraction between positively charged ACs surface and chromate ions. In the acidic range, where the Cr (VI) is predominately in the form of $HCrO_4^-$ the removal was found to exponentially decrease

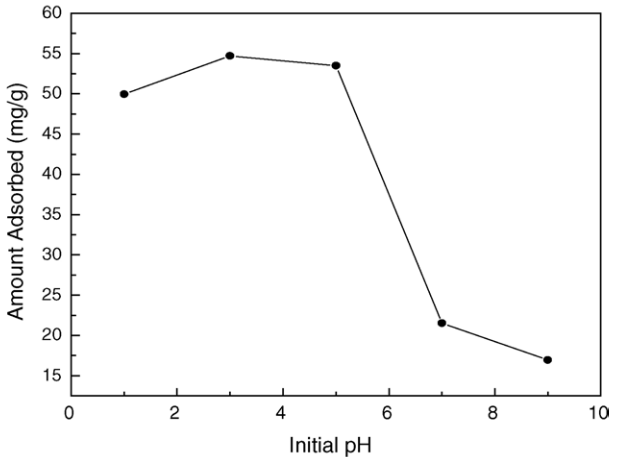

Fig. 2. Solution pH effect on the Cr (VI) adsorption.

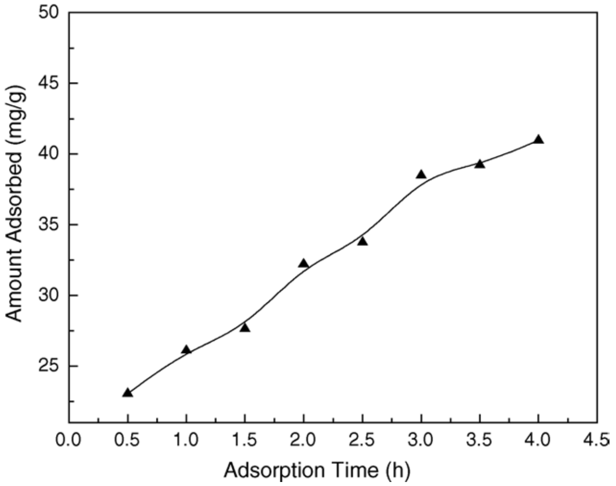

Fig. 3. Time effect on the adsorption of Cr (VI).

with increase in the pH since $HCrO_4^-$ ions has a greater affinity towards the hydrogen ions present on the surface of the activated carbon. However, at pH less than 3.0 a decrease is observed due to the chromium being present predominantly as H_2CrO_4. Adsorption of Cr (VI) on the activated carbon was not significant at pH values greater than 5.0 due to dual competition of both the anions (CrO_4^{2-} and OH^-) to be adsorbed on the surface of the adsorbent of which OH^- predominates. Maximum adsorption occurs at pH3.0 and hence it was taken as the optimal value for further adsorption studies.

3.3.2. *Effect of adsorption time*

Fig. 3 shows the effect of the time on Cr (VI) adsorption (Sample FAC2′, 0.05 g, 25 ml Cr (VI) solution of initial concentration 100 mg/L, pH 3). It is clear that the time has an evident effect on the adsorption during the first 3 h. However, the increase in adsorption becomes slow beyond 3 h. The adsorption experiments in the following text were conducted for 3 h, except indicated.

3.3.3. *Effect of adsorbent dosage*

The effect of the activated carbon dosage on Cr (VI) adsorption (Sample FAC2′, 0.05–0.15 g, 25 ml Cr (VI) solution of initial concentration 100 mg/L, pH 3) shows in Fig. 4. It is apparent that the quantity of Cr (VI) adsorption decreases with activated carbon dose increasing. It is very clear that with increase in adsorbent dose the actual number of active sites or adsorption sites per gram of adsorbent do not increase proportionately and hence there is a regular decrease in adsorbate uptake. That is because the total amount of activated carbon increases although the specific surface area of AC is constant.

On the other hand, the removal rate of Cr (VI) increases with increasing the dosage of activated carbon. That results from the increase of the total surface area, but the amount of Cr (VI) is always constant in each adsorption experiment. Accordingly the dosage of AC is 6 g/L is considered the optimum quality in this experiment.

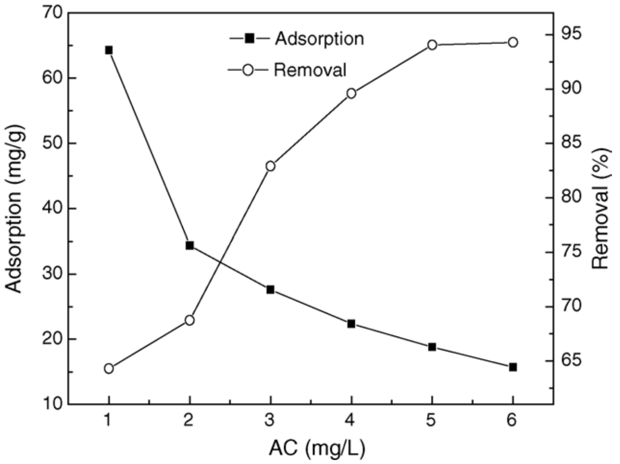

Fig. 4. The unit mass of AC on the adsorption of Cr (VI).

3.3.4. *Effect of oxygen groups on the adsorption of ACs*

By means of the above optimum adsorption experiment parameters ($T = 3$ h, pH 3, dosage of AC is 6 g/L, concentration of Cr (VI) = 100 mg/L), the adsorption of Cr (VI) on the modified activated carbons can be obtain. The results were shown in Table 4.

It can be seen that all samples after oxidation treatment and heat treatment can improve the adsorption capacity of the activated carbon. Sample FACn′ has the maximum adsorption of Cr (VI) among the all oxidized and heat-treated samples. The most important reason may relate to the oxygen groups on the surface of AC. The contents of lactonic sites on all FACn′ samples are evidently higher than that of samples modified with the other two methods, so that the adsorption property of Cr (VI) is improved distinctly. Meanwhile, the carboxylic sites were decomposed largely that may result in increasing the basic sites on the surface of AC. Many researchers have received the similar results about the effect of basic sites on the adsorption property of ACs [26,27].

Another reason of improving adsorption capacity of ACs is that the heat-treatment at high temperature probably expands the

Table 4
The adsorption amount of Cr (VI) on oxidized ACs

Sample	Adsorption of Cr (VI) (mg/g)
AC	10.90
NAC1′	13.28
NAC2′	11.50
NAC3′	11.50
NAC4′	10.78
NAC5′	12.43
HAC1′	13.03
HAC2′	13.28
HAC3′	14.05
HAC4′	13.07
HAC5′	14.47
FAC1′	15.10
FAC2′	15.45
FAC3′	15.12
FAC4′	15.25

distances of the facets of graphite hence improving the property of exchange. However, HNO_3 oxidation agent is so strong that it may destroy the micropore structure and forms macropores in ACs. So the adsorption capacity of AC will decrease in some extent.

4. Conclusions

The results presented in this paper show that Boehm titration and XPS offer the valuable technique for studying the surface chemical properties of activated carbons. By combining the two methods, the functional group species introduced to the surface as a result of chemical treatment and heat treatment at high temperature can be detected quantitatively. The activated carbon treated by oxidation has the higher adsorption property of Cr (VI) than that of the raw activated carbon. The samples treated by means of $Fe(NO_3)_3$ solution with the concentration of 10% as the oxygen agent subsequent to heat-treatment at 800 °C have the optimum adsorption property. The increasing trend of the adsorption with different modification method indicates that the interaction between adsorbate ion and adsorbent surface is chemical in nature.

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