

Intensification of adsorption process by using the pyrolytic char from waste tires to remove chromium(VI) from wastewater

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Abstract: Pyrolysis has the potential of transforming waste into valuable recyclable products. Pyrolytic char (PC) is one of the most important products from the pyrolysis of used tires. One of the most significant applications for pyrolytic char recovered is used for the removal of Cr(VI) in the wastewater effluent to control waste by waste. The surface chemistry properties of surface element distribution / concentration and chemical structure were examined for the pyrolytic char and the commercial activated carbon (CAC) respectively. The results showed that surfaces of PC possesses a large amount of ester and hydrocarbon graft, whereas there are mainly carbon functional components of C—OH, C=O and COOH on the surface of CAC. Therefore the surface electronegativity of PC is lower than that of CAC in the water. The repulsive interactions between the surfaces of PC and the negatively charged Cr(VI) ion are weaker than that of CAC, which results in an intensification of the adsorption process by the utilization of PC. The adsorption isotherms of Cr(VI) ion on the two kinds of carbons were determined experimentally. The larger adsorption amount on the PC in the case of Cr(VI) may be attributed mainly to its special surface micro-chemical environment. The mechanism of the removal Cr(VI) from aqueous solution was assumed to be the integration of adsorption and redox reaction. The adsorption was the rate-controlled step for Cr(VI) removal. The adsorption of Cr(VI) was identified as pseudo-second-order kinetics. The rate constants of adsorption were evaluated.

Keywords: waste tire; pyrolytic char; surface chemistry properties; Cr(VI); wastewater treatment; kinetics; intensification

Introduction

Waste tires cannot degrade in a short term, they will bring accidental fire and emit poisonous gases with rich dioxins. How to recycle and utilize them effectively, and prevent secondly pollution to environment has become a new tissue that the reuse of resources faces with.

W. Kaminsky *et al.* (Kaminsky, 1992) found that the solid residues are the mixture of carbon black and char forming by degradation of tire rubber. The economic feasibility of pyrolysis of waste tires depends on the value of solid residues in great extent according to A. A. Merchant *et al.* (Merchant, 1993).

Chromium in the polluted stream is mainly generated from electroplating, dyeing, leather, photo material and pigment etc. Generally, Cr(VI) is more poisonous than Cr(III). Cr(VI) is strong oxidant and has acute causticity to skin and mucous coat (Liu, 1993) and it is easy to dissolve in water. One of the most significant applications for pyrolytic char recovered is used for the removal of Cr(VI) in the wastewater effluent to control waste by waste.

Diksha Aggarwal *et al.* (Aggarwal, 1999) had studied adsorption of Cr(VI) and Cr(III) by different activated carbons from aqueous solution. Nadhem K. Hamadi *et al.* (Hamadi, 2001) had studied adsorption kinetics for the removal of Cr(VI) from aqueous solution by activated carbons derived from used tires and sawdust. But they all had not explained the process mechanism of removing Cr(VI) from aqueous solution with the properties of the carbons as adsorbents. Christian Roy *et al.* (Darmstadt, 1994; 1995; 1997; 2000) had used many different methods such as ESCA, SIMS, Auger-spectroscopy, XRD and IGC to characterize the pyrolytic char in comparison to commercial

carbon blacks used in the tire fabrication. They had not found the potential application of the pyrolytic char in removing Cr(VI) from aqueous solution.

In our research, X-ray photoelectron spectroscopy (XPS) was used to studied surface chemical state information of PC in comparison to CAC. Furthermore, in order to examine the effect of the nature of the carbon surface on the adsorption and reaction of Cr(VI) ion, the adsorption isotherms of Cr(VI) ion on the two kinds of carbons were determined experimentally. We also studied the mechanism of the adsorption, identified the adsorption kinetics, and calculated the rate constants of adsorption.

1 Experiment

1.1 Materials preparation

The CHAOYANG brand 650-16 tire tread was provided by Hangzhou Zhongce Rubber Co., Ltd. About 100 g tire shreds (10 cm × 10 cm × 10 cm) were set in a quartz tube reactor. The reactor was heated by a tubular furnace in N₂ atmosphere from room temperature to 550°C at a constant heating rate of 5°C/min. When the reactor was cooled down to ~250°C, hot air was blown into the reactor in order to remove unpleasant odor and trace oils on the surface of PC for about 10 min. The solid residue was collected and ground. Pyrolytic char was prepared.

Commercial activated carbon was analytically pure wood based powered activated carbon produced by Shanghai Activated Carbon Co., Ltd.

1.2 Characterization

The Brunauer-Emmett-Teller (BET) surface areas S_{BET} of PC and CAC were determined by N₂ adsorption and desorption isotherms measured at 77 K using an automatic

adsorption apparatus (Metermetric APAC 2100). The diameters of the PC and CAC particles were measured using the laser diffraction sizing technique (Malvern Particle Sizer 2600 Series). XPS (ESCALAB MK II X-ray spectrometer) was employed to obtain the element composition and the binding properties of atoms on the surface of the two kinds of carbons from 1 to 10 atom layers. The system pressure was normally maintained below 2×10^{-9} mbar. The XPS was equipped with an AlK α (1.486 keV) radiation source. The binding energy was ranged from 0 to 1050 eV.

1.3 Liquid-phase adsorption

An amount of 500 ml Cr(VI) solution of known concentration was added into 500 ml conical flask. The pH = 2 was adjusted either with 0.1 mol/L HCl or 0.1 mol/L NaOH. After the flask had been placed in a thermostat water bath at a constant temperature of 25°C for 30 min, about 1.0 g carbons were added into the flask and agitated with a shaking mechanism at a fixed agitation speed. The removal kinetics of the Cr(VI) was investigated by sampling mixture (5 ml) at the desired interval time. A spectrophotometer was employed at a wavelength of 540 nm with 1, 5-diphenyl carbazide reagent to determine the remaining concentration of Cr(VI) of the filtrate of each sample. The solution pH values of the initial and final solutions were measured by an acidimeter. And the following formula was used to calculate adsorption amount of Cr(VI) on the carbon materials:

q(t) = V · ΔC/1000 m. (1)

Where q is the adsorption amount (mg/g); V is the total volume of solution (ml); ΔC is the concentration variation (μg/ml) of Cr(VI) after adsorption time t; m is the total mass of the carbon (g). Furthermore, q can be expressed simply as below according to experimental condition:

q(t) = ΔC/2. (2)

2 Results and discussion

2.1 Physical properties

The Brunauer-Emmett-Teller (BET) surface areas S_{BET} of PC and CAC are 69.23 m²/g and 1355.86 m²/g respectively. The average particle diameters of PC and CAC are 1.62 μm and 0.25 μm.

2.2 Surface chemistry properties

2.2.1 Surface analysis

Fig.1 and Fig.2 are XPS wide scan spectra of PC and CAC respectively. The XPS survey spectra of PC shows lines of C, O, S and Zn. The binding energy of the S on the surface is 162.3 eV, which means S existed as S²⁻, namely ZnS. The XPS survey spectra of the commercial activated carbon shows lines of C, O, and S, the binding energy of the S on the surface is 169.4 eV, which means S exists as sulphates. The surface elemental composition of the PC and CAC is presented in Table 1.

Table 1 Surface elemental composition of PC and CAC

Carbon	Surface composition, atom %			
	C	O	Zn	S
PC	89.59	3.21	4.25	2.95
CAC	84.90	14.86	-	0.24

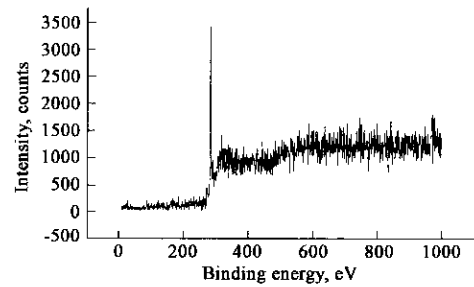


Fig.1 XPS wide scan spectra of PC

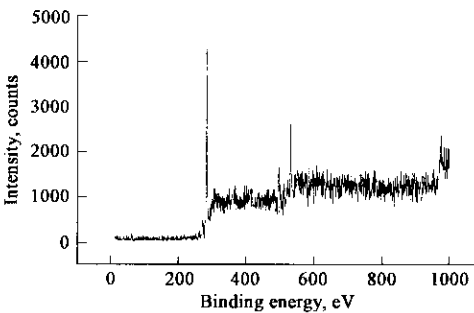


Fig.2 XPS wide scan spectra of CAC

The comparison of results in Table 1 shows that the surface elemental composition of C on PC is high. It is likely that surface of PC possesses a large amount of hydrocarbon graft.

2.2.2 C_{1s} region

The binding energy of the C_{1s} peak of the carbon on the standard silver sample surface was about 284.6 eV. All binding energies were referred to the C_{1s} peak for sample charging. The fitted curves of C_{1s} region of the PC and CAC are shown in Fig.3 and Fig.4 respectively. It was found that the two kinds of carbons could be fitted to different four line shapes. These different binding energy peaks are assigned to C—C or C—H at 284.6 eV (Carmstadt, 1994), C—OH at 286.1 eV (Liu, 1988), C—OEt at 286.6 eV (Liu, 1988), C=O at 287.6 eV (Carmstadt, 1994), COOEt at 288.9 eV (Liu, 1988), COOH at 289.6 eV and plasmon at 291.2 eV (Liu, 1988). The position, assignments and area of C_{1s} peaks of two kinds of carbons are presented in Table 2.

The results showed that surfaces of PC possesses a large amount of ester and hydrocarbon graft, whereas there are

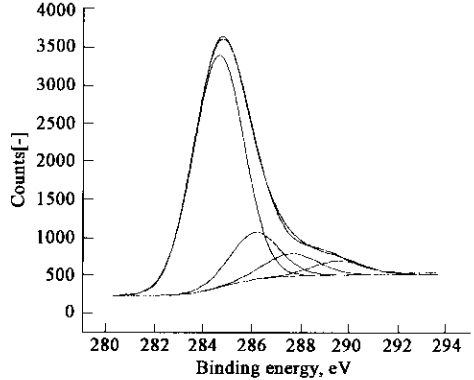


Fig.3 XPS spectra of CAC, C_{1s} region

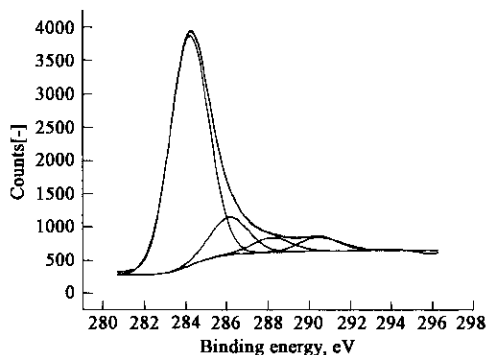


Fig.4 XPS spectra of PC, C_{1s} region

mainly carbon functional components of C—OH, C=O and COOH on the surface of CAC. The C—OH and COOH components are acidic surface groups, and they can ionize in water and produce H⁺ ions. Therefore the surface electronegativity of PC is lower than the surface of CAC in the water. In order to examine the effect of the nature of the carbon surface on the adsorption and reaction of Cr(VI) ion, the adsorption isotherms of Cr(VI) ion on the two kinds of carbons were determined experimentally.

Table 2 Position, assignments and area of C_{1s} peaks of PC and CAC

Binding energy, eV	Assignment	PC, %	CAC, %
284.6	C—C, C—H	77.6	71.9
286.1	C—OH	—	19.2
286.6	C—OEt	12.7	—
287.6	C=O	—	3.4
288.9	COOEt	5.0	—
289.6	COOH	—	5.5
291.2	Plasmon	4.5	—

2.3 Application in removing Cr(VI) from wastewater

2.3.1 Isothermal adsorption

The removal of Cr(VI) by adsorption on PC has been shown to increase with time and attains a maximum value at about 120 min, and thereafter, it remains almost constant. On changing the initial concentration of Cr(VI) solution from 50 to 100 ppm, the amount adsorbed increases from 25.00 mg/g to 48.25 mg/g at 25 °C, pH = 2 for PC(Fig.5). While for CAC, the amount adsorbed increases from 24.9 mg/g to 44.12 mg/g(Fig.6).

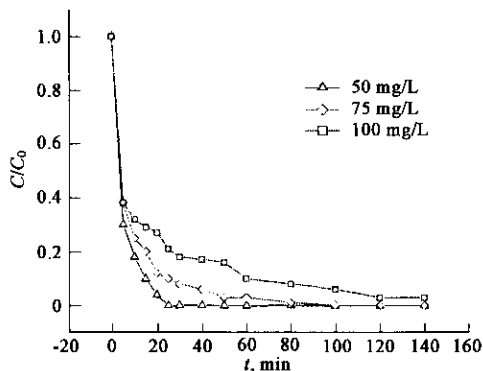


Fig.5 Time variation of Cr(VI) adsorption on PC at different initial concentrations

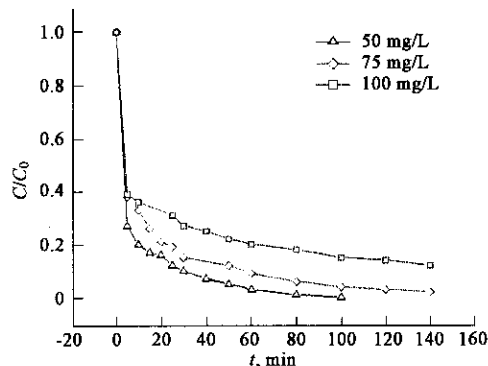


Fig.6 Time variation of Cr(VI) adsorption on CAC at different initial concentrations

on PC is higher than that on CAC. The removing rate of Cr(VI) for the PC was 99%, and the removing rate of Cr(VI) for the CAC was 88%. The final solution pH values were 2.92 and 2.80 respectively.

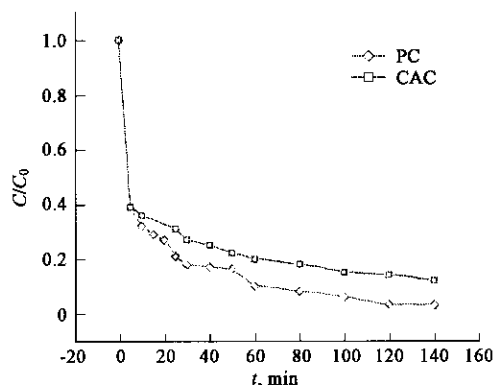
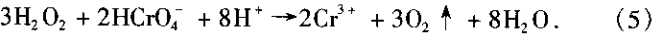
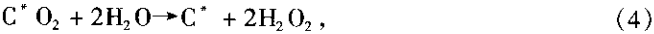


Fig.7 Comparison of time variation of Cr(VI) adsorption on PC and CAC at initial concentration 100 mg/L

Benefield *et al.* (Benefield, 1982) indicated that exists in different forms in aqueous solution and stability of these forms is dependent on the pH of the system and out of various forms of Cr(VI), HCrO₄⁻ form is the predominant species in aqueous solution within the low pH range. The mechanism of the removal Cr(VI) from aqueous solution was assumed to be the integration of adsorption and redox reaction. In general, the removal contaminants from aqueous solution by porous adsorbents included the film diffusion from the liquid phase to the particle outer surface and the intraparticle diffusion (Stephen, 1988). The redox reaction of Cr(VI) on the inner surface was considered to occur rapidly so that the adsorption was the rate-controlled step for Cr(VI) removal. The XPS results deduced that the surface electronegativity of PC is lower than that of CAC in the water. So the repulsive interactions between the surfaces of PC and the negatively charged Cr(VI) ion are weaker than that of CAC, which results in an intensification of the adsorption process by the utilization of PC. Therefore, we think that the larger adsorption amount on the PC in the case of Cr(VI) may be attributed mainly to its special surface micro-chemical environment. The surface properties of PC play a very important role in adsorbing Cr(VI) from wastewater.

From Fig. 7, we can see the adsorbed amount of Cr(VI)

And Cr(VI) ion was may reduced to Cr(III) according to the following reactions:



Where C* is the active site on the surface of the two kinds of carbons, C*O2 is the active site occupied by the oxygen.

The process was accompanied by the acid consumption. That can be confirmed by the final solution pH values.

2.3.2 Adsorption kinetics modeling

The models of adsorption kinetics correlate the solute uptake rate, so these models are important in water treatment process design.

A pseudo-second-order model (Ho, 1998; 1999) may be also described the kinetics of adsorption. The differential equation for this reaction is

dq/dt = k2(qe - q)2. (6)

Integrating Eq.(6) for the boundary conditions t = 0 to > 0 and q = 0 to > 0 and then rearranged to obtain the linear form which is shown as follows:

t/q = 1/(k2qe2) + 1/qe t, (7)
h = k2qe2. (8)

In these equations, h is the initial adsorption rate (mg/(g·min)). The kinetics plots for Eq.(7) were made for PC and CAC at different initial concentration. This plot is shown in Fig.8. Good fits were observed indicating that adsorption reaction can be approximated with the second-order kinetics model. The constant K2 is calculated and represented in Table 3. It can be observed that h (the initial adsorption rate, mg/(g·min)) is generally higher for PC than that of CAC.

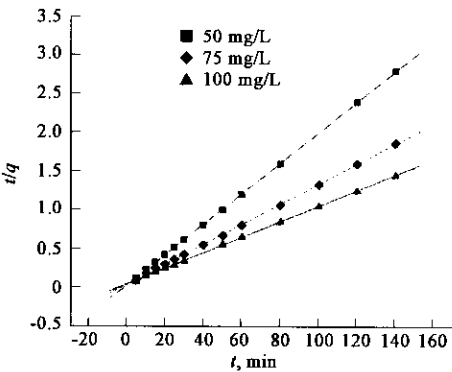


Fig.8 Second-order reaction kinetics plot for adsorption of Cr(VI) on PC at different initial concentrations

Table 3 The second-order reaction rate constants for the PC and CAC at different initial concentrations

Adsorbent	C0, μg/ml	K2, g/(mg·min)	h, mg/(g·min)	r2
PC	50	0.01603	41.08	0.99976
	75	0.00362	21.57	0.99993
	100	0.00146	14.94	0.99828
CAC	50	0.00544	14.36	0.99937
	75	0.00237	13.65	0.99940
	100	0.00170	14.02	0.99781

3 Conclusions

The integration of adsorption and redox reaction was proposed as the mechanism of the removal of Cr(VI) from aqueous solution by the PC and CAC. The adsorption was the rate-controlled step for Cr(VI) removal. And Cr(VI) ion was may reduced to Cr(III) rapidly according to the reactions of C* + O2 → C*O2, C*O2 + 2H2O → C* + H2O2, 3H2O2 + 2HCrO4- + 8H+ → 2Cr3+ + 3O2 ↑ + 8H2O. The adsorption of Cr(VI) has been identified as pseudo-second-order kinetics. The rate constants of adsorption have been evaluated.

Surface of PC has large amount of ester and hydrocarbon graft, whereas C—OH, C=O and COOH are the major carbon functional components on the surface of CAC. The surface electronegativity of PC is lower than that of CAC in the water. The repulsive interactions between the surfaces of PC and the negatively charged Cr(VI) ion are weaker than that of CAC, which results in an intensification of the adsorption process by the utilization of PC.

PC shows larger adsorption capacity of Cr(VI) than CAC. The larger adsorption amount on the PC in the case of Cr(VI) may be attributed mainly to its special surface micro-chemical environment. The surface properties of PC play a very important role in adsorbing Cr(VI) from wastewater.

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