Interactions of Cr(VI) with hybrid anion exchange/porous carbon fibers in aqueous solution at natural pH

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ABSTRACT

Novel hybrid strong anion exchange porous carbon fibers (HACAX) were synthesized and evaluated for adsorption of low concentrations of Cr(VI) at natural pH. Positive surface charge due to pyridinium groups enables HACAX to adsorb Cr(V) rapidly and with high capacity. HACAX showed stable and regenerable performance for adsorbing and converting Cr(VI) into Cr(III) with no change in pH, which is attributed to the catalytic activity of surface oxygen functional groups.

1. Introduction

Hexavalent chromium, also known as Cr(VI) or the “Erin Brockovich chemical”, is well known to the public as a notoriously toxic chemical and potential carcinogen in aqueous solutions [1, 2]. A recent survey showed that drinking water supplies in 31 out of 35 cities tested in US were contaminated with Cr(VI) [3]. Widespread public concerns and even panic ensued regarding Cr(VI) contamination in tap water [4]. To date, the USEPA has not established a legal limit for Cr(VI) in drinking water save for a 100-ppb MCL (maximum contaminant level) for total chromium to protect against allergic dermatitis [4]. A word of note: in its trivalent state, Cr is an essential human nutrient and safe with doses < 1 mg/day

[5]. Recognizing the carcinogenic potential and widespread presence of Cr(VI), California finalized the nation's first Cr(VI) MCL of 10 ppb in 2014, and the USEPA is in the process of establishing a new standard for Cr(VI) [6]. Before the regulation is established nationwide, it is critical to develop and implement an effective and reliable technologies to remove Cr(VI) in drinking water down to ppb level to protect people against this carcinogen.

In the literature, several methods and materials have been evaluated for Cr(VI) removal, including activated carbon [7], ion exchange [8], chemical reduction [9], metal oxides nanoparticles [10], membrane separation [11, 12] and precipitation [13, 14]. Activated carbons (AC) and ion exchange resins (IXR) are the two most commonly employed technologies. As the main adsorbent employed in Cr(VI) wastewater treatment [15], AC adsorbs Cr(VI) through i) electrostatic adsorption, followed by ii) surface reduction by surface functional groups which convert Cr(VI) into Cr(III) [7, 16]. Since Cr(VI) is negatively charged, effective adsorption of Cr(VI) only occurs at low pH, when the AC surface is protonated and thus positively charged [14]. Ion exchange materials adsorb Cr(VI) through electrostatic forces provided by quaternary amine functional groups which retain positive charge over a wide pH range [17]. Due to their relatively non-selective nature, IXRs suffer from a leaking issue as competing background ions flow through and exchange out Cr(VI). Additionally, both IXR and GAC suffer from slow kinetics due to the relatively large geometry of beads and granules, respectively. Critically, most of the literature for Cr(VI) removal is on the wastewater system, where it is present at ~100 to ~1000 ppm; as suggested in the literature, more studies focusing on drinking water are needed, where Cr(VI) is present at ppb to a few ppm level at natural pH [18, 19].

The objective of the current work is to design a system possessing rapid kinetics and high selectivity towards Cr(VI) at low concentration and natural pH. To this end, hybrid activated carbon/strong anion exchange materials were designed in order to: i) combine the stability of activated carbon with permanent positive charge surface of anion exchange resins, thus adsorbing Cr(VI) effectively at natural pH; and ii) provide reactive surface functional sites to convert Cr(VI) to human nutrient form of chromium (Cr(III)). The synthesis has been presented previously [20]; Current study is focusing on studying and characterizing the interactions between Cr(VI) and such hybrid materials. The fate of Cr and surface functional groups of hybrid material are elucidated, and a comprehensive mechanism of adsorption and reaction is proposed.

It is challenging to introduce quaternary amines onto porous carbon surfaces due to the difficulty of the prerequisite grafting of chloromethyl groups [21]. In the present work, a hybrid system was synthesized through an alternative route yielding pyridinium surface functional groups: polyacrylonitrile was chemically activated to form porous carbon rich with pyridinic nitrogen (PANCAF), and subsequently to form permanently charged pyridinium sites (HACAX, Scheme 1) [20]. During activation, ZnCl_2 was used to: 1) catalyze the ladder-forming reaction at lower temperature, thus preserving active N-functional groups (mainly pyridine); 2) introduce porosity by voids remaining after rinsing. Additionally, a fiber platform was adopted employing nonwoven web consisting of 6.5- μm diameter glass fibers to confine the feature size of carbon to the μm level, which facilitates mass transfer, and to improve ease of handling for containment in practical applications.

2. Materials and methods

2.1. Materials

Unless specified, all chemicals were purchased from Sigma-Aldrich and used as received. Polyacrylonitrile (PAN) $((C_3H_3N)_n, M_w \sim 150,000)$ and zinc chloride ($ZnCl_2$) were used for the synthesis of an activated carbon coating on a substrate fiber (Crane 230). Iodomethane (CH_3I), were used for the methylation reaction. Ethanol (Decon, 200 proof), dimethylformamide (DMF) (Fisher Scientific) were used as solvent. Potassium dichromate was used as a stock solution of hexavalent chromium, and 1,5-diphenylcarbazide (DPC) was used as the color reagent. Methanol (Fisher Scientific) was HPLC grade for dissolving color reagent. Reagents used for Boehm titration wet chemistry include NaOH, $NaHCO_3$ (Fisher Scientific) and Na_2CO_3 (Fisher Scientific) and HCl (Macron).

2.2. Synthesis

The synthesis scheme was described above and is based on author's previous work with minor modification [20]. Polyacrylonitrile (PAN) was dissolved in DMF at 70 °C, and then add $ZnCl_2$ to make a viscous solution. Weight ratio of PAN: $ZnCl_2$: DMF is 6.5:19:174. After $ZnCl_2$ was dissolved, a glass fiber mat (Crane 230, Crane Co) was dip-coated into the above mixture. Then dip wash the coated fiber in 5%_{wt} $ZnCl_2$ aqueous solution to make a uniform coating without losing $ZnCl_2$. After dried the samples in a fume hood overnight, put them into a furnace at 200°C for 10 hours in air to stabilize the coatings. Afterwards, put the samples in flowing N_2 by increasing heating temperature $\sim 30^\circ C/min$ to the preset temperature in-between 450°C and then held isothermed for 30 mins. After cooling down in flowing N_2 for ~ 10 hrs, sample was taken out and washed with 0.5 M HCl, DI Water, 0.5M

NaOH and DIW in sequence. The sample was vacuum dried at 110 °C overnight. Afterwards, ~ 1 g samples are soaked in 7 ml: 40 ml methyl iodide: NMP solution in a sealed container and heated at 80 °C for 18 hrs. After reaction, the solid samples were washed with ethanol and DI water to remove the residual chemicals and solvents attached on the fiber. The sample was then dried and stored for further tests and characterization.

2.3. Ion exchange properties

Ion exchange kinetics of HACAX was measured by putting small pieces of HACAX (~ 70 mg) into 200 mL 1 M NaNO₃ solution with strong stirring. 10 mL aqueous sample was taken out for iodide ion analysis at each preset time point until the iodide ion concentration was unchanged. In comparison, original PANCAF before methylation and commercially available strong base anion exchange resin IXR-B were used under the same conditions. In order to compare different materials under the same condition, both PANCAF and IXR-B were pre-exchanged with iodide as the counter ions. Iodide concentration was analyzed by iodide ISE electrode.

2.4. Cr(VI) adsorption performance

Hexavalent chromium stock solution was prepared by dissolving 0.5658 g potassium dichromate (K₂Cr₂O₇) in 200 mL DI water, giving a 1000 ppm Cr(VI). All other test solutions and standard solutions were made by diluting the 1000 ppm stock solution. The concentration of Cr(VI) was measured by UV-Vis Spectroscopy at $\lambda = 540$ nm via photometric diphenylcarbohydrazide method [18, 22]. Standard solutions were prepared at concentrations of 0, 5, 10, 20, 40, 80, 120, 400, 600, 800, 1000 ppb for calibration with $R^2 > 0.9998$. After mixing with color indicator, the sample was measured in a timely way to ensure a precise

result. In kinetic test, ICP-MS was employed to test total Cr. Cr(III) was calculated by the differences between total Cr and Cr(VI) measured by UV-Vis.

The adsorption isotherm was studied in Cr(VI) aqueous solution with different initial concentrations at room temperature. ~15 mg sample was weighed and put into solution and shaken for 6 days, and then 3 mL solution, or after appropriate dilution if necessary, was sampled and analyzed for Cr(VI) concentration. The following equation was used to calculate adsorption capacity

where Q is adsorption capacity of Cr(VI) (mg/g), C_0 and C_e means starting Cr(VI) concentration and equilibrate Cr(VI) concentration (ppm), respectively. V is the volume of the solution (mL) and W is the dry weight of active sample (g).

For pH isotherm, solutions' pH were adjusted with 0.5N NaOH or 0.5N HCl measured by pH electrode (Cole-Parmer, Cat. EW-59001-70). It was carried out in 1g HACAX per 1L 100 ppm Cr(VI) solution.

Adsorption kinetics was studied in aqueous solution at room temperature in a 250 mL flask with magnetic stirring. During the test, 150 mg sample was put into 200 mL solution with initial Cr(VI) concentration at 4 ppm. The solution was sampled at pre-set time points and stored awaiting further measurements.

Regeneration of HACAX was tested for 5 cycles. ~100 mg HACAX were soaked in between 20 mL Cr(VI) solution (1, 10, and 100 ppm) and 20 mL 1M NaNO₃ solution periodically. Sample was washed thoroughly with DI water between switching solutions to avoid residual ions attached on the surface. Sample stays in each solution for 24 hrs.

2.5.Characterizations

SEM images were obtained using a Hitachi S-4700 with mixed field emission with a 10 kV–15 kV accelerating voltage. Samples were attached on an aluminum sample holder using a carbon tape. The samples were coated with a thin layer of metals to improve conductivity using a gold palladium plasma spray.

Surface areas and pore size analysis were obtained using a Quantachrome Autosorb-1 pore surface analyzer. All samples were first dried at 110 °C under vacuum before measurement. N₂ was used to measure the surface area and pore volume at 77 K. BET equation was used to calculate the surface area using P/P₀ range from 0.05 to 0.3; The Dubinin-Radushkevitch (DR) equation was used to determine micropore (< 2 nm) volumes. The total pore volume was estimated from the amount of nitrogen adsorbed at P/P₀ = 0.95. Mesopore volume was calculated by the difference of total pore volume and micropore volume.

Coating contents were measured by TGA (Hi-Res TA Instruments 2950 Thermogravimetric Analyzer). The coating content of HACAX was measured by burning off the carbon coating at 800°C in air. Sample's coating content was calculated by the following equation:

Elemental analysis was used to quantify carbon, hydrogen, nitrogen and other heteroatoms presents in the carbon matrix. Chemical composition (C, H, and N) of samples was determined using a Model CE440 Elemental Analyzer. The detection limit for each element was 0.10% with errors 0.06%. Additionally, zinc (Zn) content was determined by

ICP/MS with detection limits on the level of ppb or even ppt. Oxygen content was determined indirectly using principles of mass balance, as estimated using the following equation:

X-ray photoelectron spectroscopy (XPS) experiments were performed on Kratos Axis ULTRA. XPS data acquisition was performed using 13 kV and 10 mA. Survey scans were accumulated from 0–1100 eV with pass energy 160 eV. High-resolution scans were performed with the pass energy adjusted to 40 eV. The inside pressure of the vacuum chamber was maintained at approximately 10^{-9} Torr during the experiments. CasaXPS program is employed to analyze elements and curve fitting. Spectrum has been calibrated to C 1s peak at 284.5 eV.

FTIR (Thermo Nicolet Nexus 670). In DRIFTs (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) mode was used to identify chemical functional groups. Fibrous samples were directly measured without KBr addition. Data acquisition was performed by Omnic[®] software with 32 scans at a resolution of 4 cm^{-1} .

Boehm titration was employed to identify surface functional groups within activated carbon. In this method, three bases (NaHCO_3 ($\text{pK}_a=6.37$), Na_2CO_3 ($\text{pK}_a = 10.25$), NaOH ($\text{pK}_a = 15.74$)) [23] with different pK_a and HCl were used to titrate activated carbon. Traditional Boehm titration assumes only surface oxygen functional groups present on the surface. In order to apply this technique in current system, a hypothesis was made here: the surface functional groups are categorized into: carboxylic acid, lactonic, phenolic, pyridinium, pyridine and pyrrolic groups. Amount of pyridine could be identified by acid

consumption; pyrrolic groups are relatively stable which won't react with any acid/base; in all functional groups, pyridinium is very unique due to its anion exchange properties. Upon soaking in base solution, pyridinium on surface can exchange iodide with OH^- and/or CO_3^{2-} and/or HCO_3^- , which are perceived as partial consumption of base by acid-base titration. Each base or acid can reacts with different acidic functional groups spectrum as shown in Table 1.

The procedure is based on recent progress in Boehm titration [24-26]; In addition, blank comparison was introduced to reduces interference from dissolved CO_2 . HACAX-Cr was soaked in concentrated NaCl and then rinsed with DIW to remove the effect of Cr on titration. Weigh four pieces of samples with each ~ 0.23 g; and then cut into small pieces and placed in glass vials containing 15 mL 0.025M NaOH, Na_2CO_3 , NaHCO_3 , HCl, respectively. A parallel set of blank solution without samples were also prepared and treated using the same procedure. All solutions were sealed and shaken for 24 hrs. Afterwards, solutions with or without samples were both filtered by syringe and membrane filters (Nylon 0.45 μm) to remove solids. Then 5 mL of filtered solutions were transferred to another container and added over amount of 0.05 M HCl (10 mL HCl for NaHCO_3 or NaOH solution, 15 mL HCl for Na_2CO_3 , or 0 mL HCl for HCl solutions). Solutions were then degassed by nitrogen for 2 hrs to remove dissolved CO_2 . Lastly, solutions were titrated by traditional acid/base titration method using phenolphthalein as indicator [23] and microburette for improved resolutions (0.004 mL/drop compared with 0.05 mL/drop for traditional burette). During titration, the solution was kept degassing by N_2 to prevent dissolution of CO_2 .

3. Results and discussion

3.1. Physical properties

Physical characterization showed as synthesized HACAX adopts a core-shell structure, with coating thickness on the order of 1 μm (Scheme 1). Porous carbon is formed as both a coating on fibers, as well as bridging between fibers. Coating content was targeted at $\sim 40\%w/w$ to balance capacity and permeability of the web.

BET pore analysis showed that the HACAX coating possesses 1045 m^2/g surface area ($R^2=0.9992$, $C=32$), with 54% mesoporous content (isotherm and BJH pore size distribution are exhibited in Fig. S1). Mesopores are critical for enhancing mass transfer by serving as a mass transport route between the external surface and micropores.

3.2. Ion exchange properties

Anion exchange activity at natural pH distinguishes HACAX from conventional activated carbon materials, and most N-rich porous carbon previously reported in the literature. Ion exchange kinetics between I^- and NO_3^- was evaluated by batch testing (Fig. 1). Despite being rich in nitrogen, PANCAF has negligible ion exchange activity; however, after methylation, HACAX displayed rapid ion exchange kinetics even comparable to commercial ion exchange resins. The combination of exchange capacity (1.7 mmol/g active coating) and kinetics highlights the significance of the conversion from pyridine to pyridinium surface.

3.3. Chromium adsorption

Cr (VI) adsorption isotherms were performed without adjusting pH (Fig.2). Due to the negative charge Cr(VI) adopts at natural pH, positively charged surface sites are critical for adsorption. Conventional granular activated carbon (GAC) exhibited limited adsorption

capacity with 20 mg/g at 22 ppm equilibrate Cr(VI). Unmodified PANCAF exhibited poor adsorption capacity of 5.2 mg/g even at 497 ppm. Both GAC and PANCAF showed almost negligible at low residual concentration. By comparison, HACAX exhibited greatly improved adsorption capacity up to 79.5 mg/g at 74 ppm equilibrate Cr(VI). The comparison with GAC and PANCAF is especially pronounced at low residual concentration: HACAX displayed adsorption capacity 9.8 mg/g at 4 ppb of Cr(VI), which is several orders of magnitude higher than other tested materials. A word of note is that, pH of initial Cr(VI) concentration 1–100 ppm ranges from 7.4 to 5.4 (Fig. S2). This implies HACAX may be suitable for treating low levels of Cr(VI) adsorption at natural pH.

Since surface charge is influenced by pH, Cr(VI) adsorption isotherms were also characterized at reduced pH (Fig.3). At $\text{pH} > 6$, PANCAF exhibited minimal adsorption capacity. In contrast, HACAX displayed excellent adsorption capacity in the range of 20–50 mg/g. At $\text{pH} < 3$, both PANCAF and HACAX exhibited very high capacity up to 160–190 mg/g based on active materials, which is among the best materials reported in literature[7]. Improved capacity at low pH for both materials suggests protonation of pyridine functional groups, which can adsorb negatively charged Cr(VI). This is consistent with the pyridinic structure possessing positive charge below its expected pK_a of ~ 4 [27]. In addition, Cr(VI) is more readily reduced to Cr(III) in the presence of carbon surface at reduced pH, according to the following electron transfer reactions :

Cr (VI) adsorption kinetics were studied with 4 ppm initial Cr(VI) concentration without adjusting solution pH (Fig.4). The performance comparison between PANCAF and HACAX exhibits the importance of strong anion exchange functionality: before methylation, PANCAF removed negligible amount of Cr(VI); After methylation, HACAX demonstrates rapid kinetics and the ability to bring Cr(VI) from ppm down to low ppb level. This illustrates the electrostatic force provided by strong anion exchange surface functional group are critical for HACAX to work in natural pH. [29] Compared with a strong base anion exchange resin (IXR), HACAX displayed faster kinetics and better selectivity. Perhaps most importantly, HACAX was not releasing Cr(VI) towards the end. Rapid adsorption kinetics are attributed to the small feature size and significant mesopore content, which greatly increases diffusion of Cr(VI) from bulk solution to active sites in the HACAX. Releasing of Cr(VI) by IXR suggests that the functional amine groups of IXR may be oxidized by accumulated Cr(VI). This implies the degradation of functional groups and reduced adsorption capacity, which agrees with recent literature findings [30][30]. In contrast, amine groups of HACAX are relatively stable—which may be critical for drinking water applications.

Stability of HACAX was further examined using regeneration tests alternating between Cr(VI) solution and 1M NaNO₃ (Fig.5). At 1, 10, and 100 ppm levels, results suggest adsorption capacities were almost unchanged after five regeneration cycles. Surprisingly, regenerable adsorption capacities (Cr (VI) exchanged out by NO₃⁻) improved after the first one or two regeneration cycles and plateaued afterwards. This suggests 1) the pyridinium structure was not damaged or oxidized by Cr(VI) accumulation; 2) Cr(VI) might be

converted to other species (e.g. Cr(III)). Previous reports in the literature indicates the conversion of Cr(VI) to Cr(III) in porous carbons only occurs low pH [31]. In order to explore what is happening, it is important to study both the fate of Cr and surface functional groups.

3.4.Characterization and Mechanism study

IR spectrum (Fig.6) reveals the surface functional groups and their changes. As discussed previously, PANCAF possess mainly pyridinic functional group (1652 cm^{-1}), while after reaction, the presence of methyl group and peak shifted from to 1644 cm^{-1} , illustrated that HACAX has been successfully methylated while possess positively charged quaternary amine functional group[20]. In addition, HACAX was characterized before and after Cr adsorption. Non obvious change in spectrum were observed, except for the emerging peaks at 940 cm^{-1} (Cr=O) for HACAX-Cr. This suggests that the presence of chromium within HACAX [32].

XPS studies were employed to understand which functional groups are responsible of converting Cr(VI) into Cr(III) at natural pH. After soaking in 1000 ppm Cr(VI) for a week, I⁻ not exchanged out by Cr(VI) still stays purely in the form of I⁻, suggesting the pyridinium structure was unaffected (Fig.7). XPS Cr 2p spectrum showed that Cr stays in two forms on HACAX surface: Cr(III) and Cr(VI), and Cr(III) represents a substantial amount (Fig.8).

Elemental analysis results of HACAX before and after Cr adsorption are listed in Table 2. Ratio of C/N is unchanged, which suggests that there is no major change in the carbon matrix. O/N ratio greatly increased, corresponding to partially adsorbed HCrO_4^- , and mostly to oxidized carbon surface; which suggests carbon surface was oxidized.

In addition, Cr (III) was also confirmed present in solution in kinetic test: ICP-MS results exhibited that 80 ppb of Cr(III) was released back into solution (Fig. 9). This implies the mechanism involves both electrostatic interaction and oxidation/reduction reactions; Cr(III) present in solution was most likely rejected from HACAX by electrostatic repulsion.

Boehm titration reveals a quantitative change of surface functional groups (Fig.10). After loading HACAX with Cr, phenol group disappeared with the concomitant increase of lactone and carboxylic acid groups. This suggests all of the phenol groups have been converted to carbonyl and/or carboxylic acid groups. Moreover, the increased amount of total acidic groups may suggest 1) non-acidic functional groups like C=C may also have been oxidized into C=O or COOH functional groups; and/or 2) there is an increase in the amount of pyridinium structure. Combined with increasing of basic functional groups as well, it implies the newly formed carboxylic acid functional groups may couple with nearby pyridine functional groups.

Combining the results provided by elemental analysis, XPS, FTIR, Boehm titration, and regeneration test, the following mechanism is proposed (Scheme 2):

- i) HACAX adsorbed Cr (VI) at natural pH due to enhancement of electrostatic attraction by pyridinium functional groups;
- ii) After accumulation of Cr(VI) on the surface, phenolic surface functional groups may reduce anionic Cr(VI) into positively charged Cr(III);
- iii) The positively charged surface repels Cr(III) back into aqueous solutions.

4. Conclusions

In conclusion, methylation of a uniquely formulated PAN-based porous carbon fiber yielded strong anion exchange groups. The resulting HACAX exhibits fast kinetics and high selectivity resulting in rapid removal of Cr(VI) down to ppb levels at natural pH. Moreover, rich surface chemistry may reduce the accumulated Cr(VI) on the surface into less toxic Cr(III) at natural pH. Conversion from Cr(VI) to Cr (III) may facilitate greater adsorption of Cr(VI), and prevent the leaking of Cr(VI) back into solution. Pyridinium anion exchange functional groups on HACAX displayed surprisingly good stability to Cr(VI) oxidation even after 5 cycles of regenerations. This work suggests the strong potential for using HACAX to remove Cr(VI) from drinking water. Other implications for such material may include that it could also potentially serve as a solid-phase PDC catalyst to convert alcohol to aldehydes and/or acid [33, 34] and antibacterial applications [35].

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References

- [1] R.M. Sedman, J. Beaumont, T.A. McDonald, S. Reynolds, G. Krowech, R. Howd, Review of the evidence regarding the carcinogenicity of hexavalent chromium in drinking water, *J Environ Sci Health C Environ Carcinog Ecotoxicol Rev* 24 (2006) 155-182.
- [2] M.D. Stout, R.A. Herbert, G.E. Kissling, B.J. Collins, G.S. Travios, K.L. Witt, R.L. Melnick, K.M. Abdo, D.E. Melarkey, M.J. Hooth, Hexavalent chromium is carcinogenic to F344/N rats and B6C3F1 mice after chronic oral exposure, *Environ. Health Perspect.* 117 (2009) 716-722.
- [3] EWG, EWG-commissioned testing for hexavalent chromium in tap water from 35 cities.
- [4] J. McGahren, H. Chajet, N. Christensen, Contamination claims could affect coal ash regulations, *Coal Age* 116 (2011) 56.
- [5] G.J. Ryan, N.S. Wanko, A.R. Redman, C.B. Cook, Chromium as adjunctive treatment for type 2 diabetes, *Ann. Pharmacother.* 37 (2003) 876-885.
- [6] CDPH, First Drinking Water Standard for Hexavalent Chromium Now Final 2014.
- [7] D. Mohan, C.U. Pittman Jr, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *J. Hazard. Mater.* 137 (2006) 762-811.
- [8] S. Rengaraj, K.H. Yeon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, *J. Hazard. Mater.* 87 (2001).
- [9] J.M.N. Chen, O.J.N. Hao, Microbial chromium-6 reduction, *Crit. Rev. Environ. Sci. Technol.* 28 (1998) 219-251.
- [10] L. Zhang, W. Xia, X. Liu, W. Zhang, Synthesis of titanium cross-linked chitosan composite for efficient adsorption and detoxification of hexavalent chromium from water, *J. Mater. Chem. A* 3 (2015) 331-340.
- [11] H. Mohammadi, M. Gholami, M. Rahimi, Application and optimization in chromium-contaminated wastewater treatment of the reverse osmosis technology, *Desalination and Water Treatment* 9 (2009) 229-233.
- [12] S. Habibi, A. Nematollahzadeh, S.A. Mousavi, Nano-scale modification of polysulfone membrane matrix and the surface for the separation of chromium ions from water, *Chem. Eng. J.* 267 (2015) 306-316.
- [13] M. Owlad, M.K. Aroua, W.A.W. Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: A review, *Water, Air, Soil Pollut.* 200 (2009) 59-77.
- [14] J. Guertin, J. Jacobs, C. Avakian, Chromium (VI) handbook, CRC Press 2005.
- [15] G. Huang, J.X. Shi, T.A.G. Langrish, Removal of Cr(VI) from aqueous solution using activated carbon modified with nitric acid, *Chem. Eng. J.* 152 (2009) 434-439.
- [16] R. Dobrowolski, E. Stefaniak, Study of chromium(VI) adsorption from aqueous solution on to activated carbon, *Adsorpt. Sci. Technol.* 18 (2000) 97-106.
- [17] A. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method, *Chemosphere* 56 (2004) 91-106.
- [18] Z. Yue, S.E. Bender, J. Wang, J. Economy, Removal of chromium Cr(VI) by low-cost chemically activated carbon materials from water, *J. Hazard. Mater.* 166 (2009) 74-78.

- [19] K. Pillay, E.M. Cukrowska, N.J. Coville, Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution, *J. Hazard. Mater.* 166 (2009) 1067-1075.
- [20] W. Zheng, J. Hu, Z. Han, Z. Wang, Z. Zheng, J. Langer, J. Economy, Synthesis of porous carbon fibers with strong anion exchange functional groups, *Chem. Commun.* 51 (2015) 9853-9856.
- [21] W. Lukens, Final Report: SERDP SEED Project ER-1428 - SERDPMModified Activated Carbon Perchlorate Sorbents, Lawrence Berkeley National Laboratory, 2007.
- [22] E. Pehlivan, S. Cetin, Sorption of Cr(VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV-visible spectrophotometer, *J. Hazard. Mater.* 163 (2009) 448-453.
- [23] T. Bandosz, *Activated Carbon Surfaces in Environmental Remediation*, Elsevier Science & Tech 2007.
- [24] S.L. Goertzen, K.D. Thériault, A.M. Oickle, A.C. Tarasuk, H.A. Andreas, Standardization of the Boehm titration. Part I. CO₂ expulsion and endpoint determination, *Carbon* 48 (2010) 1252-1261.
- [25] Y.S. Kim, S.J. Yang, H.J. Lim, T. Kim, K. Lee, C.R. Park, Effects of carbon dioxide and acidic carbon compounds on the analysis of Boehm titration curves, *Carbon* 50 (2012) 1510-1516.
- [26] A.M. Oickle, S.L. Goertzen, K.R. Hopper, Y.O. Abdalla, H.A. Andreas, Standardization of the Boehm titration: Part II. Method of agitation, effect of filtering and dilute titrant, *Carbon* 48 (2010) 3313-3322.
- [27] J.R. Pels, F. Kapteijn, J.A. Moulijn, Q. Zhu, K.M. Thomas, Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis, *Carbon* 33 (1995) 1641-1653.
- [28] W. Liu, J. Zhang, C. Zhang, L. Ren, Preparation and evaluation of activated carbon-based iron-containing adsorbents for enhanced Cr(VI) removal: Mechanism study, *Chem. Eng. J.* 189–190 (2012) 295-302.
- [29] W. Zheng, J. Hu, Z. Han, Z. Wang, Z. Zheng, J. Langer, J. Economy, Synthesis of porous carbon fibers with strong anion exchange functional groups, *Chem. Commun.* (2015).
- [30] K. Xiao, F. Xu, L. Jiang, N. Duan, S. Zheng, Resin oxidization phenomenon and its influence factor during chromium(VI) removal from wastewater using gel-type anion exchangers, *Chem. Eng. J.* 283 (2016) 1349-1356.
- [31] D. Park, Y.S. Yun, J.M. Park, Comment on the removal mechanism of hexavalent chromium by biomaterials or biomaterial-based activated carbons, *Industrial and Engineering Chemistry Research* 45 (2006) 2405-2407.
- [32] Y.G. Ko, U.S. Choi, T.Y. Kim, D.J. Ahn, Y.J. Chun, FT-IR and isotherm study on anion adsorption onto novel chelating fibers, *Macromol. Rapid Commun.* 23 (2002) 535-539.
- [33] P. Zhang, Y. Gong, H. Li, Z. Chen, Y. Wang, Selective oxidation of benzene to phenol by FeCl₃/mpg-C₃N₄ hybrids, *RSC Adv.* 3 (2013) 5121-5126.
- [34] K. Chen, P. Zhang, Y. Wang, H. Li, Metal-free allylic/benzylic oxidation strategies with molecular oxygen: Recent advances and future prospects, *Green Chemistry* 16 (2014) 2344-2374.

[35] H. Luo, C. Gu, W. Zheng, F. Dai, X. Wang, Z. Zheng, Facile synthesis of novel size-controlled antibacterial hybrid spheres using silver nanoparticles loaded with poly-dopamine spheres, RSC Adv. 5 (2015) 13470-13477.

Table 1 Titration with proposed different model compounds

Titration	NaOH	Na ₂ CO ₃	NaHCO ₃	HCl	Calculated or Perceived as
Surface Groups	a	b	c	d	
Carboxylic Acid	Yes	Yes	Yes	No	c
Lactonic	Yes	Yes	No	No	b-c
Phenolic	Yes	No	No	No	a-b
Pyridinium	Partially	Partially	Partially	No	Partially of <i>a</i> , or <i>b</i> , or <i>c</i>
Pyridine	No	No	No	Yes	d
Pyrrolic	No	No	No	No	

Table 2 Elemental Analysis of HACAX before and after Cr(VI) Adsorption

Samples	Weight percent					Atomic Ratio		
	C	H	N	O	Cr	C/N	O/N	Cr/N
HACAX	25%	1.2%	7.8%	8%	-	3.8	0.9	-
HACAX-Cr	20.9%	1.2%	6.5%	10%	2.54%	3.8	1.4	0.0005

Scheme 1 Synthesis of porous carbon with strong anion exchange functional group (HACAX)

Fig. 1 I^- and NO_3^- exchange as a function of time for of PANCAF, HACAX and commercial ion exchange resins IXR-B

Fig. 2 Cr(VI) adsorption isotherm at natural pH by PANCAF, HACAX and commercially available Granular Activated Carbon (GAC)

Fig. 3 Cr(VI) adsorption isotherm at different pH

Fig. 4 Cr(VI) adsorption kinetics with initial 4 ppm Cr(VI) at neutral pH by PANCAF, HACAX and GAC and a commercial ion exchange resin

Fig. 5 Adsorption and regeneration of Cr(VI) isotherm at 1, 10, 100 ppm Cr(VI). 1M NaNO₃ was used as regeneration solution.

Fig. 6 FTIR of HACAX before and after interactions with Cr (VI)

Fig. 7 XPS spectrum of Iodide

Fig. 8 XPS Spectrum of Cr before and after adsorbing Cr(VI)

Fig. 9 Conversion from Cr(VI) to Cr(III) by HACAX at neutral pH;

Fig. 10 Boehm Titration of HACAX before and after Cr (VI) adsorption.

Scheme 2 Mechanism of Interactions between Cr(VI) with HACAX surface functional groups. Step 1: attraction from bulk to carbon surface, accumulation, migration to nearby functional groups; Step 2: Oxidation/reduction reaction, migration, adsorption and repelling Cr^{3+} back to bulk.

STEP 1 - Attraction, accumulation, and migration to nearby functional groups

STEP 2 - Oxidation/reduction, migration, adsorption & repeling Cr^{3+}