

Effect of acidic surface functional groups on Cr(VI) removal by activated carbon from aqueous solution

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Abstract

The activated carbon with high surface area was prepared by KOH activation. It was further modified by H₂SO₄ and HNO₃ to introduce more surface functional groups. The pore structure of the activated carbons before and after modification was analyzed based on the nitrogen adsorption isotherms. The morphology of those activated carbons was characterized using scanning electronic microscopy (SEM). The surface functional groups were determined by Fourier transform infrared spectroscopy (FTIR). The quantity of those groups was measured by the Boehm titration method. Cr(VI) removal by the activated carbons from aqueous solution was investigated at different pH values. The results show that compared with H₂SO₄, HNO₃ destructs the original pore of the activated carbon more seriously and induces more acidic surface functional groups on the activated carbon. The pH value of the solution plays a key role in the Cr(VI) removal. The ability of reducing Cr(VI) to Cr(III) by the activated carbons is relative to the acidic surface functional groups. At higher pH values, the Cr(VI) removal ratio is improved by increasing the acidic surface functional groups of the activated carbons. At lower pH values, however, the acidic surface functional groups almost have no effect on the Cr(VI) removal by the activated carbon from aqueous solution.

Keywords: activated carbon; surface functional groups; removal; modification; chromium(VI)

1. Introduction

Activated carbon (AC) has been widely used to remove inorganic and organic pollutants from aqueous or gaseous media as adsorbent for purifying environment. The high adsorption capacity of AC is attributed to its huge surface area, well-developed pore structure, and special surface chemical properties. The surface area and pore structure can be controlled during the activation process such as activation time, activation agent, and temperature. The surface chemical properties depend on surface oxygen functional groups on AC such as carboxyl, phenol, and lactone [1-2], and can be made or changed by means of oxidation treatment, thermal treatment, etc. To improve the adsorption capacity and selectivity of AC on a certain adsorbate, modification of surface functional groups on AC was often applied [3-5].

Chromium is a highly toxic pollutant generated from many industrial processes such as leather tanning, electroplating, and manufacturing of dye, paint, and paper. Chromium exists in the aquatic environment mainly in two states: trivalent Cr(III) and hexavalent Cr(VI). The latter form is far

more toxic than the former. Contact with Cr(VI) can cause severe health problems from simple skin irritation to lung carcinoma [6]. Cr(VI) removal from wastewater by AC has been widely used and proved economically favorable and technically easier [7-9]. Recently, many studies on improving the adsorption capacity of AC to Cr(VI) have focused on chemical modification aiming to increase surface functional groups. Zhao *et al.* [10] reported that treatment with HNO₃, H₂O₂, and Fe(NO₃)₃ increased the weakly acidic functional group of AC and increased the adsorption capacity of the AC to Cr(VI) by a factor of 1.4. This effect was also reported by Rios *et al.* [11], where the adsorption capacity of AC to Cr(VI) was increased by a factor of 1.7 through treating AC with HCl. However, adsorption capacity decreased by a factor of approximately 4.3 when AC was modified by HNO₃ due to the presence of acidic surface groups in the study of Aggarwal *et al.* [12]. Thus, it is still unclear what role the acidic surface groups play on the adsorption capacity of AC to Cr(VI).

In this work, using anthracite as raw material, AC was prepared by KOH activation. H₂SO₄ and HNO₃ were em-

ployed to modify the AC to increase the acidic surface groups. The Cr(VI) removal by the ACs from aqueous solution was investigated at different pH values. The relationship between acidic surface groups and adsorption performance was analyzed.

2. Experimental

2.1. Carbon adsorbents

The AC with high surface area (parent AC) was prepared using inexpensive Ningxia (China) coal as raw material and KOH as active reagent according to the method as shown in previous work [13]. It was further treated by $9 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4 and $6 \text{ mol}\cdot\text{L}^{-1}$ HNO_3 in a water bath of shaker at a temperature of 90°C for 4 h, respectively. Then, the treated ACs were filtered, washed, and dried at 120°C . The sample modified by H_2SO_4 is named as AC-S and that modified by HNO_3 is named as AC-N.

N_2 adsorption isotherms of the above ACs at 77 K were measured on a Quantachrome Autosorb-1 equipment. The specific surface area was determined by the five-point Brunauer-Emmett-Teller (BET) method, and micropore volumes were calculated by the Dubinin-Radushkevich (DR) equation. The pore size distribution was determined by the density functional theory (DFT) method. The morphology was measured using GEOL-6700F scanning electronic microscopy (SEM). The acidic surface groups of adsorbents were analyzed by Fourier transform infrared spectroscopy (FTIR, Jasco FT/IR-660) qualitatively and the Boehm titration method [14] quantitatively. The Boehm method is described as follows: 0.5 g of the carbon sample was added to a series of flasks that contain 50 mL of $0.05 \text{ mol}\cdot\text{L}^{-1}$ NaOH, Na_2CO_3 , and NaHCO_3 solutions, separately. The flasks were then sealed and shaken for 24 h at room temperature. The suspension was then filtered and 10 mL of the filtrate was titrated with $0.05 \text{ mol}\cdot\text{L}^{-1}$ HCl. The number of acidic groups was calculated based on the assumption: NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; and NaHCO_3 neutralizes only carboxylic groups.

2.2. Adsorption experiments

All the chemicals used in adsorption experiments are of analytical reagent grade. Cr(VI) solution was prepared by dissolving potassium dichromate in distilled water. A series of 200 mL conical flasks were filled with 50 mL of Cr(VI) solution with the initial concentration of $50 \text{ mg}\cdot\text{L}^{-1}$. Each solution was adjusted to the designed pH value (1-9) with dilute H_2SO_4 ($0.1 \text{ mol}\cdot\text{L}^{-1}$) and KOH ($0.1 \text{ mol}\cdot\text{L}^{-1}$). Then, 0.03 g of adsorbent was added. The mixture was shaken in a water bath of shaker with the design temperature of 25°C .

Adsorption time of 40 h was designed, since primary experiment indicated that 40 h was required for the adsorption equilibrium. After that, the sample solution was filtered. The concentrations of residual Cr(VI) and total Cr including not only Cr(VI) but Cr(III) in the filtrate were analyzed to obtain the removal ratio of chromium.

$$\text{Removal ratio} = \frac{c_0 - c_e}{c_0} \times 100\% \quad (1)$$

where c_0 is the initial concentration of chromium in the solution, $\text{mg}\cdot\text{L}^{-1}$; c_e is the equilibrium concentration of Cr(VI) or total Cr in the solution, $\text{mg}\cdot\text{L}^{-1}$.

The concentration of Cr(VI) was determined by a modified diphenylcarbohydrazide spectrophotometric method (GB7467-87). Total Cr was determined by first converting all chromium to Cr(VI) then determining Cr(VI) concentration according to Chinese standard method (GB7466-87).

3. Results and discussion

3.1. Pore structure characteristic of adsorbents

The N_2 isotherms and pore size distributions of the ACs before and after modification are shown in Figs. 1 and 2. It is noted that N_2 adsorption capacity of the AC modified by

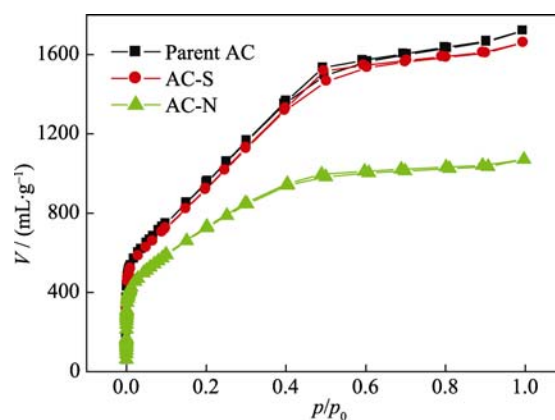


Fig. 1. N_2 isotherms of the ACs.

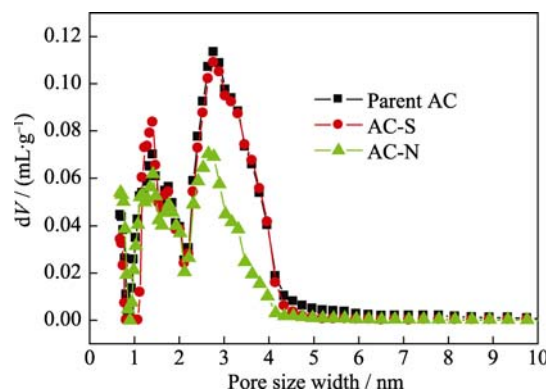


Fig. 2. Pore size distributions of the ACs.

HNO₃ (AC-N) decreases remarkably whereas that of the AC modified by H₂SO₄ (AC-S) decreases a little relative to the parent AC. Accordingly, there are remarkable decrease on surface area and pore volume of AC-N and less decrease on those of AC-S compared with parent AC (Table 1). Seen from the pore size distributions, the micropores whose pore size width is at ~1.5 nm increase for AC-S, which leads to larger DR micropore volume of AC-S than that of the parent AC. Particularly, mesopores whose pore size ranges from 2 to 4 nm reduce notably for AC-N sample, which leads to the decrease of average pore size of AC-N. It

is indicated that H₂SO₄ modifier produced small amount of fresh micropores while it broke some original pores of parent AC and made not much change for the pore structure of parent AC. However, HNO₃ destroyed the original pore of parent AC severely due to its strong oxidation. This is in accordance with the results reported in many literatures [4, 15]. Furthermore, it is observed that the surfaces of ACs were all destroyed to some degree after modification from the SEM images of the ACs (Fig. 3). Nevertheless, the surface of AC-N was destroyed more than that of AC-S.

Table 1. Physical characteristics of the ACs

AC samples	$S_{\text{BET}} / (\text{m}^2 \cdot \text{g}^{-1})$	$V_{\text{total pore}} / (\text{cm}^3 \cdot \text{g}^{-1})$	$V_{\text{micropore (DR)}} / (\text{cm}^3 \cdot \text{g}^{-1})$	Average pore size / nm
Parent AC	3892	2.668	1.702	2.741
AC-S	3744	2.574	1.919	2.750
AC-N	1726	1.646	1.195	2.416

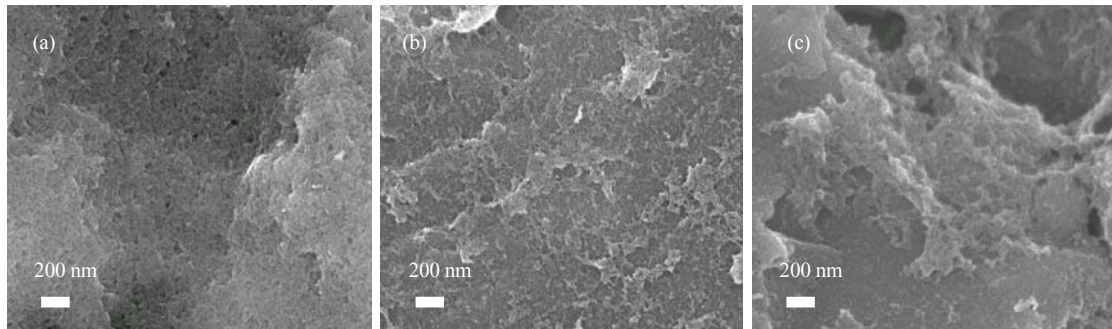


Fig. 3. SEM images of the ACs: (a) parent AC; (b) AC-S; (c) AC-N.

3.2. Surface chemical characteristic of adsorbents

3.2.1. FTIR spectra

The chemical modifiers not only changed the pore structure but also brought alteration of the surface functional groups to some extent. The FTIR spectra of the ACs are shown in Fig. 4. Among them, the spectrum of the parent AC is simplest. Obviously, a stronger broad adsorption band at ~3400 cm⁻¹, which is ascribed to O–H stretching vibration, appears on FTIR spectra of the ACs after modification, especially AC-N. More complex adsorption bands which are assigned to carbonyl C=O, C=N, and C–H vibrations at ~1700–1300 cm⁻¹ are also shown on the FTIR spectra of AC-S and AC-N. The bands observed at 1000–1300 cm⁻¹ are assigned to asymmetric and symmetric C–O–C stretching [16], which are also strengthened on the spectra of ACs after modification. However, compared with AC-S, the adsorption bands on the FTIR spectrum of AC-N are stronger, suggesting that HNO₃ modifier induced more surface oxygen-containing groups to the parent AC.

3.2.2. Boehm titration

Table 2 shows the amount of the acidic surface functional

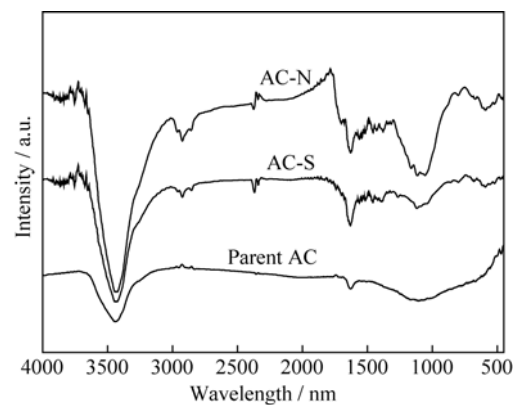


Fig. 4. FTIR spectra of the ACs.

groups of the ACs involved in this study, which is the result of Boehm titration. It is clear that the number of acidic surface functional groups increases after treatment with H₂SO₄ and HNO₃ in varying degree. HNO₃ treatment increases the amount of carboxylic, lactone, and phenol groups notably, particularly carboxylic group, indicating the strong oxidation of HNO₃. H₂SO₄ increases the amount of these acidic

Table 2. Amount of surface acidic functional groups on the ACs (mmol·g⁻¹)

Sample	Carboxylic	Lactonic	Phenolic
Parent AC	0.000	0.045	0.155
AC-S	0.223	0.174	0.302
AC-N	0.410	0.215	0.381

surface groups less than HNO₃. This is in accordance with the results attained from FTIR spectra.

3.3. Adsorption experiments

The chromium removal ratio of the studied ACs at different pH values is shown in Figs. 5-7. It is clearly seen that as the pH value decreases, the Cr(VI) removal ratio increases always. The same trend is for total Cr removal ratio at high pH values (>3 or 4). However, the total Cr removal ratio drops sharply or increases less than the Cr(VI) removal ratio with the decrease in pH values in the low pH range. When the pH value is above 7, the chromium removal ratio is very low. It is indicated that the pH value of Cr(VI) solution plays a key role in adsorption capacity of the ACs. A less removal ratio of total Cr than Cr(VI) implies that Cr(VI) was

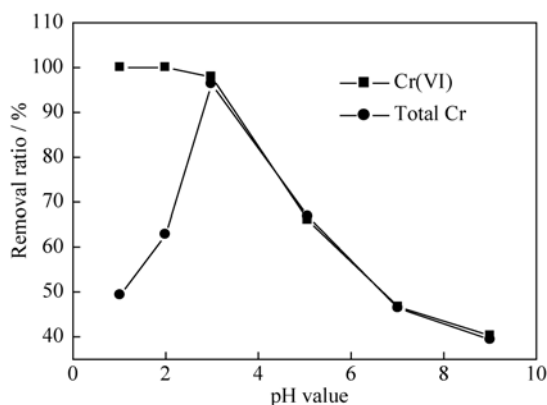


Fig. 5. Removal ratio of the parent AC to Cr(VI) and total chromium at different pH values.

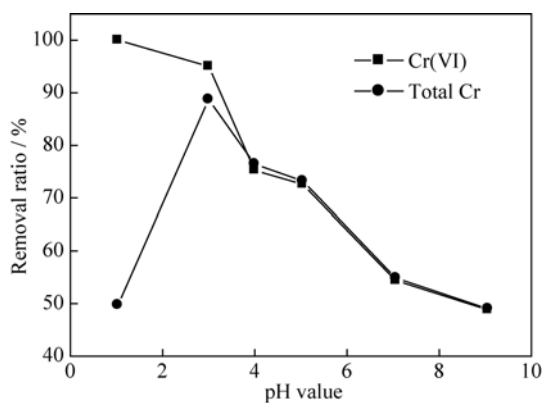


Fig. 6. Removal ratio of AC-S to Cr(VI) and total chromium at different pH values.

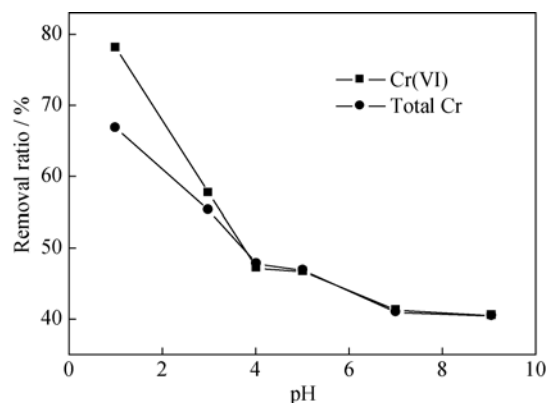


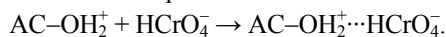
Fig. 7. Removal ratio of AC-N to Cr(VI) and total chromium at different pH values.

reduced by carbon to Cr(III) but not adsorbed at low pH values, which was also observed by some researchers [17-18].

In aqueous solution, the following equilibrium exists among different species of Cr(VI):



The main type of species which Cr(VI) exists in depends on the pH value of aqueous solution and the concentration of Cr(VI). When the concentration of Cr(VI) is below $\sim 1 \text{ g}\cdot\text{L}^{-1}$ and the pH value ranges from 1 to ~ 6.5 , HCrO_4^- is the main species. And CrO_4^{2-} predominates at the same concentration of Cr(VI) and $\text{pH} > \sim 6.5$ [19]. Thereby, HCrO_4^- or CrO_4^{2-} , negatively charged ion, is the main type of species in the studied solution range. In the acidic solution, acidic surface groups on ACs are protonated and charged positively [11]. Thus, the complexes form between adsorbents and adsorbates due to electrostatic attractive power, which causes the chemical adsorption:



However, surface groups on ACs are de-protonated and electron-rich in the basic solution; meanwhile, the electrostatic repulsive force exists between adsorbates and adsorbents, leading to a less adsorption of Cr and Cr removal ratio. At a lower pH value (< 3 or 4), the electrostatic repulsive force also exists between protonated ACs and Cr(III), positively charged ions, resulting in little adsorption to Cr(III) and the decrease of total Cr removal ratio. Different from the parent AC and AC-S, total Cr removal of AC-N always increases with the decrease of pH values. Possibly, this is ascribed to more carboxylic groups on AC-N surfaces, which increase the cation exchange capacity and lead to a higher

adsorption capacity of AC-N to Cr(III) at low pH values.

It is noted that the pH value at which Cr(VI) starts to be reduced to Cr(III) is different for the ACs. The pH value is ~ 3 for the parent AC while the pH value is ~ 4 for AC-S and AC-N. Thereby, it is possible that the reducibility of ACs enhances because of the increase of surface acidic functional groups.

To purify waste water containing Cr, not only Cr(VI) but Cr(III) should be removed. The comparison of total Cr removal ratio of the ACs is shown in Fig. 8. When the pH value is above 5, the Cr(VI) removal ratio of AC-S is higher than that of the parent AC. It is speculated that more acidic surface functional groups result in a stronger polarity and a more positive density on the surface of AC-S, which causes its higher adsorption capacity to polar Cr(VI) anions. At lower pH values (3, 4), the Cr removal ratio of the parent AC is higher than that of AC-S. This should be attributed to a bigger surface area and pore volume of the parent AC as the protonation almost donates the same polarity and positive charge to the surface of all ACs. The Cr removal capacity of AC-N is far lower than that of the others at $\text{pH} < \sim 7$, which is caused by its far lower specific surface area and pore volume. However, AC-N has almost the same Cr removal ratio with the parent AC at a higher pH value (~ 9). It is suggested that abundant acidic surface functional groups of AC-N counteract the deprotonation on the surface of ACs partly and reduce the electrostatic repulsive force between adsorbates and adsorbents, leading to a higher physical adsorption. Consequentially, the Cr(VI) adsorption capacity of ACs depends mainly on their specific area and pore volume at a lower pH value, but mainly on their acidic surface functional groups at a higher pH value.

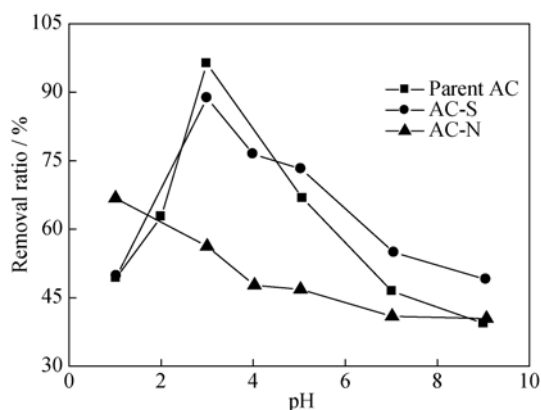


Fig. 8. Comparison of total chromium removal ratio of the ACs.

4. Conclusion

The AC with high surface area was prepared by KOH ac-

tivation and was further modified by H_2SO_4 and HNO_3 . Compared with H_2SO_4 , HNO_3 destructs the original pore of the AC more seriously, which leads to the lower surface area and pore volume of the AC modified by it. At the same time, it induces more acidic surface functional groups on the AC. As the pH value decreases, the Cr(VI) removal ratio always increases. Nevertheless, at $\text{pH} < 3$ or 4, Cr(VI) is reduced to Cr(III), leading to the decrease of total Cr removal ratio. The ability of reducing Cr(VI) to Cr(III) by the ACs is related to acidic surface functional groups. At higher pH values, the Cr(VI) removal ratio is improved by increasing acidic surface functional groups on the ACs. At lower pH values, the Cr(VI) removal ratio increases with the increase of surface area and pore volume of the ACs, whereas acidic surface functional groups on the ACs almost have no effect on it.

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