Activated carbon with excellent chromium(VI) adsorption performance prepared by acid–base surface modification

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Abstract

In the present work, activated carbon (AC) with excellent Cr(VI) adsorption performance especially at low concentrations was prepared by an acid–base surface modification method. Raw activated carbon (AC_0) was first oxidized in boiling HNO_3 (AC_1), then treated with a mixture of NaOH and NaCl (AC_2). Batch equilibrium and continuous column adsorption were conducted to evaluate the adsorption performance. Boehm titration, elemental analysis, and N_2/77 K adsorption isotherm methods were used to characterize the surface properties and pore structure of modified ACs. The results revealed that the modified AC exhibited excellent Cr(VI) adsorption performance in terms of adsorption capacity and adsorption rate: $AC_2 > AC_1 > AC_0$. Modification caused S_{BET} to decrease and the total number of surface oxygen acidic groups to increase. HNO_3 oxidization produced positive acid groups, and subsequently NaOH treatment replaced H^+ of surface acid groups by Na^+, and the acidity of AC decreased. The main cause of higher Cr(VI) adsorption capacity and rate for AC_2 was the presence of more oxygen surface acidic groups and suitable surface acidity. HNO_3–NaOH modification shows potential for the preparation of high quality AC for the effective removal of low concentrations of Cr(VI).
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1. Introduction

Removal of hazardous metal ions especially in low concentrations from industrial effluent is of great interest due to the large quantity of material processed. Metals ions such as Cr, Hg, Cd, Ni, As, Pb, etc. have a harmful effect on human physiology and other biological systems [1]. Chromium, which is on the top priority list of toxic pollutants as defined by the EPA, is present in the electro-plating, metallurgy, and chemical engineering wastewater as Cr(VI) in the form of oxidized species, such as chromates (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), and dichromate ($HCrO_4^-$), depending on pH and Cr(VI) concentration [2]. Due to its high solubility, Cr(VI) is most hazardous, since it can accumulate in the food chain and cause several ailments. The stricter environmental regulations related to the discharge of heavy metals make it necessary to develop efficient processes for Cr(VI) removal from wastewater. Several methods were studied for the treatment of wastewater containing chromium compounds. Among those, adsorbent adsorption is effective and widely used [3]. Activated carbon (AC) either in powder or in granular form can offer a relatively efficient technology for removal of Cr(VI).

Recently, numerous studies were conducted to reveal the relationship between surface characteristics of oxidized activated carbon with its adsorption capacity for toxic metal ions [4]. However, most studies are focused on the highly concentrated Cr(VI), it is rare to find work conducted for the low concentrations of Cr(VI) in wastewater despite its large quantity and different adsorption mechanism.

Cr(VI) can simultaneously adsorb onto AC by an ion exchange mechanism and oxidization mechanism [5].

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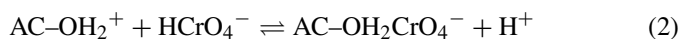*E-mail address:* liushouxin@126.com (S.X. Liu).
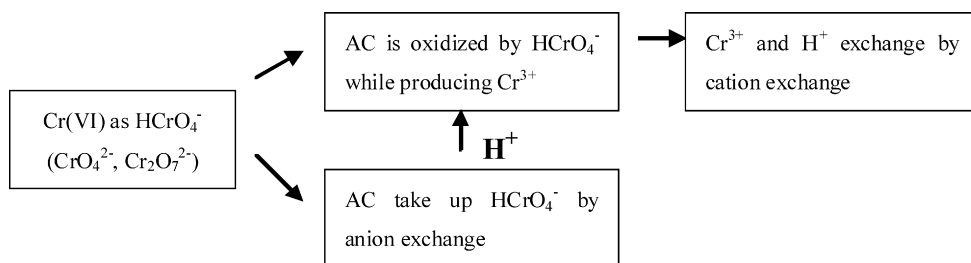
The oxidization mechanism is shown according to the following equation:

$$E(HCrO_4^-/Cr^{3+}) = E^0 + \Delta E_{(HCrO_4^-/Cr^{3+})} + \Delta E\,pH$$
$$= E^0_{(HCrO_4^-/Cr^{3+})} + 0.018\,\log C(HCrO_4^-)/$$
$$C(Cr^{3+}) - 0.126\,pH \quad (1)$$

$E(HCrO_4^-/Cr^{3+})$ was dependent on Cr(VI) concentration and pH. An increase in pH and a decrease in Cr(VI) concentration causes the value of $E(HCrO_4^-/Cr^{3+})$ to drop dramatically. So, for low concentrations of Cr(VI), most wastewater (except those under strongly acidic conditions, pH < 1), removal of Cr(VI) through an oxidization mechanism was difficult. Results from Kratochvil revealed that the uptake of Cr(VI) (720 mg/L) at pH 7 was indeed negligible and no Cr(III) was detected in the liquid in equilibrium [3]. So, the ion exchange mechanism was dominant for the removal of Cr(VI) at low concentrations.

The ion exchange mechanism of activated carbon was due to the presence of surface functional groups, such as carboxylic, hydroxyl, and lactones, which have a high affinity for and are the main sites for metal ion adsorption. The nature and amount of these acidic functional groups depend on the nature of the carbon and the history of its formation. It is commonly known that oxidation of activated carbon can significantly enhance the adsorption capacity of Cr(VI) on AC [6]. Oxidative treatment in an oxidized gas atmosphere or a reaction with a strong acid such as HNO$_3$ can increase the total amount of acidic functional groups on AC, leading to increased adsorption capacity for Cr(VI) [2,4,6].

Based on the equilibrium constants for Cr(VI) hydrolysis, HCrO$_4^-$ and CrO$_4^{2-}$ are the two major species in the solution [1]. Adsorption of HCrO$_4^-$ and CrO$_4^{2-}$ on activated carbon were as follows [7,8]:

$$AC–OH_2^+ + HCrO_4^- \rightleftharpoons AC–OH_2CrO_4^- + H^+ \quad (2)$$

$$AC–OH_2^+ + CrO_4^{2-} \rightleftharpoons AC–OHCrO_4^{2-} + H^+ \quad (3)$$

When activated carbon was treated with boiling nitric acid, oxygen acidic groups –COOH, –OH, –COOR were initially produced. This may be the reason for the higher capacity of AC$_1$ and AC$_2$ than AC$_0$. Oxygen acidic groups then further reacted with H$^+$ formed positive hydronium ions such as –COOH$_2^+$, –OH$_2^+$, =C=OH$^+$. Because of the reversible characteristics of above reactions, the pH of aqueous solutions decreased with adsorption progress, and the counter reaction became dominant. Therefore, more of positive hydronium ions that are present, the less metal ions can be adsorbed. So, surface pH control may be crucial for the low concentration Cr(VI) removal.

Due to the different adsorption removal mechanism, the objective of this work was to prepare activated carbon with excellent Cr(VI) adsorption performance especially for low concentrations of Cr(VI). Using a simple method, HNO$_3$–NaOH surface modification over commercial AC was adapted and the related mechanism was elucidated.

2. Materials and methods

Commercial coconut activated carbon ($S_{BET} = 873\ m^2/g$, particle size 2–4 mm) was used, which has been specifically used for water treatment and kindly supplied by Jianxin company (Tangshan, China). Prior to usage, the carbon sample was washed with boiled deionized water and oven-dried at 120 °C for 24 h (marked AC$_0$). Activated carbon modification was as follows: 10 g AC$_0$ was added into 50 ml nitric acid solution with concentration of 7 mol/L, shaken slowly at 90 °C for 12 h, then dried at 105 °C for 24 h, and marked as AC$_1$. Then AC$_1$ was added to the mixed solution of 1 mol/L NaOH and 1 mol/L NaCl with the ratio of 20 mL/g-carbon, shaken at 30 °C for 48 h, then dried at 105 °C for 24 h, and marked as AC$_2$. Cr(VI) aqueous solution was prepared by dissolving analytical grade K$_2$Cr$_2$O$_7$ in deionized water.

Elemental analysis was conducted on Euro EA-3000 Element Analysis Spectrometer, N$_2$ was used as carrier gas with a flow rate of 11.3 mL/min, and H$_2$ was the combustion gas with a flow rate of 80 mL/min. The concentration of Cr(VI) was determined spectrophotometrically by TAS-900 atomic adsorption spectroscopy at 365 nm. pH was determined by a PHS-3C pH meter. S_{BET} was determined at 77 K using a micrometrics ST-2000 automatic apparatus. The surface functional groups containing oxygen were determined according to the Boehm titration method [9,10]. The surface pH of the ACs studied was measured according to ASTM D3838 based on boiling and sonic slurry method.

The equilibrium adsorption measurement of Cr(VI) from the dilute aqueous solution happened as follows: 0.2 g activated carbon sample was added to a series of 100 mL Cr(VI) solutions with concentrations from 5 to 50 mg/L. The bottles were sealed with paraffin film and then shaken at 30 °C at a frequency of 90 strokes/min. The adsorbed amount of Cr(VI) was measured according to the change in Cr(VI) concentration. A continuous column adsorption experiment was conducted on a quartz glass adsorption column with a 20 mm diameter and a 200 mm height. Five grams of activated carbon was added and the height of carbon bed was 1.5 cm. One liter of Cr(VI) aqueous solution with concentration of 50 mg/L was circulated into the column by
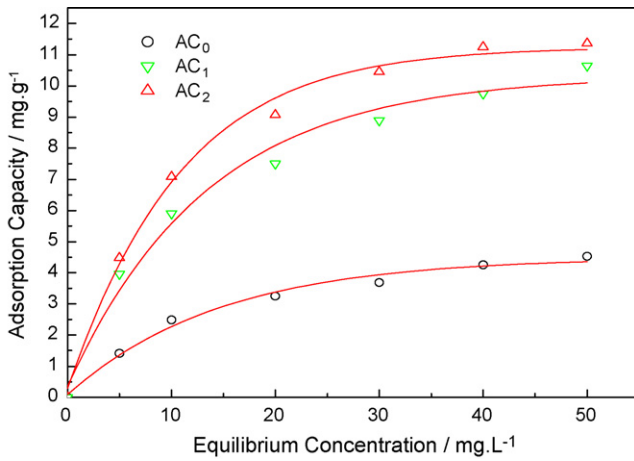
Fig. 1. Adsorption isotherm of Cr(VI) onto activated carbons at 30 °C.

Fig. 2. Adsorption of Cr(VI) on various carbons treated by Langmuir equation.

a peristaltic pump. The aqueous samples (5 mL) were taken at preset time intervals and the species concentration was similarly measured.

3. Results and discussion

The data obtained from the equilibrium and kinetics column adsorption experiments were analyzed to determine the adsorption capacity and rate of the modified and received AC. For all equilibrium systems in this work, no Cr(III) was detected. This result further demonstrated the different adsorption mechanism for low concentrations of Cr(VI).

Cr(VI) adsorption isotherms of AC_0, AC_1, and AC_2 were shown as Fig. 1. According to the data, adsorption of Cr(VI) on all carbons fitted the Langmuir isotherm well and exhibited type I behavior according to the IUPAC classification. This may be an indicator that mono-molecular layer chemical adsorption occurred. Langmuir isotherm constants were calculated from the following equation and the parameters obtained are presented in Table 1 (Fig. 2).

$$\frac{c}{q} = \frac{c}{q_m} + \frac{1}{q_m k_L} \tag{4}$$

Where q_m and k_L are Langmuir constants determined from the slope and intercept of the plot, and indicative of maximum adsorption capacity (mg g^{-1}) of activated carbon and energy adsorption, respectively. c, q are equilibrium concentration and equilibrium amount of adsorbed. Compared to AC_0 (Table 1, $AC_0 = 7.6138$ mg g^{-1}), the adsorption capacity of modified AC was greatly enhanced. The first modification of HNO_3 oxidation increased the adsorption capacity significantly ($AC_1 = 13.7457$ mg g^{-1}); the subsequent second treatment pro-

cess can induce a further increase, but this increase is small ($AC_2 = 13.8889$ mg g^{-1}).

The continuous column adsorption result was shown as Fig. 3. It must be noted that, although the second treatment process was slightly beneficial to the adsorption capacity, it could significantly enhance the adsorption rate. The order of the adsorption rates was found to be $AC_2 > AC_1 > AC_0$.

The large adsorption capacity and fast adsorption rate of AC_2 revealed its great potential in extremely low concentrations of Cr(VI) in the wastewater treatment field.

Oxygen is an important heteroatom for Cr(VI) adsorption which commonly occurs in the form of carboxylic acid groups, phenolic hydroxyl groups, and quinone carbonyl groups. Activated carbons assume an acidic character when exposed to oxygen between 200 and 700 °C or to an oxidant such as hydrogen peroxide, nitric acid, and sulfuric acid mixtures in the solution [11,12]. Generally, the higher the oxygen content, the more acidic the dispersions can be when activated carbon is added into the aqueous dispersion. It can be seen from Table 2 that more acidic oxygen surface functional groups have been intro-

Table 1
Langmuir parameters of Cr(VI) adsorption on various carbons

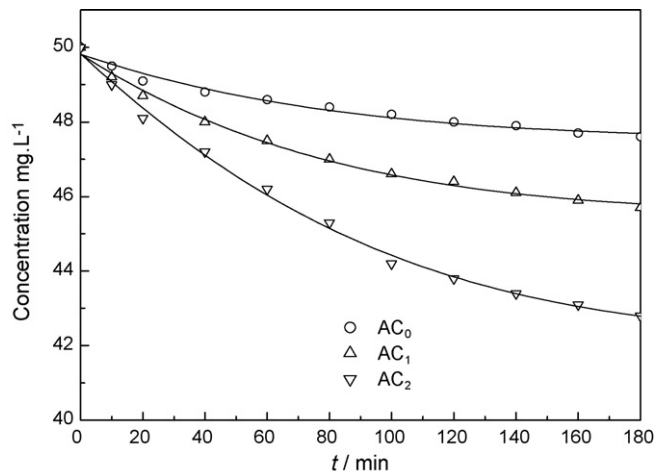| Sample	q_m (mg g^{-1})	k_L
AC_0	7.6138	0.0343
AC_1	13.7457	0.0630
AC_2	13.8889	0.0998

Fig. 3. Concentration profiles of Cr(VI) continuous column adsorption on various carbons.

Table 2
Boehm titration results for oxide groups on carbons

Sample	–COOH (mmol g^{-1})	–COOR (mmol g^{-1})	–OH (mmol g^{-1})	Total (mmol g^{-1})
AC_0	0.25	0.60	0.45	1.30
AC_1	1.50	4.37	8.37	14.25
AC_2	0.75	4.12	7.37	12.25

Table 3
Elemental analysis results for various carbons

Sample	$w(C)$ (%)	$w(H)$ (%)	$w(N)$ (%)	$w(O)$ (%)	$w(O)/w(C)$	$w(H)/w(C)$	$w(N)/w(C)$	$w(O)/w(H)$
AC_0	94.615	0.598	0.455	4.332	0.0458	0.0063	0.00480	7.227
AC_1	70.748	0.930	1.734	26.588	0.3758	0.0131	0.0245	29.542
AC_2	79.220	0.523	1.259	18.998	0.2398	0.0066	0.0159	36.535

duced by HNO_3 oxidation. The number of carboxylic, phenolic, carbonyls on the carbon surface increased. After NaOH treatment, the total number of acidic groups slightly decreased. The results of the Boehm titration indicated that the increased acidity is primarily explained by the formation of carboxylic acid and phenolic hydroxyl groups. Clearly, the distribution of chemical groups on the carbon surface is significantly affected by the oxidation of HNO_3.

Adsorption of Cr(VI) was more effective in the case of acid treated activated carbons, resulting from an increase of acidic functional groups [12]. Data in Table 2 suggested that the adsorption capacity of AC_0, AC_1, and AC_2 was proportional to the total amount of acidic surface functional groups on carbon. But the different adsorption capacity and adsorption rate of AC_2 and AC_1 revealed that higher acidity may result worse adsorption performance.
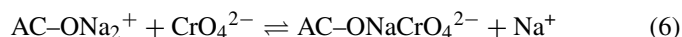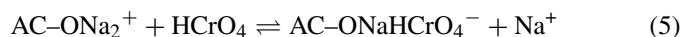
BET surface area measurement results according to N_2 adsorption at 77 K were as follows: $S_{BET-AC_0} = 873$ m^2/g, $S_{BET-AC_1} = 853$ m^2/g, and $S_{BET-AC_2} = 851$ m^2/g. Because of erosive action, the first HNO_3 oxidation treatment leads to 20 m^2/g loss of total surface area due to the collapse of the micropore wall. The second modification step has almost no effect on S_{BET}. For physical adsorption, the capacity was proportional to S_{BET}. However, AC_2 and AC_1 exhibited better adsorption performance than AC_0 in spite of their lower S_{BET}. The increased capacity may result from changing chemical properties and acidic surface functional groups were thought to play a dominant role.

AC_2 was prepared by the replacement of H$^+$ by Na$^+$ on AC_1. However, the difference in AC_2 suggested that the release of H$^+$ may be detrimental. The result of surface pH tests (pH$_{AC_0}$ 7.1, pH$_{AC_0}$ 4.2, pH$_{AC_0}$ 8.7) showed a difference from H$^+$ that had been released into the aqueous solution. Obviously, AC_1 released more H$^+$ than AC_2.

The data in Table 3 show differences in the elemental analysis results. For AC_1, the total numbers for oxygen, hydrogen, and nitrogen are much higher. The change in the elemental ratio of $w(O)$ to $w(C)$, $w(H)$ to $w(C)$ revealed that HNO_3 oxidation can increase the oxygen content of the AC surface, as well as the H content. This agreed well with the results of the Boehm titration, in which carboxylic and hydroxyl acid groups increased

during HNO_3 oxidation. Compared with AC_1, the $w(H)/w(C)$ ratio of AC_2 decreased significantly and almost with the same with AC_0. This result indicates that on carbon surfaces, H$^+$ can be replaced by Na$^+$; and carboxylic/sodium carboxylate complex groups were developed.

The result of the Boehm titration indicated that the total amount of oxygen acidic groups on AC_2 and AC_1 were almost the same, but they exhibited different adsorption capacities and rates. When activated carbon was treated with HNO_3, oxygen acid groups –COOH, –OH, –COOR were produced at first, then further reacted with H$^+$ to form positive hydronium ions such as –COOH$_2^+$, OH$_2^+$, =C=OH$^+$. When AC_1 was further treated by NaOH, H$^+$ of carbon surface acidic groups can be replaced by Na$^+$, which then causes surface acidity to decrease. The reason for the different performance of AC_2 and AC_1 was mainly due to the surface acidity change. The prepared AC_2 exhibited slight higher adsorption capacity and a significantly faster rate than AC_1. Therefore, controlling the pH of the solution to favor the adsorption region of metal ions is crucial. When H$^+$ is replaced by Na$^+$, adsorptions of $HCrO_4$ and CrO_4^{2-} may be as follows:

$$AC-ONa_2^+ + HCrO_4 \rightleftharpoons AC-ONaHCrO_4^- + Na^+ \qquad (5)$$

$$AC-ONa_2^+ + CrO_4^{2-} \rightleftharpoons AC-ONaCrO_4^{2-} + Na^+ \qquad (6)$$

The main cause of the higher Cr(VI) adsorption capacity and rate for AC_2 can be attributed to more oxygen surface acidic groups, and suitable solution pH provided by surface groups. HNO_3–NaOH modification showed potential for the preparation of high quality AC for the effective removal of low concentrations of Cr(VI).

4. Conclusion

For low concentrations of Cr(VI) in wastewater under normal conditions (not under strongly acidic conditions, pH < 1), Cr(VI) removal occurs only through an ion exchange mechanism. Surface pH of AC is crucial in terms of Cr(VI) adsorption capacity and rate. HNO_3–NaOH modification can enhance the Cr(VI) adsorption capacity onto AC significantly. HNO_3 oxidization produced positive acidic groups, subsequent NaOH/NaCl treatment replaced the H$^+$ of acidic groups by Na$^+$ and the acidity of

AC decreased. The main cause for the higher Cr(VI) adsorption capacity and rate for AC_2 was that there were more oxygen surface acidic groups, and suitable surface acidity. HNO_3–NaOH modification shows potential for the preparation of high quality AC for the effective removal of low concentrations of Cr(VI).

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