Research article

Removal of chromium Cr(VI) by low-cost chemically activated carbon materials from water

Zhongren Yue [a,b,*], Samantha E. Bender [a], Jinwen Wang [a], James Economy [a,**]

[a] Department of Materials Science & Engineering, University of Illinois at Urbana-Champaign, 1304 W Green St., Urbana, IL 61801, United States
[b] The University of Tennessee Space Institute, 411 B. H. Goethert Parkway Tullahoma, TN 37388, United States

A B S T R A C T

Low-cost, chemically activated carbon materials, Pellet-600 and PVA-300, were prepared at relatively low temperatures and show more effective removal efficiency of Cr(VI) from water than commercially available activated carbons tested. The Pellet-600 is a pelletized carbon material with high mesoporous volumes and surface area, and the PVA-300 is composed of a high surface area carbon coating on a fiberglass mat substrate. A much faster adsorption kinetics and a much higher adsorption capacity for Cr(VI) are achieved by the Pellet-600. At very low concentrations of Cr(VI), the PVA-300 displays a strong adsorption ability for Cr(VI). XPS data show an increase in the atomic ratio of Cr/C and oxidation of carbon materials after adsorption of Cr(VI). These results suggest that a high content of mesopores with a high surface area and surface functional groups greatly improve the Cr(VI) removal efficiency from water.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Chromium (Cr) compounds are widely used in industry such as electroplating, metal finishing, leather tanning, pigments, etc. The predominant use of chromium in industry unfortunately introduces an environmental concern. Cr exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state. In the environment Cr(III) is typically not a problem, its relative toxicity is low. In contrast, Cr(VI) compounds are toxic chemicals and genotoxic carcinogens [1]. Thus, the presence of Cr(VI) ions in the environment is posing serious problems and causing great public concern [2,3]. Currently, the United States Environmental Protection Agency (US EPA) has set a Maximum Contaminant Level (MCL) for chromium at 0.1 parts per million (ppm) in drinking water [4]. The increasing concern with Cr(VI) pollution, significantly motivates the investigation and development of new and improved materials to address the problems.

A wide range of technologies have been investigated for the removal of Cr(VI) from water [5–11]. Adsorption using activated carbons proved to be the most efficient technique [7–11]. To further improve the removal efficiency of Cr(VI) ion from water, the commercially available activated carbons were chemically modified with acid and different oxidizing agents such as HNO_3, H_2O_2 and $Fe(NO_3)_3$ [7,8]. It was found that the adsorption mechanism and rate of Cr(VI) are affected by the modified pore structure and surface properties of the activated carbons.

A family of chemically activated carbon materials has been developed by a new approach in our laboratory [12]. This new method provides the carbon materials with relatively low-cost, high surface area, high mesopore volumes, and some unusual pore surface chemistries [13–17]. Some of these activated carbon materials, without any post-chemical treatments, contain high concentration of functional groups. In most cases, these groups include –OH, =O, and –COOH. Some other groups such as >P(O)OH and –P(O)(OH)$_2$ may exist on the activated materials made from certain raw materials and H_3PO_4 activation [16]. The previous studies have shown that those kinds of materials have improved removal efficiency for trace toxic organics over the granular activated carbons (GACs) [17–20]. Therefore, the novel activated carbon materials with tailored porosity and surface chemistry are expected to have great potential as highly effective adsorbents for removal of Cr(VI) from water.

In this work, two chemically activated carbon materials with highly mesoporous volumes and functional groups were prepared and then tested in comparison to standard activated carbons for Cr(VI) removal. The Cr(VI) adsorption kinetics and adsorption isotherms were performed to demonstrate the superior activity of the new materials. The effect of porous and chemical structures on the adsorption of Cr(VI) was also elucidated.

---

* Corresponding author at: The University of Tennessee Space Institute, 411 B. H. Goethert Parkway Tullahoma, TN 37388, United States. Tel.: +1 931 393 7362; fax: +1 931 393 7530.
** Corresponding author. Tel.: +1 217 333 9260; fax: +1 217 333 2736.
E-mail addresses: zyue@utsi.edu (Z. Yue), jeconomy@uiuc.edu (J. Economy).

2. Experimental

2.1. Synthesis of materials

Two chemically activated carbon materials, Pellet-600 with a pellet form and PVA-300 with a fiber mat form, were laboratory prepared using a patented approach [12]. A granulated carbon Pellet-600 and a fiber form material PVA-300 were synthesized in the following ways.

2.1.1. Pellet-600

Cellulose powder with ~20 μm particle size (Aldrich Chemical Company) was dissolved in 66 wt% of $ZnCl_2$ aqueous solution. The weight ratio of cellulose, $ZnCl_2$, and H_2O in the solution is 2.5:33:16. 1 g of carbon black (Pearls 2000, Cabot Corporation) with particle size of ~12 nm was mixed with 7 g of the solution. The mixture was pelletized and then activated with $ZnCl_2$ inside the material in N_2 at 600 °C for 30 min. The pellets were washed with HCl and deionized (D.I.) water and then fully dried at 150 °C under vacuum. The resulting pellets have a cylinder form with a diameter of 1.6 mm and a length of 1.3 mm. In this experiment, $ZnCl_2$ plays an important role for the preparation of Pellet-600. Its aqueous solution is used as a solvent for cellulose binder; subsequently it acts as a catalyst to activate the cellulose binder to high surface area porous carbon binder. Nanosize carbon black with very high geometric surface combining with the porous carbon binder provides the Pellet-600 with a high porosity.

2.1.2. PVA-300

1 g of polyvinyl alcohol (PVA) (99+% hydrolyzed, Avg. M.W. 50,000, Aldrich Chemical Company) was dissolved in 10 g of hot water (~90 °C). After cooling, 1 g of H_3PO_4 (86%) was added into the solution. A non-woven fiberglass mat, CRANEGLAS 230 (0.015 in. nominal thickness, fiber diameter of 6.5 μm and 7 wt% of PVA binding), was dip-coated with the above solution. The coated mat was dried at 120 °C and then activated with H_3PO_4 inside the coating at 300 °C in air for 60 min. The activated fiber mat was washed with a NaOH (0.5 M) solution and D.I. water, then rinsed thoroughly with HCl (0.5 M) and D.I. water, and finally dried at 150 °C under vacuum.

As a comparison, two commercially available activated carbons, granular activated carbon GAC-F400 from Calgon Co. and activated carbon fiber ACF-10 from Kynol Co., were employed in this study, since they have a close surface area and microporous volumes to the Pellet-600 and PVA-300, respectively.

2.2. Adsorption of Cr(VI)

$K_2Cr_2O_7$ was used to prepare a stock solution with a concentration of 1000 ppm Cr(VI) which was diluted for preparation of standard and test solutions. Standard solutions were prepared at concentrations of: 0, 5, 10, 20, 40, 80, 125, 200, 400, 600, 800, and 1000 ppb. The pH of test solutions is in a range between 4.8 and 6.8 based on the concentration of Cr(VI). The adsorption of Cr(VI) was carried out in a shaking machine at room temperature. Color reagent for the analysis of Cr(VI) was prepared according to Refs. [21,22]. 250 mg of 1,5-diphenylcarbohydrazide was dissolved into 50 ml of methanol (HPLC-grade). 250 ml of H_2SO_4 solution (contains 14 ml of 98% H_2SO_4) was added into the above solution, which was then diluted with D.I. water to 500 ml. The fresh color reagent is a very clear solution and can be used for several days until any color appears.

Adsorption kinetics of Cr(VI) were studied at room temperature with an initial Cr(VI) concentration of 4 ppm at pH 6.0, an initial volume of 200 ml, and a sample weight of 176–179 mg. One mL samples were removed at different times for the analysis of Cr(VI)

concentration. Although there is a minor error for the reported data due to an increasing solid to solution ratio with sampling, this test method can be used to compare the removal efficiency of Cr(VI) on different activated carbons.

Adsorption isotherms were performed at concentrations of: 0.5, 1, 2, 4, 8, 12, 20, and 40 ppm (pH changed from 6.8 to 4.8). For each solution, 30–40 mg of each adsorbent was added and the samples were shaken for 7 days at room temperature.

6 ml of water samples were treated, after dilution if necessary, with 2 ml of the above color reagent. The color was developed upon addition of the color reagent. The solutions were measured within 2 h at λ = 540 nm using a Shimadzu 2100 UV–vis spectrophotometer. The concentration of Cr(VI) prior to and after adsorption was calculated by means of standard solutions.

2.3. Characterization

Brunauer–Emmett–Teller (BET) surface area and micro- and mesoporous volumes were carried out on an Autosorb-1 apparatus (Quantachrome). All samples were degassed at 150 °C until the outgas pressure rise was below 5 μHg/min prior to analysis. N_2 isotherm results at 77 K in the appropriate relative pressure ranges were used for subsequent calculations. The BET equation was used to determine the surface area. The Dubinin–Radushkevich (DR) equation was used to deduce micropore (<2 nm) volumes. The total pore volume was estimated from the amount of nitrogen adsorbed at $P/P_0 = 0.95$. The volume of mesopores (2–50 nm) was calculated by subtracting the volume of micropores from the total pore volume at a relative pressure of 0.95.

The ash or fiberglass content of activated carbon materials was measured using a Hi-Res TA Instruments 2950 Thermogravimetric Analyzer (TGA) by burning off the carbon materials (~20 mg) in air at 800 °C.

X-ray photoelectron spectroscopy (XPS) data were obtained from the carbon materials using a Physical Electronics PHI Model 5400 surface analysis system. Before analysis all samples were washed with D.I. water and then fully dried. XPS spectra were obtained using an achromatic Mg Kα (1253.6 eV) X-ray source operated at 300 W. Survey scans were collected from 0 to 1100 eV with a pass energy equal to 178.95 eV. High-resolution scans were performed with the pass energy adjusted to 35.75 eV. The pressure inside the vacuum system was maintained at approximately 10^{-9} Torr during all XPS experiments. A non-linear least squares curve fitting program (XPSPEAK4.1 software) with a symmetric Gaussian–Lorentzian sum function and Shirley background subtraction was used to deconvolve the XPS peaks. The carbon 1s electron binding energy corresponding to graphitic carbon was referenced at 284.5 eV for calibration [23].

3. Results and discussion

3.1. Comparison of different adsorbents

The BET surface area and microporous and mesoporous volume of the four carbon materials are listed in Table 1 comparing chemically activated carbon materials Pellet-600 and PVA-300 with commercially available products GAC-F400 and ACF-10. Pellet-600 has the highest surface area, microporous and mesoporous volumes which contributed from porous carbon binder and nanosize carbon black. PVA-300 fiber has a 33-wt% of carbon coating on a fiberglass substrate so that it has a lowest surface area of 549 m²/g which is mainly contributed from the activated coating material. Pellet-600 and PVA-300 were prepared with chemical activations at relatively low temperatures. Previous studies have demonstrated

Table 1
Comparison of porosity parameters of adsorbents.

Adsorbent	Pellet-600	PVA-300	GAC-F400	ACF-10
Activation method	ZnCl$_2$ at 600 °C	H$_3$PO$_4$ at 300 °C	–	–
Material form	Pellet	Fiber mat	Granule	Fabric
BET surface area (m^2/g)	1357	549 (1664[a])	1053	730
DR micropore volume (cm^3/g)	0.49	0.22	0.41	0.25
Mesopore volume (cm^3/g)	0.94	0.07	0.19	0.05
Total volume (cm^3/g)	1.43	0.29	0.60	0.30
Ash or fiberglass[*] (wt%)	1.72	67.0[*]	5.97	2.10

[a] BET surface area (m^2/g of carbon). Calculation based on the carbon coating.

[*] Adsorbent consists of porous carbon and fiberglass.

that low temperature, chemically activated materials possess more functional groups [13–17].

3.2. Adsorption kinetics

Cr(VI) removal with four adsorbents vs. adsorption time is shown in Fig. 1. The Pellet-600 displays superior activity as compared to the other materials tested and demonstrates the fast kinetics of the material. After 540 min the Pellet-600 had removed the Cr(VI) below the EPA MCL of 100 ppb, and it continued to remove the Cr(VI) to below 6 ppb. It is suggested that high mesoporous volumes and surface area in the Pellet-600 improve the removal efficiency of Cr(VI) from water. The commercial granular form, GAC-
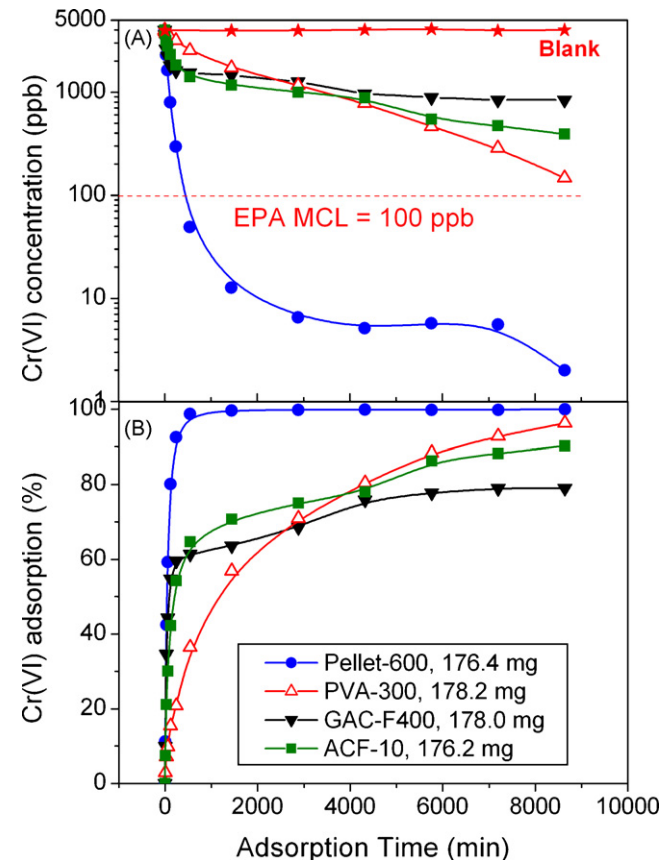
F400, was not able to reach the MCL set by the EPA as it only removed down to 840 ppb after 6 days. Although the PVA-300 had slower kinetics, it was still able to come close to the MCL after 6 days, whereas the commercial fiber form, ACF-10 only reached about 400 ppb. The slower removal of Cr(VI) by the PVA-300 is probably due to the lower carbon content (33.0 wt% of the carbon coating) on the fiberglass mat vs. the ACF-10 which is 97.9% carbon.

3.3. Adsorption isotherms

The adsorption isotherms for the materials are shown in Fig. 2. The Pellet-600 shows a high capacity in both low concentration and high concentration regimes. The capacity was much greater than other materials. The isotherm for PVA-300 shows a very high capacity in the low concentration regime, but fell below commercial products at high concentration. This is again due to the lower amount of carbon in the PVA-300. The log–log plot can be seen in Fig. 2(B) long with the best-fit lines. The lines for all materials are shown to fit well with a Freundlich isotherm model $Q = KC_e^{1/n}$ (or $\log Q = \log K + 1/n \times \log C_e$), where Q is mass of the target compound adsorbed per unit mass of adsorbent (mg/g); C_e is equilibrium concentration of the adsorbate in the liquid (mg/l); K is the adsorption equilibrium constant (mg/g)(mg/l)$^{-1/n}$; and n is a constant indica-

Fig. 1. Cr(VI) removal vs. adsorption time. (A) Change in Cr(VI) concentration and (B) change in the ratio of Cr(VI) adsorption.
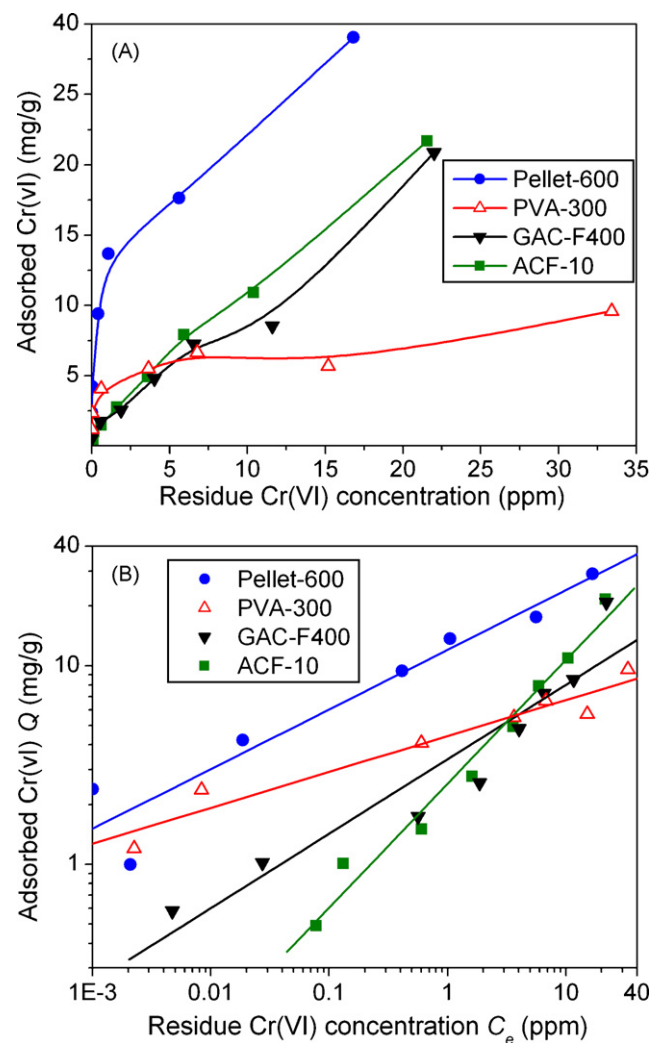

Fig. 2. Adsorption isotherms of Cr(VI) for materials tested. (A) Linear-type plot and (B) log-type plot with best-fit lines.

Table 2
Freundlich model parameters for adsorbents.

Adsorbent	K	1/n	r
Pellet-600	12.05	0.300	0.960
PVA-300	4.43	0.181	0.969
GAC-F400	3.38	0.375	0.948
ACF-10	2.54	0.624	0.988

tive of adsorption intensity. For an effective adsorption system, high adsorption capacity (Q) and low equilibrium concentration of target compound (C_e) after adsorption are needed. Thus, the larger the K value and smaller the $1/n$ value, the more effective the adsorbent is for adsorption.

The calculated Freundlich parameters and the best-fit correlation coefficient values (r) are listed in Table 2. The Pellet-600 and PVA-300 show higher K and lower $1/n$ values as compared to the commercial products GAC-F400 and ACF-10. This indicates that the chemically activated Pellet-600 and PVA-300 are effective materials for the removal of Cr(VI) from water. It is suggested that the improved adsorption affinity of Cr(VI) on the Pellet-600 and PVA-300 might be related to the pore surface chemistry of the materials as well as their proper pore structures.

3.4. XPS analysis

In order to future characterize the surface characters of the prepared materials, XPS data were obtained for Pellet-600 and PVA-300 prior to and after adsorption of Cr(VI). XPS survey spectra (see Figs. 3 and 4) show carbon and oxygen atoms on the Pellet-600 and carbon, oxygen, and silicon atoms on the surface of PVA-300 prior to adsorption. Silicon should derive from SiO$_2$, which is the main constituent of the fiberglass substrate. For both materials, Cr atom was detected on the surface after adsorption of Cr(VI). The surface elemental analysis from high-resolution XPS spectra is listed in Table 3. The atomic ratio of Cr/C greatly increased in both materials after adsorption. For the Pellet-600 the atomic ratio of Cr/C increased from 0 to 0.037 and O/C increased from 0.110 to 0.206. For the PVA-300, Cr/C increased from 0 to 0.022, the change in O/C was omitted due to an error from a contribution of O in the SiO$_2$.
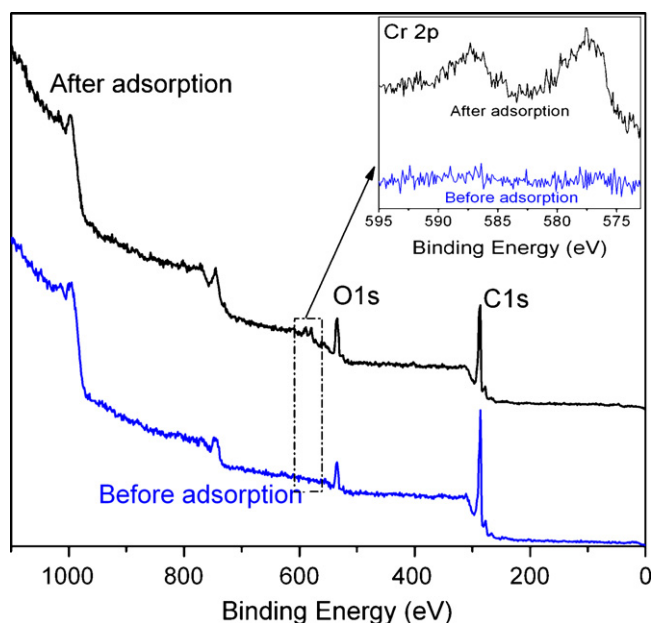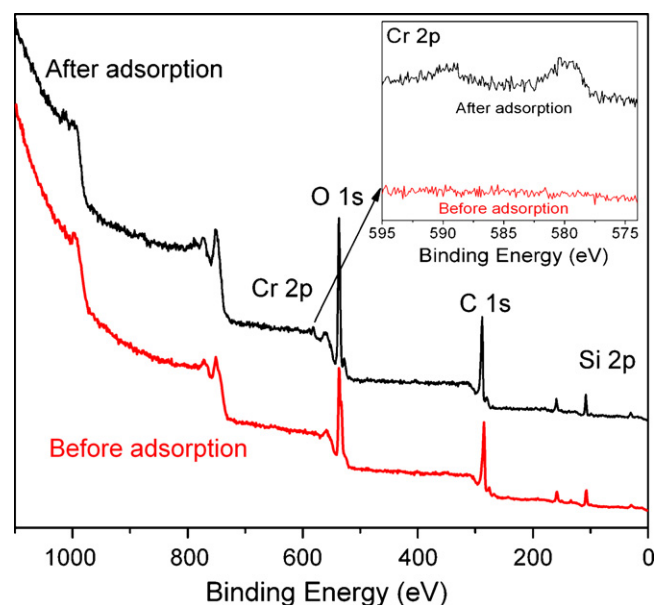

Fig. 4. XPS survey spectra of PVA-300 before and after adsorption.

Table 3
XPS surface elemental analysis of the Pellet-600 and PVA-300.

	Pellet-600		PVA-300
	O/C	Cr/C	Cr/C
Before adsorption	0.110	0	0
After adsorption	0.206	0.037	0.022

To explain the increase in O/C on the surface of the Pellet-600, High-resolution XPS C1s spectra (Fig. 5) were deconvoluted into four peaks. Based upon literatures [24,25], the four peaks in the spectra represent carbon in C*–H and C*–C (peak I, 284.5 eV), carbon present in phenolic, alcohol, and ether groups (peak II, around 285.5 eV), carbonyl or quinone groups (peak III, 287.5 eV), and carboxyl or ester groups (peak IV, around
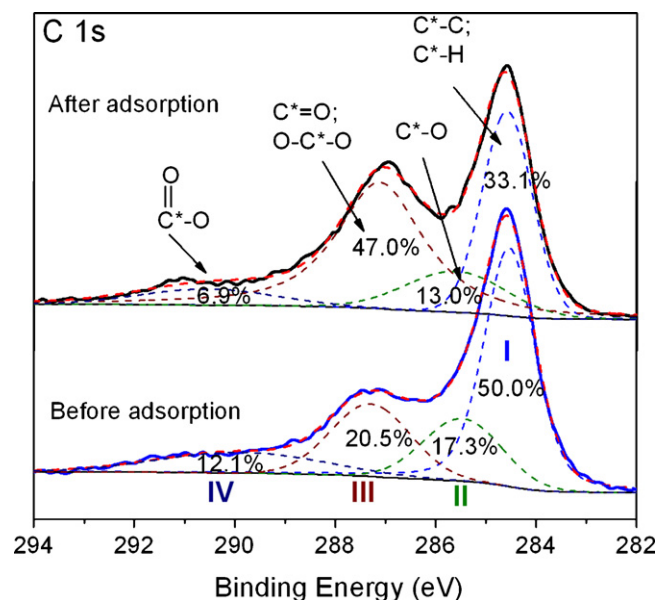

Fig. 3. XPS survey spectra of Pellet-600 before and after adsorption.

Fig. 5. High-resolution XPS C1s spectra of the surface of Pellet-600 before and after adsorption.

290 eV). There is a significant decrease in the relative content of peak I while a significant increase in the peak III is observed after adsorption. This suggests that the carbon in the Pellet-600 was oxidized ($\equiv$C–H $\rightarrow$ $\equiv$C–OH $\rightarrow$ $=$C$=$O) after the adsorption of Cr(VI).

It is reasonable to hypothesize that the part of adsorbed Cr(VI) is reduced to Cr(III) with oxidation of the functional groups C–H and C–OH in the Pellet-600. The reduction of Cr(VI) to Cr(III) on activated carbons was reported in literatures [26–28]. It was found that small amount of Cr(III) may not be adsorbed in the pores, instead, it may begin to dissolve back into solution around pH 4–5. However, in the case of this study, if Cr^{3+} ion was formed, it is likely to be adsorbed by ion exchange groups, such as –COOH, which presents a relatively higher concentration in the chemically activated carbon materials.

4. Conclusions

Two activated carbon materials, Pellet-600 and PVA-300, were synthesized with chemical activation at low temperatures. Both materials show an improved adsorption efficiency in removing Cr(VI) from water as compared to the commercial products GAC-F400 and ACF-10. The following features of the materials are summarized as follows:

(1) The Pellet-600, a granulated carbon material activated with $ZnCl_2$ at 600 °C in a N_2 flow, has high mesoporous volumes and surface area. The PVA-300, a fiber form material activated with H_3PO_4 at 300 °C in air, has high surface area carbon coated on a fiberglass substrate. Both carbon materials are low cost and considered to have high concentration of functional groups on the surface due to the low temperature activation.
(2) The Pellet-600 shows much faster adsorption kinetics than other materials for the removal of Cr(VI) from water. Its high mesoporous volume and high surface area are considered to be the main factors for the improvement.
(3) Cr(VI) adsorption isotherms show that the Pellet-600 has a higher adsorption capacity than other materials. The PVA-300 has a stronger adsorption affinity for Cr(VI) over other materials at very low concentrations of Cr(VI).
(4) XPS analyses show an increase in the atomic ratios of Cr/C and O/C on the surface of the carbon materials after adsorption of Cr(VI). The peak-fitting of C1s spectra demonstrates a conversion of carbon bonds from C*–H to C*$=$O. These results suggest that the adsorption of Cr(VI) onto carbons is achieved partially by a redox reaction between the Cr(VI) and carbon materials.

References

[1] D. Blowes, Tracking hexavalent Cr in groundwater, Science 295 (2002) 2024A–2025A.
[2] R.R. Leonard, Lauwerys, carcinogenicity and mutagenicity of chromium, Mut. Res. 76 (1980) 227–239.
[3] S.D. Flora, M. Bagnasco, D. Serra, P. Zanacchi, Genotoxicity of chromium compounds. A review, Mut. Res. 238 (1990) 99–172.
[4] U.S. Environmental Protection Agency. National Primary Drinking Water Standards, 2003. http://www.epa.gov/safewater/consumer/pdf/mcl.pdf.
[5] C.S. Brooks, Metal Recovery from Industrial Waste, Lewis, Michigan, USA, 1991.
[6] B. Deng, L. Lan, K. Houston, P. Brady, Effects of clay minerals on Cr(Vi) reduction by organic compounds, Environ. Monitor. Assess. 84 (2003) 5–18.
[7] S.J. Park, Y.S. Jang, Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr(VI), J. Colloid Interface Sci. 249 (2002) 458–463.
[8] N. Zhao, N. Wei, J. Li, Z. Qiao, J. Cui, F. He, Surface properties of chemically modified activated carbons for adsorption rate of Cr (VI), Chem. Eng. J. 115 (1–2) (2005) 133–138.
[9] D.D. Dharani, M. Ranjit, P. Jyotsnamayee, N.D. Surendra, S.T. Ravindra, Removal of Cr(VI) from aqueous solution using activated cow dung carbon, J. Colloid Interface Sci. 232 (2000) 235–240.
[10] P.C. Manuel, M.M. Jose, T.M. Rosa, Chromium(VI) removal with activated carbons, Water Res. 29 (1995) 2174–2180.
[11] A. Diksha, G. Meenakshi, R.C. Bansal, Adsorption of chromium by activated carbon from aqueous solution, Carbon 37 (1999) 1989–1997.
[12] J. Economy, C.L. Mangun, Z. Yue, Activated organic coatings on fiber substrates, US Patent 6,517,906 (2001).
[13] Z. Yue, C.L. Mangun, J. Economy, Preparation of fibrous porous materials by chemical activation 1. $ZnCl_2$ activation of polymer coated fibers, Carbon 40 (2002) 1181–1191.
[14] Z. Yue, J. Economy, G. Bordson, Preparation and characterization of NaOH-activated carbons from phenolic resin, J. Mater. Chem. 26 (2006) 1456–1461.
[15] Z. Yue, J. Economy, Synthesis of highly mesoporous carbon pellets from carbon black and polymer binder by chemical activation, Micropor. Mesopor. Mater. 96 (2006) 314–320.
[16] Z. Yue, C.L. Mangun, J. Economy, Characterization of surface chemistry and pore structure of H_3PO_4-activated poly(vinyl alcohol) coated fiberglass, Carbon 42 (2004) 1973–1982.
[17] Z. Yue, J. Economy, K. Rajagopalan, G. Bordson, M. Piwoni, L. Ding, V.L. Snoeyink, B.J. Marinas, Chemically activated carbon on a fiberglass substrate for removal of trace atrazine from water, J. Mater. Chem. 16 (2006) 3375–3380.
[18] L. Ding, V.L. Snoeyink, B.J. Marinas, Z. Yue, J. Economy, Effects of powdered activated carbon pore size distribution on the competitive adsorption of aqueous atrazine and natural organic matter, Environ. Sci. Technol. 42 (2008) 1227–1231.
[19] Z. Yue, J. Economy, Nanoparticle and nanoporous carbon adsorbents for removal of trace organic contaminants from water, J. Nanopart. Res. 7 (2005) 477–487.
[20] Z. Yue, C.L. Mangun, J. Economy, P. Kemme, D. Cropek, S. Maloney, Removal of chemical contaminants from water to below USEPA MCL using activated carbon fiber filter, Environ. Sci. Technol. 35 (2001) 2844–2848.
[21] Dionex, Technical Note 26, Determination of Cr(VI) in water, waste water, and solid waste extracts, 1996. http://www1.dionex.com/en-us/webdocs/4428_TN26_16May07_LPN034398-02.pdf.
[22] S. Morales-Muñoz, J.L. Luque-García, M.D. Luque de Castro, A continuous approach for the determination of Cr(VI) in sediment and soil based on the coupling of microwave-assisted water extraction, preconcentration, derivatization and photometric detection, Anal. Chim. Acta 515 (2004) 343–348.
[23] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: J. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Eden Prairie, MN, 1992, p. 216.
[24] Y. Xie, P.M.A. Sherwood, X-ray photoelectron spectroscopic studies of carbon fiber surfaces. 11. Differences in the surface chemistry and bulk structure of different carbon fibers based on poly(acrylonitrile) and pitch and comparison with various graphite samples, Chem. Mater. 2 (1990) 293–299.
[25] Z. Yue, W. Jiang, L. Wang, S.D. Gardner, C.U. Pittman Jr., Surface characterization of electrochemically oxidized carbon fibers, Carbon 37 (1999) 1785–1796.
[26] C.P. Huang, M.H. Wu, The removal of chromium(VI) from dilute aqueous solution by activated carbon, Water Res. 11 (1977) 673–679.
[27] D.C. Sharma, C.F. Forster, Removal of hexavalent chromium from aqueous solutions by granular activated carbon, Water SA 22 (1996) 153–160.
[28] J. Fang, Z. Gu, D. Gang, C. Liu, E.S. Ilton, B. Deng, Cr(VI) removal from aqueous solution by activated carbon coated with quaternized poly(4-vinylpyridine), Environ. Sci. Technol. 41 (2007) 4748–4753.