

# Study on activated carbon in chromium-containing wastewater treatment by XPS

Yang Jun, Wang Yunxiu

Shandong University of Technology, Jinan 250014, China

Zhang Yinsheng

Shandong Non-Metallic Material Research Institute, Jinan 250014, China

**Abstract**— The mechanism of activated carbon treatment with chromium-containing wastewater by X-ray photoelectron spectroscopy (XPS) and that of adsorption and reduction reaction of the activated carbon with hexavalent chromium solution are presented in this paper. The XPS results show that at  $\text{pH} < 1$ , the activated carbon does not adsorb any chromium ion, and the main reaction is reduction process of  $\text{Cr(VI)}$ ; at  $1 < \text{pH} < 6$ , both reduction process of  $\text{Cr(VI)}$  and adsorption process of  $\text{Cr(VI)}$  and  $\text{Cr(III)}$  occur on the carbon surface; at  $\text{pH} > 6$ , the main process is adsorption of the carbon to  $\text{Cr(VI)}$ . The optimum range of treatment is at  $\text{pH}$  3–6, in which removal efficiency of adsorption and reduction is relatively high. It demonstrates that the reduction mechanism is a heterogeneous acid catalysis process.

**Keywords:** wastewater treatment; X-ray photoelectron spectrometry; activated carbon.

## 1 Introduction

The electroplating wastewater is one of the main pollution resources. Its treatment by activated carbon has been considered as a prospective method from economical and technical points of view. The activated carbon method is an advanced process which can remove certain organic and inorganic compounds by virtue of its adsorption characteristics of large specific surface and rich pore structure. Beginning in the 1960s, the method was extensively applied to environmental protection and used in treatment of chromium-containing wastewater in China in the 1970s (Cheng, 1983). But the reaction mechanism studied by XPS has not ever been reviewed. The results in this paper are only our preliminary study on the carbon with XPS due to the complication of the activated carbon.

## 2 Experiment

### 2.1 Apparatus

Perkin-Elmer PHI 5300 ESCA system. X-ray source: Mg K $\alpha$  (energy 1253.6 eV), power 300W, 15kV. Pass energy 17.90 eV for narrow spectra.

### 2.2 Preparation of test samples

#### 2.2.1 Standard samples

Graphite (C. P.), Cr sheet (99.99%), Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (A. R.).

K<sub>2</sub>CrO<sub>7</sub> (primary standard), K<sub>2</sub>CrO<sub>4</sub> (A. R.).

#### 2.2.2 ZJ-15 granular activated carbon (Xinhua Chemical Factory, China).

#### 2.2.3 Samples of ZJ-15 activated carbon (AC) after the reaction with various pH scales of Cr(VI) solution.

Make a series of Cr(VI) solution of 50.00 ml with different pH scales: 0.34, 0.76, 1.63, 2.71, 3.48, 4.30, 5.76, 6.44, 7.85 and 11.93 in a 250 ml cone bottle. 2.00g AC is added to each bottle. The bottles are shaken for 4 hours, then go on with filtering and washing. Finally, the Cr(VI) content and total chromium of filtered liquid are determined with ferrous sulfate titration. The separated AC are put in an electric vacuum drying oven for 10 hours, and then grind it into powder.

### 2.3 Procedures

2.3.1 To locate the AC power on the double-side adhesive plaster and carry out survey scanning and narrow scanning on the samples at 20 °C, and to get the XPS spectra.

2.3.2 To calibrate binding energy (BE) of C<sub>1s</sub> in ZJ-15 activated carbon and the BE of Cr2p in standard samples by the method of gold precipitation amount calibration curve (Huang, 1986).

2.3.2 To calibrate the BE of Cr2p adsorbed on the AC surface with the BE of C<sub>1s</sub> of the AC as inner standard.

## 3 Results and discussions

### 3.1 The elements and structures on the AC surface

#### 3.1.1 The determination of elements.

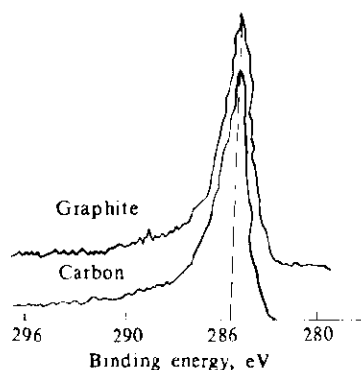
In order to collect the complete information, we carry out the survey scanning on the carbon samples with the maximum pass energy of 178.95 eV. The content of various elements is shown in Table 1.

**Table 1** Atomic concentration of various elements in the activated carbon

Elements	C	O	S	Si	Al	N	Cl
Atomic conc., %	83.5	13.1	1.2	1.2	0.6	0.3	0.1

### 3.1.2 Kind of structures

From the XPS spectra of  $C_{1s}$  (Fig. 1) of the AC and graphite the  $C_{1s}$  spectrum of the AC exists obviously trailing in high binding energy, which is similar to the  $C_{1s}$  spectrum of graphite. The  $C_{1s}$  BE (284.5 eV) of the AC is just equal to that of graphite, but the  $C_{1s}$  BE of other nongraphite polymers is generally within 285.0–285.5 eV, which changes with chemical environment around carbon atom. The XPS spectra of the AC, therefore, further prove that the activated carbon is analogous to graphite structure.

Fig. 1  $C_{1s}$  spectra of AC and graphite

### 3.2 The $Cr_{2p}$ XPS spectra and BE in standard samples

Fig. 2 shows the  $Cr_{2p}$  spectra and Table 2 demonstrates  $Cr_{2p}$  BE (eV) in related standard samples. The BE difference between  $Cr(VI)$  and  $Cr(III)$  is 2.0 eV, and that of  $Cr(VI)$ ,  $Cr(0)$  is about 5.0 eV. Therefore, the valence of chromium adsorbed on the carbon can be distinguished with chemical shift. There are some differences in BE between the adsorbed chromium on the carbon surface and the chromium ion of standard samples, but the mechanism of various valence chromium is primarily similar.

**Table 2**  $Cr_{2p}$  BE (eV) in related standard samples

Sample	$K_2Cr_2O_7$	$K_2CrO_4$	$Cr_2(SO_4)_3$	Cr sheet
Valence	Cr(VI)	Cr(VI)	Cr(III)	Cr(0)
$Cr_{2p}$ BE, eV	579.3	579.2	577.1	574.3

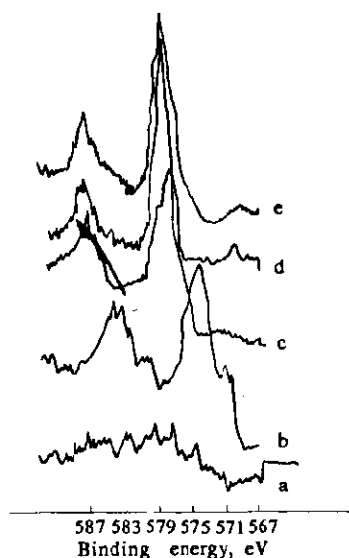


Fig. 2 Cr2p spectra from standard samples

a. unadsorbed AC; b. Cr sheet;  
c.  $\text{Cr}_2(\text{SO}_4)_3$ ; d.  $\text{K}_2\text{CrO}_4$ ; e.  $\text{K}_2\text{Cr}_2\text{O}_7$

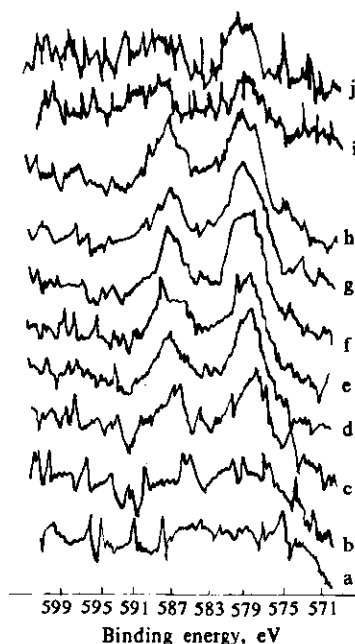


Fig. 3 Cr2p spectra on the AC surface under various pH

a. 0.34; b. 0.76; c. 1.63; d. 2.71; e. 3.48;  
f. 4.30; g. 5.67; h. 6.44; i. 7.85; j. 11.93

### 3.3 The analyse of chromium ions on the AC surface

#### 3.3.1 The relation between chromium content and pH scale of solution

The XPS spectra of adsorbed Cr2p on the AC which reacts with Cr(VI) solution of different pH scales are demonstrated in Fig. 3. The adsorbed Cr/C atomic concentration ratio on the carbon surface is shown in Table 3. According to Table 3,

**Table 3** The Cr2p/ $\text{C}_{1s}$  atomic concentration ratio on the activated carbon surface

No.	a	b	c	d	e	f	g	h	i	j
pH	0.34	0.76	1.63	2.71	3.48	4.30	5.67	6.44	7.85	11.93
(Cr/C) $\times 10^8$	0.0	0.0	0.3	0.4	1.2	2.0	1.0	0.8	0.0	0.0

at  $\text{pH} < 1$ , the AC adsorbs neither Cr (VI) nor Cr(III); at  $\text{pH} 3-6$ , the carbon surface adsorbs a great deal of chromium ion and the adsorbed amount achieves maximum at  $\text{pH} 4.30$ ; at  $\text{pH} > 6$ , the adsorbed amount of chromium ions decreases; at

pH 7.85 or 11.93, the carbon adsorbs neither Cr(VI) nor Cr (III).

### 3.3.2 Valence analysis of chromium ions

There exists a 2eV "platform" between 577 eV and 579 eV at the Cr2p spectrum peak (at pH 3.48 and 4.30) in Fig. 3. As the BE value reflects the chemical surroundings around an element and the changing of the element valent situation, it is obvious that this "platform" is caused by overlapping of Cr2p peak of different valent chromium ions. In order to compare the different valences of chromium ion on the carbon surface, we carry out the curve which fits those XPS spectra. According to the BE of Cr2p in the standard samples, we consider the chromium ions with over BE 578.0 eV as the poisonous high-valent chromium ions, those with below BE 578.0 eV as non-poisonous low-valent chromium ions. According to the simulating results, the atomic concentration percentage of the high-valent and low-valent chromium ions on the AC for the different pH scale solution are obtained (Table 4). Although the above-mentioned classification method is not quite appropriate, it can preliminarily reflect relative contents of different valent chromium ions on the carbon surface.

**Table 4 The relative contents of different valent chromium ions on the carbon surface**

pH	2.71	3.48	4.30	5.67
Cr, high-valence, %	38.6	18.4	52.3	72.9
Cr, low-valence, %	61.4	81.6	47.7	27.1

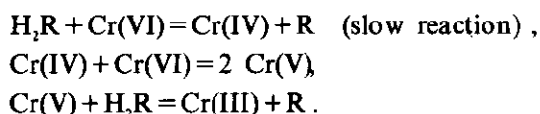
By analysis on the XPS spectra (Fig. 3), at pH 0.34 and 0.76, the AC does not adsorb chromium ions, at pH 1.63, the adsorbed chromium ion on the carbon is mainly Cr(III), at pH 2.71, the amount of adsorbed Cr(III) decreases, while Cr(VI) increases; at pH 2.71–5.67, there are different valent chromium ions on the carbon surface; at pH 3.48, the content of low-valent chromium ions is maximum, then the low-valent chromium ions decrease as pH is increasing; at pH > 6, the adsorbed chromium ions are mainly high-valent chromium ions.

### 3.3.3 The discussion of reaction mechanism of the activated carbon with hexavalent chromium ion solution

From the analyses of XPS and chromium ion valences, we know that at pH < 1, the activated carbon does not adsorb Cr (VI) or Cr(III) and this process may mainly includes the reduction of Cr(VI). At pH > 6, the process is mainly adsorption of Cr (VI) on the activated carbon. Within pH 1–6, the processes are both adsorption and reduction. The adsorption reduction ability of activated carbon is strongest at pH 3–6. At pH > 6, the amount of adsorbed Cr(VI) decreases. At pH 7.85 and 11.93,

the carbon does not adsorb any chromium ion.

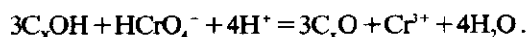
The XPS results almost coincide with the chemical analysis. The results of XPS analysis show that the carbon does not adsorb Cr(VI) or Cr(III). That reduction of Cr(VI) only occurs on the external surface of carbon may explain the results. This explanation is identical with the Huang's one (Huang, 1978). If the reduction occurs on the internal surface, then Cr(VI) and Cr(III) would be detected by XPS. Therefore, the reduction reaction carries out on the external carbon surface in high acidity. The reduced low-valent chromium ions are unstable, and they can complex with the groups of the carbon body and produce more stable chromium complex ions. The low-valent chromium ions are probably Cr(V), Cr(IV), Cr(III) and Cr(II). The possible reaction processes of  $\text{Cr}_2\text{O}_7^{2-}$  with organic compounds ( $\text{H}_2\text{R}$ ) may be as follows (Cotton, 1972):



The changing trend of the high-valent chromium ions adsorbed on the carbon surface varies with increasing pH values of wastewater solution, which may be explained as follows: at pH 2.71, the adsorbed content of low-valent chromium ions on the carbon surface is still little. At pH 3.48, the strong hydrolysis adsorption would occur for the low-valent chromium ions (Hassler, 1974), and it would bring about the competitive adsorption of high-valent with low-valent chromium ions on the carbon surface. As the hydrolysis adsorption is stronger than the electrostatic adsorption, the adsorbed content of low-valent chromium ions is more than that of high-valent ones. At pH 4.30–5.67, the reduction is very weak and the adsorbed content of low-valent chromium ions decreases, while that of high-valent ones increases gradually. These results show that the processes of reduction and adsorption of activated carbon change with the pH scales of wastewater solution.

### 3.3.4 The discussion on reduction process mechanism

Combining with the results of kinetic experiments of reduction of the activated carbon with hexavalent chromium at  $\text{pH} < 1$ , we hold that the reduction process is a heterogeneous acid catalysis and its mechanism can be discussed as follows (Yang, 1989): a. Oxygen-containing groups hydrolyses on carbon surface; b. Chromium anions such as  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ , diffuse oriently only on carbon surface membrane; c. Chromium anions carry out chemical complex adsorption with the oxygen-containing groups on the carbon surface; d. Its acid catalysis reduction occurs as follows:



e. Reduced products desorb from carbon surface. The activated carbon does not adsorb Cr(III) component in high acidity. As pH increases, Cr(III) component is adsorbed in hydrolysis form; f. Reduced low-valent products transmit from carbon surface to bulk phase.

## 4 Conclusion

The XPS analysis shows that the relations of adsorption and reduction processes of the activated carbon with the hexavalent chromium-containing solution along with the change of pH value are as follows: at  $\text{pH} < 1$ , only the reduction process of Cr(VI) goes on the external carbon surface; at  $\text{pH} > 6$ , only the adsorption process of Cr(VI) goes on the carbon surface; at  $1 < \text{pH} < 6$ , both the adsorption and reduction processes occur simultaneously on the carbon surface.

The results of XPS analysis demonstrate that the optimum pH ranges of chromium-containing wastewater treatment by the activated carbon is at pH 3–6.

The adsorption of the activated carbon for tri-valent chromium ion is hydrolysis adsorption in high acidity. It is possible that there are products of Cr(II), Cr(IV) and Cr(V) which exist in complex forms.

The mechanism of reduction process is probably a heterogeneous acid catalysis.

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(Received September 21, 1992)