Title:

Enhancement of Cr(VI) removal by modifying activated carbon developed from *Zizania caduciflora* with tartaric acid during phosphoric acid activation

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Abstract

Tartaric acid (TA) was employed to modify *Zizania caduciflora* (ZC)-based activated carbon during phosphoric acid activation for improving its Cr(VI) removal from aqueous solutions. The original activated carbon (AC) and TA-modified activated carbon (AC-TA) were characterized by N_2 adsorption/desorption, Boehm's titration and X-ray photoelectron spectroscopy (XPS) analysis. The Cr(VI) removal abilities of AC and AC-TA were evaluated by batch sorption experiments. The residual Cr(VI) and total Cr concentration were determined to investigated the "Sorption-coupled reduction" mechanism. Equilibrium data for the Cr(VI) removal on AC and AC-TA were well described by the Freundlich model. The AC-TA exhibited much higher Cr(VI) and total Cr sorption capacities than AC. After blocking of carboxyl and hydroxyl functional groups, the carbons showed obviously higher Cr(VI) and total Cr removal than the original AC and AC-TA, indicating that electrostatic attraction played an important role on Cr(VI) removal. The higher Cr(VI) removal on AC-TA was attributed to its higher amount of oxygen-containing functional groups, which provided more electrons for Cr(VI) reduction and more positive sites for the produced Cr(III) sorption.

Keywords: *Zizania caduciflora*; Tartaric acid; Activated carbon; Cr(VI)

1. Introduction

It is well known that chromium (Cr) is carcinogenic and mutagenic to living organisms. Cr in wastewaters and in the aquatic environment mainly exists in two stable oxidation states (hexavalent chromium Cr(VI) and trivalent chromium Cr(III)). Since it is much more mobile, water soluble and bioavailable, Cr(VI) is about 300 times more toxic than Cr(III) [1]. Cr(VI) compounds have been considered as a priority pollutant and classified as class A human carcinogens by the US Environmental Protection Agency (USEPA) [2, 3]. In addition, the USEPA has set the maximum contaminant level for Cr(VI) in domestic water supplies to be 0.05 mg/L [4] [5]. Thus, in order to prevent the poisonous impact of Cr(VI) on ecosystem and public health, it is important the removal of Cr(VI) compounds from wastewater before discharging them into aquatic environments. Sorption onto activated carbon is the most versatile and widely used technology for treatment of Cr(VI) contaminated wastewater due to its low invest and cost, easy operation and insensitivity to toxic substances [6].

"Sorption-coupled reduction" mechanism is widely accepted as the true of Cr(VI) removal by carbon materials under acidic conditions: (1) the anionic Cr(VI) species can be adsorbed to the protonated active sites of the adsorbent mainly by electrostatic attraction; and (2) the Cr(VI) is then reduced to Cr(III) on the adsorbent, followed by sorption on the adsorbent or release into solution. In our previous work [7], removal of Cr(VI) by T. natans husk-based activated carbon at initial pH of 4.0 was studied and we found that more than 85% Cr adsorbed on the carbon's surface was present as

Cr(III). Villaescusa et al. [8] also reported the similar result that the ratio of Cr(III) and Cr(VI) adsorbed on yohimbe bark was 2.75/1 at initial pH of 3.0. These results indicated that the reduction of Cr(VI) and the following sorption of Cr(III) was the leading mechanism for Cr(VI) removal by carbonaceous materials. For reduction of Cr(VI) to Cr(III), both protons in solution and electrons supplied by adsorbent are required [9, 10]. It is well-demonstrated that carboxylic, carbonyl and hydroxyl groups can play a role as electron donors [11]. These groups also can efficiently adsorb Cr(III) ions by cation exchange, electrostatic attraction or surface complexation. Hence, induction of oxygen-containing groups can be an effective method to enhance the removal of Cr(VI).

Zizania caduciflora (ZC) is an annual hydrophyte that is planted widely in many Asian countries as an important and popular cash crop and widely used in constructed wetlands for wastewater treatment. A large number of ZC residues are generated every year. However, most of such biomass wastes is often abandoned or burned as firewood. Disposal of such solid wastes has become a difficult environmental problem. ZC has a developed caudex system, which may offer a good basis for the production of an effective activated carbon. A survey of literature showed that no work has been done so far on utilization of ZC as a low-cost material to prepare activated carbon.

Utilization of phosphoric acid as activating agent for preparation of activated carbons with well-developed porosity and excellent sorption ability towards heavy-metal ions from various hydrophyte residues has been well established in our previous works [12-14]. Since tartaric acid (TA) has multiple groups (two carboxyl and hydroxyl groups) that can easily bind on the adsorbent's surface, impregnating tartaric acid onto adsorbent (activated carbons and lignocellulose materials) was used to improve their sorption ability towards various metal ions [15-17]. However, thus far no relevant studies have been performed on modifying activated carbon with TA during the preparation process. At high temperature, phosphoric acid as a good catalyst could promote not only the hydrolysis of lignocelluloses, but also the etherification and esterification between ZC and TA. Thus, this modification method may enhance the oxygen content of the produced activated carbon.

The objective of this paper is to improve the Cr(VI) removal ability by modifying ZC-based activated carbon with TA during phosphoric acid activation. The Cr(VI) removal mechanisms on the carbons were investigated by bath Cr(VI) sorption studies and XPS analysis.

2. Materials and methods

2.1. Materials

Reagent-grade potassium dichromate ($K_2Cr_2O_7$) was used to prepare the stock metal solutions. Zizania caduciflora (ZC) was collected from Nansi Lake in Shandong Province (China). ZC was washed repeatedly with distilled water to remove the dust and soluble impurities, dried at 105 ^oC for 12 h and shattered to pieces. ZC with a particle size fraction of 0.45-1.0 mm was used as precursor for preparation of activated carbon.

2.2. Synthesis of activated carbons

ZC (10 g) was fully soaked in H_3PO_4 solution (40 wt.%) at a ratio of 0.2/10 (mol H_3PO_4/g ZC) and with different mount of TA (0-0.05 mol). After impregnation at room temperature for 10 h, the samples were heated up to the desired temperature of 450 °C and maintained for 1 h in a muffle furnace under oxygen-limited conditions. After cooling to room temperature, the carbonized materials were thoroughly washed with distilled water until the pH of washing liquid was steady. Finally, the carbons were filtered, dried at 105 ^{o}C for 10 h and sieved to 100-160 mesh with standard sieves (Model Φ200). The resulting activated carbons were named as AC-TA-X, where X is amount of TA added (0.01, 0.02, 0.03 and 0.05) for 10 ZC.

2.3. Characterization methods

The pore structure characteristics of the carbons were determined by N_2 adsorption/desorption at 77 K using a surface area analyzer (Quantachrome Corporation, USA). Surface elemental composition and chemical oxidation state of the carbons was quantified using an X-ray photoelectron spectrometer (XPS) (Perkin-Elmer PHI 550 ESCA/SAM) with Mg Kα irradiation source. All the spectra were calibrated by C 1s peak at 284.6 eV. Boehm's titration method [18] was used to quantify the amount of acidic functional groups on the carbons' surfaces.

2.4. Blocking of carboxyl and hydroxyl groups

The carboxyl and hydroxyl groups on the carbons were blocked by the methods described by Gardea-Torresdey et al. [19] and Chen and Yang [20]. About 0.5 of carbon was soaked in anhydrous CH_3OH (100 mL) with concentrated HCl (2 mL) or formaldehyde (100 mL) for 12 h. The resulted carbon was then filtered, repeatedly washed with deionized water to remove excess HCl and CH_3OH or formaldehyde, freeze dried and stored for subsequent use. The blocking reactions are as follows:

$$RCOOH + CH_3OH \xrightarrow{H^+} RCOOH_3 + H_2O \quad (1)$$

$$2R - OH + HCHO \longrightarrow (R - O)_2\,CH_2 + H_2O \quad (2)$$

2.5. Batch sorption experiments

Batch sorption experiments were performed by adding 40 mg carbon into 50 mL Cr(VI) solution to investigate the effect of initial Cr(VI) concentration and initial pH on the sorption. The samples were shaken at room temperature of 22±1 ^{o}C and 120 rmp for 48 h to ensure that sorption equilibrium was reached. Duplicate samples were prepared for all sorption experiments.

After equilibrium, the samples were filtered through a 0.45 µm membrane filter. The concentration of Cr(VI) was determined by a UV–vis spectrophotometer (UV-5100, Shanghai) at the wavelength of 540 nm, using 1,5-diphenylcarbazide as chromogenic reagent, H_2SO_4 and H_3PO_4 as buffering agent. The residual concentrations of total Cr were measured with an atomic absorption spectrophotometer (180-80, Hitachi, Japan). The trivalent chromium concentration was determined from the difference between total chromium and Cr(VI) concentrations.

The amounts of Cr ions adsorbed on the carbons, Q_e (mg/g), were calculated using the following equation: $Q_e = (C_0 - C_e)V/M$, where C_0 and C_e are the initial and equilibrium concentrations of the heavy metal ions in the aqueous solution (mg/L), respectively, V is the volume (L) of the solution, and M is the mass of adsorbent used (g).

3. Results and discussion

3.1. Sorption capacity

The sorption isotherm experiments were evaluated at the initial Cr(VI) concentration ranged from 10 to 50 mg/L. The pH values of the solutions were fixed at 5.00±0.02. The sorption data were fitted with the Langmuir model ($Q_e = Q_m K_L C_e/(1 + K_L C_e)$) and Freundlich model ($Q_e = K_F C_e^{1/n}$), where Q_m (mg/g) is the maximum sorption capacity, K_L (L/mg) represents the Langmuir constant, K_F ($mg^{1-1/n}$ $L^{1/n}$/g) is the Freundlich affinity coefficient, and n is the Freundlich linearity index.

Fig. 1 shows the sorption isotherms of Cr(VI) for the carbons. The isotherm constants calculated by using nonlinear regressive were presented in Table 1. The values of correlation coefficient (R^2) derived from Freundlich model were much more close to 1 than those obtained from Langmuir model, which indicated that the sorption of Cr(VI) on the carbons is simulated better by Freundlich model than by Langmuir model. The comparison of experimental points and fitted curves in Fig. 1 also demonstrated this result. The maximum Cr(VI) sorption capacity (Q_m) of the TA-modified carbons were much higher than that of AC, indicating that TA modification during H_3PO_4 activation enhanced the Cr(VI) removal of the produced carbons. The values of K_F calculated from the Freundlich model for the TA-modified carbons were much higher than that for AC, which suggested that the TA-modified carbons had a higher sorption affinity towards Cr(VI). For the TA-modified carbons, AC-TA-0.3 showed the highest Q_m. In the following parts of the paper, the TA-modified sample using the TA additive amount of 0.3 was employed as the TA-modified carbon (AC-TA) for further studies.

3.2. Removal of Cr(VI) as influenced by initial pH

The effect of pH on Cr(VI) removal was studied by adjusting initial pH from 2.0 to 11.0 with 0.1 M HCl or NaOH. In order to investigate the consumption of H^+ ions for Cr(VI) removal on the carbons at acidic condition, 40 mg of carbon sample was added into 50 mL solution with different pH in the present of or in the absence of Cr(VI). As shown in Fig. 2a, the equilibrium pH levels of the sorption samples were higher than that of control samples. This result suggested that the removal of Cr(VI) consumed a large amount of H^+ ions, indicating the occurrence of reduction of Cr(VI) to Cr(III). It also can be confirmed from the higher removal of Cr(VI) compared to that of total Cr (Fig. 2b). In general, the removal of Cr(VI) and total Cr by AC-TA was 20-30% higher than AC. The carbons showed higher Cr(VI) and total Cr removal at low pH of 2.0-3.0. The removal of Cr(VI) by the carbons was high (about 100%) at low initial pH (2.0-3.0), followed by a remarkable decrease between initial pH of 4.0 and 11.0. It is known that Cr(VI) exists in aqueous solution as anion ($[HCrO_4]^-$,

$[CrO_4]^{2-}$ or $[Cr_2O_7]^{2-}$). The extent of protonation/depotonation of the carbons' surfaces decreased/increased with increasing solution pH. Thus, the electrostatic attraction at low pH and the electrostatic repulsion at high pH between the carbons' surfaces and Cr(VI) anions would promoted and hindered the Cr(VI) removal, respectively. In additional, the redox potential of Cr(VI)/Cr(III) is much higher at low pH than that at high pH. Therefore, a part of Cr(VI) ions was reduced to Cr(III), as noted above. As a result, the carbons showed high removal of Cr(VI) at low pH due to the reduction of Cr(VI) and electrostatic attraction. It was also found from Fig. 2b that the removal for total Cr by the carbons increased when pH was increased from 2.0 to 3.0, followed by an obvious decrease as increasing pH. At low pH, a part of Cr(VI) was reduced to Cr(III). The produced Cr(III) ions could be released into aqueous solution by electrostatic repulsion between positively charged Cr(III) ions and protonated surfaces of the carbons or adsorbed by the carbon. The lower total Cr removal at pH of 2.0 compared to that at pH of 3.0 were mainly due to the competition of excess H^+ ions for sorption sites and the strong electrostatic repulsion between Cr(III) ions and positive charged carbon surface.

3.3. Physical and chemical properties of the carbons

The performance of carbons was strongly depended not only on the porosity but also on the chemistry of the surface. A well-developed pore structure would provide a good environment for adsorbate to transport to the internal pores and also could removal pollutants by pore-filling effect. The O-containing groups (ketone, carboxylic and hydroxyl groups) and unsaturated C=C bond are the Lewis base and could play a role as electron donors. For the Cr species, Cr(VI) could accept these electrons and reduce to Cr(III), and the produced Cr(III) could be bonded by these O-containing groups by formation of coordinate covalent bond.

The BET surface area (S_{BET}) and pore size distribution were determined by using the Brunauer-Emmett-Teller (BET) theory and Density Functional Theory (DFT) method. The micropore surface area (S_{mic}), external surface area (S_{ext}) and micropore volume (V_{mic}) were evaluated by the t-plot method. Total pore volume (V_{tot}) was determined from the amount of N_2 adsorbed at a P/P_0 around 0.95. Fig. 3 shows the N_2 adsorption isotherms for AC and AC-TA. The N_2 adsorption/desorption isotherms are classified as type IV according to the IUPAC classification, with a wider hysteresis loop at high relative pressures, indicating that both AC and AC-TA had a mixed microporous and mesoporous structure. It can be observed from Fig.3 that only slight difference in N_2 adsorption/desorption isotherms existed for AC and AC-TA samples. The porous structure parameters for the carbons were listed in Table 1. The ZC-derived activated carbon (AC) has a well-developed porosity with high S_{BET} (1270 m^2/g) and large V_{tot} (1.37 m^3/g). Only slightly decrease in the specific surface area and total pore volume was observed for the activated carbon after TA modification. The two carbons were mainly mesoporous with V_{mic}/V_{tot} of 22.6% for AC and 24.3% for AC-TA.

The results of Boehm's titrations were given in Table 3. AC-TA contained much higher acidic groups than AC, indicating TA-modification dramatically enhanced the surface acidity of the produced carbon, which is coincident with the XPS results (see later). The amounts of acidic groups on the carbons' surfaces were as follows: phenol > lactone > carboxyl.

3.4. XPS analysis

XPS analysis was used to evaluate the differences of AC and AC-TA in the surface elemental composition the chemical oxidation state. As illustrated in Fig. 4, the XPS survey spectra revealed the different content of carbon and oxygen on the carbons' surfaces. Table 3 also lists the carbon and oxygen atomic concentrations on the carbons' surface. The O/C ratio on the carbon's surface increased form 75% to 110% after TA modification, suggesting that the oxygen containing groups introduced onto AC-TA.

Fig. 5 shows the typical high-resolution and curve fitting of C 1s spectra of AC and AC-TA. The C1s spectra of the carbons have been deconvoluted into five components corresponding to: (peak I) graphitic carbon at 284.6 eV; (peak II) C–O bond in hydroxyl or ether groups at 286.0 eV; (peak III) C=O groups at 287.5 eV; (peak IV) carboxyl groups at 289.0 eV; and (peak V) π-π^* transitions in the aromatic system at 291.0 eV [21, 22]. According to the area-simulating curve, the percentage of each component was calculated and listed in Table 4.

Fig. 5 shows the high resolution C 1 s spectra of AC-TA before and after Cr(VI) sorption. It can be observed that the binding energies of C 1s for peaks 2-5 were increased slightly, suggesting the occurrence of chemical coordination between Cr ions and these surface functional groups. The area ratio of peak 1 (graphitic carbon) for AC-TA after Cr(VI) sorption decreased from 56.4% to 53.2% and area ratio of peak 1 (C-O groups) and peak 4 (carboxyl groups) increased slightly. These results indicated that some graphitic carbon was oxidized by hexavalent chromium. Similar phenomenon was also observed in previous works [7, 23]. The high resolution XPS spectrum of Cr(2p3/2) on the Cr(VI)-loaded AC-TA was shown in Fig. 6. The BEs at 577.3 eV and 578.9 eV were assigned to Cr(III) and Cr(VI). According to the XPS results about 85% adsorbed chromium predominantly existed in trivalent form (atomic ratio), indicating the sorption of the produced Cr(III) was the leading mechanism for Cr(VI) uptake to the carbons.

According to the differences of AC and AC-TA in physiochemical characteristics and Cr(VI) removal results (see Tables 1-3), a conclusion can be drawn that the higher Cr sorption capacity of AC-TA compared to AC was mainly due to its higher amount of oxygen-containing groups. Chromium sorption mainly depends on the availability of chromium ions in solution and on the occurrence of redox reactions between the surface groups and the Cr(VI) which lead to the formation of Cr(III). The more amount of oxygen-containing groups (such as carboxyl, hydroxyl and carbonyl groups) on the carbons' surfaces could provide more electron-donors for Cr(VI) reduction to Cr(III), and then adsorbed more Cr(III) ions by cation exchange, electrostatic attraction or surface complexation [24, 25].

3.4. Removal of Cr(VI) as influenced by blocking of carboxyl and hydroxyl groups

After blocking, the -COOH and R-OH groups were transformed to esters (-COOC-) and ethers (C-O-C). It has been proved that both -COOH and R-OH groups before and after blocking can act as electron-donor groups [10, 26]. Our previous studies have confirmed that these esters and ethers also could adsorb metal cations by chemical complexation [12, 27]. Thus, the different Cr removal between the original and blocked carbons was mainly caused by the change of carbons' surface charges. As shown in Fig. 6a, the removal of Cr(VI) and Cr_{total} by the blocked carbons was obviously enhanced. For these carbons, the removal of Cr(VI) and Cr_{total} is ordered as follows: hydroxyl groups-blocked carbon (AC-OH and AC-TA-OH) > carboxyl group-blocked carbon (AC-COOH and AC-TA-COOH) > original carbon (AC and AC-TA). The high resolution XPS spectra of Cr(2p3/2) on the Cr(VI)-loaded AC-TA, AC-TA-OH and AC-TA-COOH were shown in Fig. 6b, c and d. The ratio of Cr(III)/Cr_{total} on the carbons' surfaces followed an order of AC-TA-Cr (84.8%) > AC-TA-COOH (77.9%) > AC-TA-OH (76.5%). It is evident that blocking of -COOH or R-OH groups promoted the sorption of Cr(VI). After blocking, the dissociation of free -COOH and R-OH groups was restrained, resulting in the reduction of electrostatic repulsion between Cr(VI) anions and these dissociated groups. As a result, the surfaces of blocked carbons are more accessible for Cr(VI) anions and more Cr(VI) was adsorbed by the positive charged sorption sites or reduced by the electron-donor groups. As shown in Table 2, the AC and AC-TA contained much more phenolic groups than carboxyl groups. Since the carboxyl groups were much easier to dissociate than phenolic groups, the AC-OH and AC-TA-OH only showed a slight higher removal of Cr(III)/Cr_{total} than AC-COOH and AC-TA-COOH. These results indicated that electrostatic attraction plays an important role for Cr sorption on the carbons.

The results discussed above suggested removal mechanism includes three steps: (1) Firstly, Cr(VI) anions were bounded on carbons' surfaces by electrostatic attraction; (2) Secondly, some of adsorbed Cr(VI) anions were reduced to Cr(III) by adjacent electron-donor groups of the carbons; and (3) Finally, the produced Cr(III) were released into the aqueous phase or adsorbed by the oxygen-containing groups on the carbons' surfaces. After Cr(VI) sorption (dosage= 40 mg/50 mL; C_0 = 20 mg/L; and initial pH = 5.00±0.02), the values of Cr(III)/Cr_{total} on AC and AC-TA were 81.5% and 84.8%. The amount of Cr(VI) on AC-TA (2.7 mg/g) was similar to that on AC (2.0 mg/g), whereas, the amount of Cr(III) on AC-TA (15.4 mg/g) was much higher than that on AC (8.9 mg/g). These results indicated that much higher oxygen-containing groups of AC-TA promoted the Cr(VI) reduction and Cr(III) sorption, eventually enhancing its Cr_{total} removal ability. It also suggested the main Cr(VI) removal mechanism was Cr(VI) reduction (Cr(VI) to Cr(III)) and then sorption of Cr(III).

4. Conclusion

Activated carbon prepared from Zizania caduciflora (ZC) by phosphoric acid activation has well-developed porosity (V_{tot}, 1.37 m^3/g) and high specific surface area (S_{BET}, 1270 m^2/g). Modification of activated carbon with tartaric acid (TA) during phosphoric acid activation obviously enhanced the Cr(VI) removal ability of the carbons. The Cr(VI) removal showed strong dependence on solution pH and the optimum removal performance of Cr(VI) and Cr_{total} for the carbons was obtained at pH of 2.0-3.0. After blocking carboxyl (R-COOH) and hydroxyl groups (R-OH), the removal efficiencies of Cr(VI) and Cr_{total} by the carbons were enhanced, indicating the important role of electrostatic attraction on Cr(VI) removal. For the carbons, Cr(VI) was adsorbed on the carbons by electrostatic attraction and was subsequently reduced from to Cr(III), followed by sorption on the carbons or release into aqueous solution. The enhanced Cr(VI) removal efficiency of AC-TA was attributed its higher amount of oxygen-containing groups. The present work provided a new method to promote the Cr(VI) removal from aqueous solution.

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Figure captions

Fig. 1. Sorption isotherm of Cr(VI) on AC and AC-TA (dosage = 40 mg/50 mL; initial pH = 5.00±0.02; t = 48 h; and temperature = 22±1 °C).

Fig. 2. Effect of initial pH on equilibrium pH in the present of or in the absence of Cr(VI) (a) and Cr removal on the carbons (b) (dosage = 40 mg/50 mL; C_0 = 20 mg/L; t = 48 h; and temperature = 22±1 °C).

Fig. 3. N_2 adsorption/desorption isotherms (a) and pore size distribution (b) of AC and AC-TA.

Fig. 4. XPS survey scans of AC and AC-TA.

Fig. 5. High-resolution XPS spectra of C 1s for the carbons before and after Cr(VI) sorption.

Fig. 6. Removal of Cr(VI) and Cr_{total} by AC and AC-TA before and after blocking of carboxyl and hydroxyl functional groups (a) (dosage= 40 mg/50 mL; C_0 = 20 mg/L; t = 48 h; and temperature = 22±1 °C). Cr 2p 3/2 XPS spectra of original AC-TA (b), AC-TA-COOH (c) and AC-TA-OH (d) after Cr(VI) sorption.

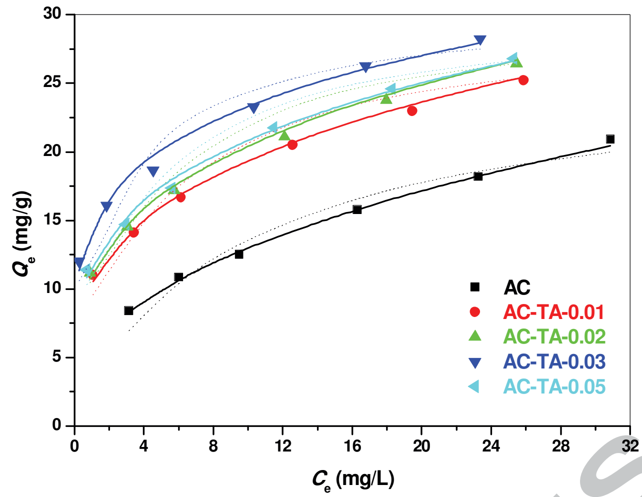

Fig. 1. Sorption isotherm of Cr(VI) on AC and AC-TA (dosage = 40 mg/50 mL; initial pH = 5.00±0.02; t = 48 h; and temperature = 22±1 °C).

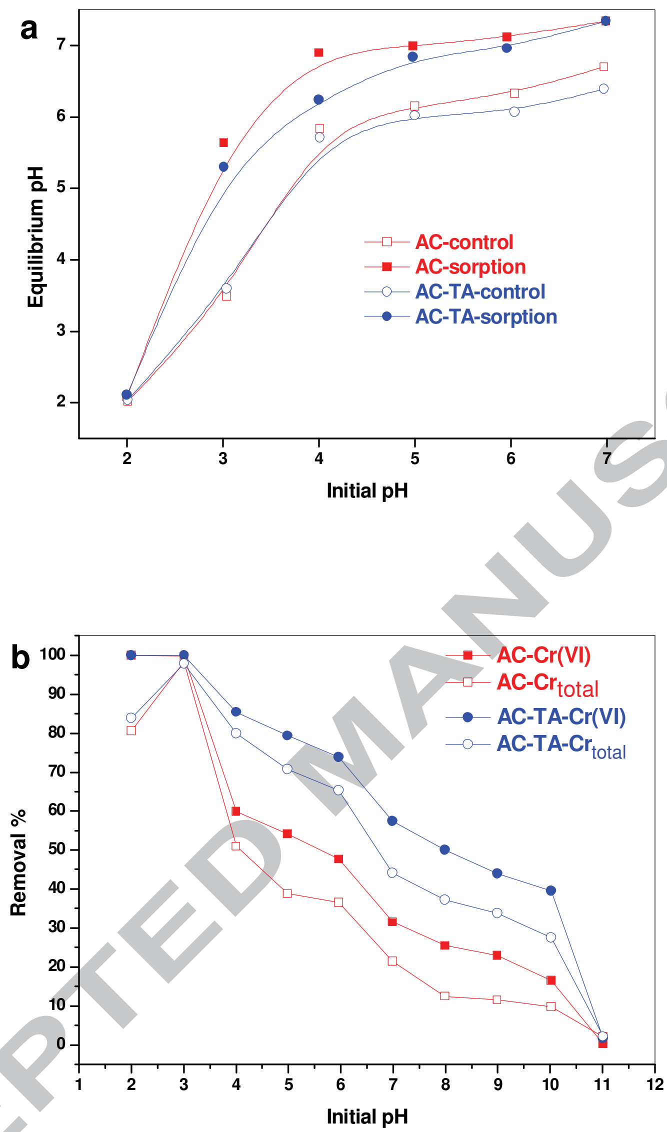

Fig. 2. Effect of initial pH on equilibrium pH in the present of or in the absence of Cr(VI) (a) and Cr removal on the carbons (b) (dosage = 40 mg/50 mL; C_0 = 20 mg/L; t = 48 h; and temperature = 22±1 °C).

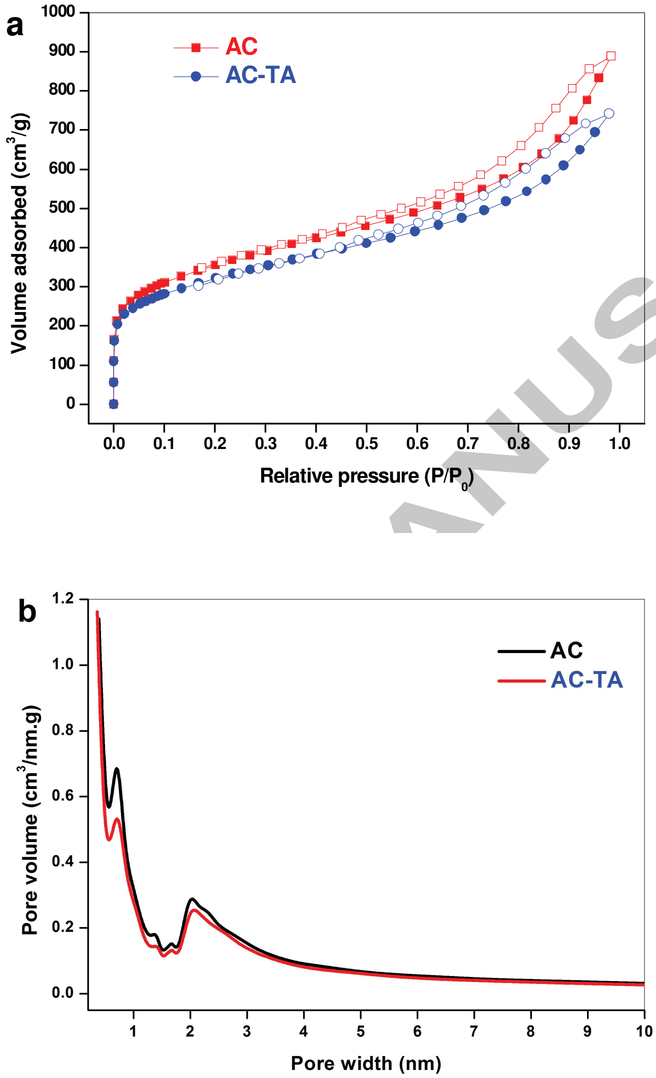

Fig. 3. N_2 adsorption/desorption isotherms (a) and pore size distribution (b) of AC and AC-TA.

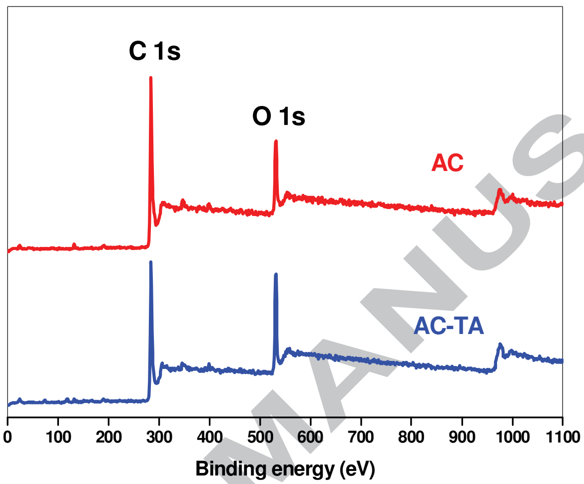

Fig. 4. XPS survey scans of AC and AC-TA.

1

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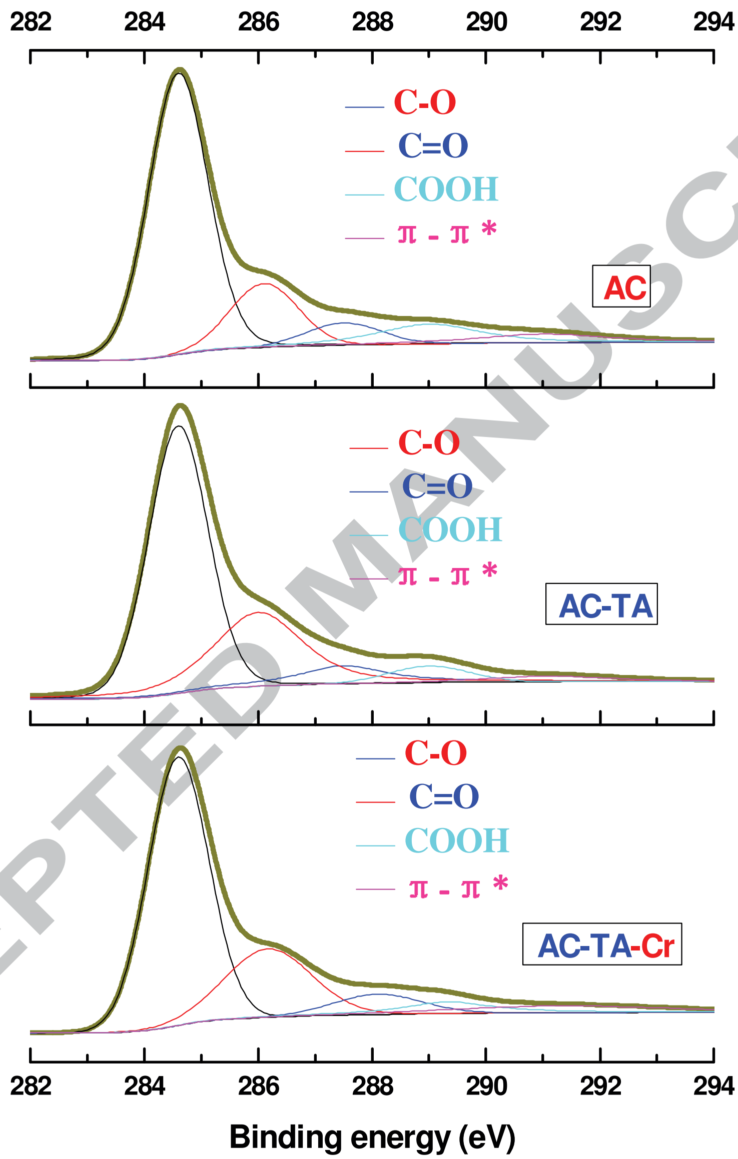

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4 **Fig. 5.** High-resolution XPS spectra of C 1s for the carbons before and after Cr(VI)

5 sorption.

6

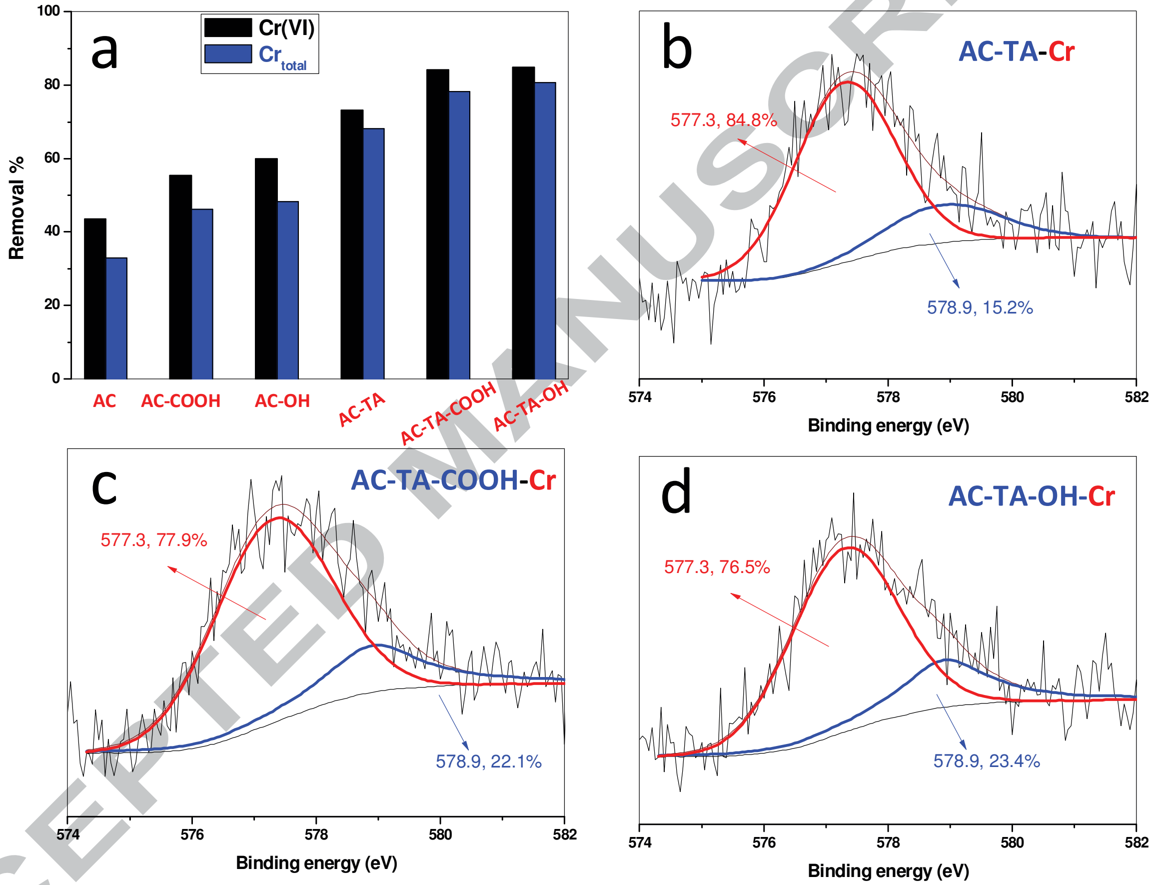

Fig. 6. Removal of Cr(VI) and Cr_{total} by AC and AC-TA before and after blocking of carboxyl and hydroxyl functional groups (a) (dosage= 40 mg/50 mL; C_0 = 20 mg/L; initial pH = 5.00±0.02; t = 48 h; and temperature = 22±1 °C). Cr 2p 3/2 XPS spectra of original AC-TA (b), AC-TA-COOH (c) and AC-TA-OH (d) after Cr(VI) sorption.

Table 1

Isotherm parameters for Cr(VI) sorption onto the carbons.

Samples	Langmuir			Freundlich		
	Q_m/mg· g^{-1}	K_L/L· mg^{-1}	R^2	K_F/ mg^{1-n}L^n/g	1/n	R^2
AC	23.5	0.123	0.9525	5.28	0.395	0.9966
AC-TA-0.1	29.0	0.274	0.9279	10.4	0.276	0.9916
AC-TA-0.2	29.8	0.304	0.9299	11.0	0.273	0.9905
AC-TA-0.3	31.0	0.498	0.9074	14.9	0.201	0.9827
AC-TA-0.5	29.7	0.338	0.9422	11.8	0.252	0.9901

Table 2

Surface area and pore volume parameters elemental compositions of the carbons.

Samples	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_{mic} (cm^3/g)	V_{mic}/V_{tot} (%)	V_{mes} (cm^3/g)	V_{tot} (cm^3/g)
AC	1270	645	625	0.31	22.6	1.06	1.37
AC-TA	1145	588	557	0.28	24.3	0.87	1.15

Table 3

Concentrations of surface functional groups of the carbons.

Samples	Carboxyl (mmol/g)	Lactone (mmol/g)	Phenolic (mmol/g)	Total acidic (mmol/g)	C wt.%	O wt.%	O/C %
AC	0.40	0.57	0.89	1.86	57.2	42.8	75.0
AC-TA	0.61	0.72	1.31	2.64	47.5	52.5	110.3

Table 4

Relative Concentration of components forming C1s XPS spectra of AC and AC-TAC before and after Cr(VI) sorption.

Samples		Peak from C 1s spectrum				
		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
	Binding energy (eV)	284.6	286.0	287.6	289.0	291.0
AC	Relative content (%)	62.5	15.7	6.0	9.9	5.9
AC-TA	Relative content (%)	56.4	28.2	8.1	4.6	2.8
AC-TA-Cr	Binding energy (eV)	284.6	286.1	288.1	289.3	291.3
	Relative content (%)	53.2	30.1	5.8	6.9	4.0

- *Zizania caduciflora* was used as carbon precursor for activated carbon preparation.
- Activated carbon was modified with tartaric acid during phosphoric acid activation.
- Tartaric acid modification enhanced Cr(VI) sorption capacities of the carbons.
- XPS analysis was used to investigate the Cr(VI) sorption mechanisms.