SYNTHESIS OF ANION EXCHANGE/ACTIVATED CARBON FIBER HYBRID MATERIALS FOR AQUEOUS ADSORPTION OF TOXIC HEXAVALENT CHROMIUM

BY
WEIHUA ZHENG

THESIS
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Adviser:
Professor James Economy
ABSTRACT

Hexavalent chromium, also known popularly as the “Erin Brockwich chemical”, has recently been identified as a carcinogen by ingestion. Unfortunately, it is present in drinking water supplies in United States. An effective, Point-of-Use (POU) based technology to remove Cr(VI) in tap water is urgently needed to protect human beings against this carcinogen. Due to the inadequate state-of-the-art technology for rapid, selective removal of Cr(VI), a unique hybrid activated carbon/anion exchange system (HACAX) has been developed for the first time in our group. HACAX was synthesized by methylation of PAN based Chemically Activated Carbon Fibers. The HACAX was characterized by BET, SEM, XPS,TGA and elemental analysis. The ion exchange property and adsorption performance towards Cr(VI) were also studied comprehensively. HACAX displays not only very high mesopore content with a surface area up to 1085 m²/g based on coating, but also good strong base ion exchange capacity up to 1.5 meq/gC and exceptionally fast kinetics due to multi-scale facilitated mass transfer. Compared with conventional activated carbon and ion exchange resin systems, HACAX has excellent adsorption capacity towards Cr(VI) even at natural pH and very low concentrations of Cr(VI); besides, HACAX has very fast kinetics and high selectivity which can remove Cr(VI) from 4 ppm down to ppb levels or below; moreover, this hybrid material is also able to convert Cr(VI) to non-toxic Cr(III) to prevent the leaking of Cr(VI). These results showed that HACAX is a unique and effective adsorbent for POU Cr(VI) removal and potentially other anion treatments.
To My Love and Be Loved Family….
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1.1 Drinking Water Contamination - Cr(VI)

Hexavalent chromium, also named chromium-6 or Cr(VI), is a toxic anion in aqueous solutions. Cr(VI) is well known as a notorious chemical to the public from the movie “Erin Brockovich”, which highlighted the lawsuits on the drinking water contaminated by Cr(VI) in Hinkley, California. The case was settled in 1996 for $333 million, which was the largest settlement ever paid in US history[1, 2].

After 15 years, it turns out that Hinkley was not alone: according to a recent nationwide drinking water supply survey conducted in December 2010, 31 out of 35 cities in the United States tested were contaminated by Cr(VI)[3]; more importantly, Cr(VI) in drinking water not only causes health issues like anemia, damage of gastrointestinal tract and kidney/ liver malfunctions, but also was recently identified as carcinogen which causes stomach cancer [4-7]. The widespread carcinogenic Cr(VI) in drinking water supply has already aroused wide public concerns and panic about whether their tap water was contaminated by this carcinogen[8, 9].

To date, USEPA hasn’t established a legal limit for Cr(VI) in drinking water yet; but an MCL (maximum contaminant level) for total chromium has been set as 100 ppb to protect against allergic dermatitis[10]. The state of California has established a very strict public health goal (PHG) of 0.02 ppb for Cr(VI) as of July, 2011[11, 12].

Recognizing the carcinogenic character and widespread presence of Cr(VI), currently EPA is in the process of establishing a new standard for Cr(VI)[13, 14]. However, before the new regulations come out demanding better treated drinking water by Public Water Systems
it is critical to develop and implement an effective, Point of Use (POU) based technology to remove Cr(VI) in tap water and thus protect against this carcinogen, especially for those vulnerable populations and areas.

1.2 Treatment Technology

In the past few decades, several technologies have been developed for wastewater Cr(VI) removal, including chemical precipitation[16], ion exchange[17], membrane separation[18], sedimentation[19], reduction[20] and adsorption[21], etc. Of all these methods, activated carbon emerges out as the most popular and widely used adsorbent in wastewater treatment applications due to its high surface area, porous internal structure, controllable surface chemistry, cost-effectiveness and ease of use[22].

While the effectiveness of commercially available Granular Activated Carbon (GACs) for wastewater treatment of Cr(VI) at levels of 100-1000 ppm worth noted, GACs suffer from a number of drawbacks including slow adsorption kinetics, poor selectivity and low capacity for Cr(VI). These features limit its application for drinking water treatment, where Cr(VI) ions are present at very low levels of ppm or even ppb[3, 23]. Besides, GACs needs to be operated under low pH for adequate capacity, which is impractical for POU application [21, 24, 25]. There remains no indication of an adequate material for fast and selective removal of Cr(VI) from drinking water in the literature. So it is very important to develop a novel technology to be able to selectively and rapidly to remove this carcinogen at trace level.

1.3 Activated Carbon Fiber System Development and Derivation

To address the slow kinetics of GACs, the Economy group [26-33] has developed a new family of chemically activated carbon fibers by using low-cost glass fibers coated with the activated carbon fibers (CAFs). CAFs offers a number of advantages over GACs,
including lower activation temperatures < 450 °C; cost-effectiveness ($1-2/lb) due to use of glass fiber as core substrate; excellent wear characteristics; and more importantly, the ~7 µm diameter of CAFs greatly improved contact efficiency and thus provides much faster intraparticle adsorption kinetics compare with the mm size of GACs. CAFs are very effective in removing trace levels of organic contaminants in drinking water below 1 ppb, such as BTEX (benene, toluene, ethylbenzene and p-xylene)[33], TCE (trichloroethylene), atrazine, half mustard, humic acid, etc.[28].

In 2002, in order to expand this novel system for inorganic ions removal, the Economy group[34, 35] developed a hybrid activated carbon/cation exchange (HACCX) system through sulfonation of phenolic based activated carbon coated on glass fibers. HACCX combines a cation exchange functional group in a micropore structure of activated carbon fibers, which shows excellent adsorption properties towards cationic heavy metals such as Cs\(^+\), Sr\(^{2+}\), etc.[35].

1.4 Objective and Organization

Motivated by the need to address the problem of Cr(VI) in drinking water as well as the inadequate state-of-the-art technology, the current study was undertaken to design a novel materials system with rapid kinetics and good selectivity to bring trace Cr(VI) down to below ppb level. In light of success of cation exchangeable activated carbon system for cation heavy metal removal[35], a concept of novel anion exchangeable activated carbon system is proposed and explored in this work for Cr(VI) anion removal.

Analogous to the HACCX system [34, 35], this hybrid activated carbon/anion exchange (HACAX) material would have high surface area with more active sites consisting of a permanently positive charged surface to attract and adsorb anions such as Cr(VI), and greatly improved kinetics due to hydrophilic surface and the small fiber diameter of 7 µm.
All of these characteristics would contribute to the feasibility for POU applications of this hybrid material bring trace level of Cr(VI) down to below the ppb level. To the author’s knowledge, there is no work done on this novel material yet, since it is very difficult to introduce a permanently positive charge onto the surface of activated carbon, which makes it exhibits anion exchange property at natural pH.

In this work, positive charge functional group was introduced to the surface by choosing a special nitrogen-rich PAN (polyacrylonitrile) as precursor to make chemically activated carbon fiber (CAFs). CAF has pyridine-like ladder structure, which could be further methylated to introduce a methyl group onto pyridine-N, and thus display a permanent positive charge for anion exchange adsorption.

In Chapter 2, basic background information of Cr(VI) and state-of-the-art technologies for Cr(VI) removal are reviewed, and feasibility of design of the hybrid material is justified.

In Chapter 3, experimental procedures and methods are described for the synthesis, characterization and Cr(VI) adsorption test for the HACAX material.

In Chapter 4, in the first part, the ion exchange properties and characterization of the hybrid materials is discussed. In the second part, Cr(VI) adsorption kinetics and equilibrium performance at trace level is discussed, including the characterization by XPS, elemental analysis and adsorption kinetic tests, an novel Cr(VI) electrostatic attraction – Cr(VI) accumulation – Cr(VI) surface reduction to Cr(III) – Cr(III) repulsion adsorption mechanism for this hybrid material is proposed. In the end, a summary and a future work plan will be described.

1.5 References


CHAPTER 2
LITERATURE REVIEW

2.1 Chromium

2.1.1 Sources and Uses

Chromium (Cr) is a steely-gray, lustrous, hard, transition metal, and it is the 21st most abundant element in Earth’s crust[1]. Cr is widely used in industry such as electroplating, leather tanning and wood preserving, etc.[2]. Due to its high corrosion resistance and hardness, Cr is a crucial element for producing stainless steel and superalloys. United States is one of the biggest consumers for Cr with 538,000 tons chromium consumption annually. 80% of Cr is used for stainless steel industry, and currently there is no viable substitute for it.

Due to extensive use in industry, Cr has become one of the major contaminants in drinking water. In some places, chromium is released into natural water on level of 5 ppm via leakage, unsuitable storage or improper disposal practices[2, 3]. In 1988, 142,000 tons of chromium was discharged into drinking water around the world[4], which presents serious environmental and human health problems[5, 6].

2.1.2 General Chemistry

In natural water, Cr exists almost exclusively as Cr(III) oxidation state or Cr(VI) oxidation state. Cr(III) is a hard acid, and it is insoluble in water and thus immobile under ambient conditions; Cr(III) could exist as Cr$^{3+}$, CrOH$^{2+}$, Cr(OH)$_3$, Cr(OH)$_4$$^-$, the form of which depends on the pH of aqueous solution.
Cr(VI) is a strong oxidizer and it exists only in oxygenated states which are highly soluble in natural water. Cr(VI) exists as $\text{CrO}_4^{2-}$, $\text{HCrO}_4^-$ and $\text{Cr}_2\text{O}_7^{2-}$ depends on pH and concentration of solution[7]. Most of these three forms of Cr(VI) are very soluble and mobile in natural water [8, 9], which pose a high risk to the spread of its toxicity.

Chromium is a redox active contaminant with dramatic alterations in its mobility and toxicity with different states. The following diagram shows the pH and redox potential between state of Cr(VI) and Cr(III)[10].

![Stability diagram of chromium at various equilibrium potential and pH in aqueous solution](image)

Cr(VI) could be reduced to Cr(III) easily especially at low pH, which provides a pathway for Cr(VI) removal at low concentrations.

### 2.1.3 Health Effects

Cr(III) is an essential compound for human beings at low concentration. Cr(III) is a critical trace element nutrient for glucose metabolism. Together with Insulin, Cr(III) is responsible for reducing blood sugar levels and control of diabetes.
Besides, Cr(III) can also regulate blood cholesterol level by reducing low density lipoproteins in blood and aid fat metabolism [2].

In contrast to Cr(III), Cr(VI) is dangerous to human beings due to its high toxicity and carcinogenetic properties[9]. It has been well-known for half a century that inhalation or skin contact of Cr(VI) causes acute toxicity, irritation and ulceration of the nasal septum, asthma, dermatitis and even cancers [2, 7, 11].

However, Cr(VI) by ingestion was not commonly accepted as a carcinogen before 2009. The reason is that a forged paper published in the Journal of Occupational and Environmental Medicine in 1997 [12] claimed that Cr(VI) ingestion would not cause cancer. This work greatly influenced EPA to make MCL assessments for Cr(VI) as well as held back research study activities on carcinogenicity of Cr(VI).

It was not until 2005 when this error was uncovered by the Environmental Working Group (EWG) and the Wall Street Journal[13]. It turned out that the paper was forged and financially supported by Pacific Gas & Electric Co. (PG&E), an energy company who provides 2/3 of California’s natural gas and electricity, as well as disposing large amounts of chromium into water. Interestingly, PG&E is also the company who contaminated the drinking water in Hinkey with Cr(VI) and then was defeated by Erin Brockovich and paid $333 million in fines. Apparently, PG&E hired people to forge this paper in order to avoid the strict standard for Cr(VI) in drinking water by EPA[13].

After that, this journal editor retracted the paper, and researchers and regulators started a new round of re-evaluation research activities to investigate the toxicity as well as human and animal cancer studies by ingestion of Cr(VI) from drinking water, in order to estimate cancer risk and establish possible new regulations[14].
In 2006, Sedman et al. [15] studied toxicokinetic and genotoxicity of Cr(VI) to animal cells. The result shows that part of hexavalent chromium ingested can be absorbed and enters cells of several different tissues and causes DNA damage.

After that, California EPA conducted a rigorous re-analysis of the original data[16] from the forged publications, which showed that there is a statistically significant increase in stomach cancer by Cr(VI) exposure compared with general populations without exposure[13].

Moreover, National Toxicology Program (NTP, part of NIH (National Institutes of Health)) [17, 18] carried out comprehensive animal studies in 2008 and 2009. The results revealed statistically significant, dose-related increases in tumors in the duodenum and the small intestine of mice, and tumors in the oral cavity of rats. This report provided additional evidence of the link between Cr(VI) to cancer.

The increases in stomach tumors in both human and animal studies, along with the toxicology and mechanistic data suggest that Cr(VI) ingested orally poses a carcinogenic risk and more strict standards for Cr(VI) in drinking water should be considered.

2.1.4 Spread of Cr(VI) in Drinking Water

2.1.4.1 Cr(VI) in U.S.

In United States, monitoring of Cr(VI) in drinking water supply was not mandatory in most states except in California, due to the lack of regulations by USEPA as there was no connection between cancer and Cr(VI) by ingestion before. In 2010, EWG conducted a nationwide survey of drinking water supplies in 35 cities in the U.S, which showed that 31 cities’ of 35 (89%) drinking water supply was contaminated by carcinogenic Cr(VI)[13]; Moreover, 25 cities in this survey have even higher levels than California’s proposed public health goal (PHG); The highest
one, Norman city from Oklahoma has Cr(VI) in their drinking water measured at 200 times California’s proposed safe limit, as shown in Figure 2.2.

In the survey by EWG, the contaminated cities’ drinking water served more than 26 million people, and it is estimated that at least 74 million people in 42 states are affected by Cr(VI) contaminated drinking water, as indicated in Figure 2.3.
Additionally, nearly 40% of California drinking water sources tested was contaminated by hexavalent chromium above safety levels.

This survey has been cited and reported by major newspapers including The New York Times, The Washington Post, Los Angeles Times, Chicago Tribune, CBS News, etc., which brought public concerns and EPA’s quick response to promise to speed up the new regulation process[19-24].

There are also several Cr(VI) contamination at very high levels in United States. In 2009, the ground water in Midland, Texas had Cr(VI) levels up to 5.25 ppm[25][25]. Another occurrence of Cr(VI) in groundwater with 0.58 ppm was in Hinkley, California, which was brought to the public attentions by the efforts of Erin Brockovich[26].
2.1.4.2 Cr(VI) around the world

Water contamination with hexavalent chromium is also a worldwide problem. In Sukinda, India, which is regarded as the world’s most polluted locale by the Times Journal, 60% of drinking water contains double the Cr(VI) as compared with WHO standards of 50 ppb[27]. With an exposed population of 2.6 million, it was estimated that 85% of the deaths in this areas were due to chromium related diseases. In Jinzhou, China, due to the chromium ore processing, the drinking water was polluted by an industry wastestream which led to higher cancer risk for local residents. Dr. Zhang’s survey and investigation was the first time that scientists found statistically significant relations between human cancers and chromium in drinking water [16]. In Aug., 2011, a chemical plant in Qujing, China dumped 5,000 tons of chromium waste near Chachong Reservoir, whose downstream river feeds the Pearl River, one of China’s longest waterways and threaten the water sources for tens of millions of residents[28]. In Greece, ground water associated with industrial waste in central Euboea and Asopos valley was contaminated by Cr(VI) at levels higher than 50 ppb. Assopos aquifer also showed a wide range of Cr(VI) concentrations from 2 to 180 ppb [29].

2.1.5 Regulations and New Regulation Progress

2.1.5.1 U.S.EPA

Starting from 1992, EPA has set a MCL (maximum contaminant level) for total chromium at 100 ppb in order to protect against allergic dermatitis. This standard includes both nutrient Cr(III) and toxic Cr(VI) [3].

In recent years, as more and more scientific evidence was published that Cr(VI) may cause stomach cancer by ingestion [16-18], EPA began a rigorous and comprehensive review of Cr(VI) health effect to establish a more strict standard. In
September 2010, EPA proposed to classify Cr(VI) as likely to be carcinogenic to humans via ingestion[3], and a final determination about the carcinogenicity of Cr(VI) will be made by 2011[30]. On December 22, 2010, in correspondence to 89% of the cities in the USA is contaminated by Cr(VI), EPA administrator Lisa Jackson announced that EPA is re-evaluating how wide-spread and prevalent this contaminant is, and that “it is likely that EPA will tighten drinking water standards to address the health risks posed by Cr(VI)”[30].

2.1.5.2 California EPA

As a frontier in environmental regulations, California currently regulates total chromium under 50 ppb as MCL. In 2009, in response to the risk of gastrointestinal tumors caused by Cr(VI) in drinking water studied by NTP[17, 18], California EPA proposed setting a public health goal (PHG) of 0.06 ppb for Cr(VI) in drinking water[31]. In December 2010, in order to better protect human health, California EPA announced a new draft PHG of 0.02 ppb Cr(VI) in drinking water[32].

2.1.5.3 Other Countries

Most countries, including the supranational European Union (EU) have currently established a limit of 50 ppb for total chromium in drinking water [33, 34]. India has set a India Standard (IS) of 50 ppb for Cr(VI) in drinking water[35]. Currently China has set a standard for the Cr(VI) at 50ppb in drinking water[36]. Italy has a more strict regulation in that Cr(VI) in drinking water needs to be lower than 5ppb[34, 37].

2.2 Cr(VI) Removal Technologies

In literature, several methods have been developed for Cr(VI) removal from wastewater and drinking water, including adsorption[7], ion exchange[38],
reduction[39], membrane separation[40], precipitation[41], etc. These methods are reviewed in the following sections.

2.2.1 Membrane Separation

Membrane processes have been studied for chromium removal majorly from wastewater. Aroua et al.[42] removed Cr(VI) from 10 ppm concentration in water using either chitosan, PEI or pectin-enhanced ultrafiltration (UF) process with 30% rejection rates. Muthukrishnan et al.[43] used two nanofiltration (NF) composites polyamide membranes for Cr(VI) removal. At initial concentration of 1000 ppm Cr(VI), the rejection rates are 94% and 99%, respectively. Reverse Osmosis (RO) has also been applied for Cr(VI) removal both in wastewater and drinking water. At both feed concentration of 10,000 ppm and 10 ppm, the rejection rate are up to 99%,[44], [45].

However, the current removal efficiency of UF and NF still needs improvement in order to achieve ppb levels. Although RO membranes can achieve higher effluent water purity, they must operate at higher pressure which can be expensive, and there is no data available on removing Cr(VI) at the ppb level.

2.2.2 Ion Exchange

Ion Exchange Resins (IXR) have been widely used in industry for separation of inorganic ions. The main advantages of ion exchange are high affinity towards Cr(VI). Sapari et al.[46] studied Dowex 2-X4 anion exchange resin which can remove Cr(VI) down to detection limit after 8 bed volumes of 8 ppm. Pehlivan et al.[9] studied two macroporous strong base IXR (Lewatit MP64 and Lewatit MP 500), which shows 20 mg/g adsorption capacity at 52 ppm initial Cr(VI) concentration and pH 5.0.
Strong base ion exchange resins have charge sites which can attract and adsorb Cr(VI) through electrostatic forces thus improving kinetics[47]. However, ion exchange resins have some disadvantages: it is more expensive compare with other adsorbents; the size of ion exchange resin is on the level of 1mm. Thus, the kinetics for removing Cr(VI) is still very slow at the ppb level of contaminants, and flow rate for flow-through test is remarkably slowed down[48]. This limits its applicability to POU treatment (requires fast flow rate ~ 10 BV/min); also, there is still no indication of capacity of ion exchange materials at drinking water contamination level. Moreover, ion exchange resin does not have a pathway for converting Cr(VI) to less toxic forms, such as Cr(III). This might lead to leaking of toxic Cr(VI) in POU applications as more background ions flow through and exchange out the adsorbed Cr(VI). All these factors limit use of ion exchange resins for POU treatment.

2.2.3 Activated Carbon

Activated Carbon is the main adsorbent in wastewater treatment due to its low cost, effectiveness and ease of operation [49]. Activated carbon has a well developed pore structure and a very high surface area from 500 to 1500 m\(^2\)/g. Also, a wide spectrum of surface functional groups could be prepared which interact, oxidize or reduce the target compounds to enhance adsorption. All these properties make activated carbon and its derivatives widely used in the treatment of Cr(VI) contaminated waters[8].

Commercial activated carbon such as GACs has been studied for Cr(VI) removal extensively. In the literature, most of the studies investigate the adsorption performance at low pH and initial Cr(VI) concentration from 10 ppm up to 1000 ppm[7, 8, 50]. Han et al. [51] studied Filtrasorb 400 commercial activated carbon (GACs) for Cr(VI), and the result showed an adsorption capacity of 0.18 mg/g.
Activated Carbon Fibers (ACF)\cite{52} has also been used for Cr(VI) removal, and has shown better adsorption capacity up to 22.29 mg/g and improved kinetics due to the geometry of the fiber which is relatively small\cite{53}.

In order to improve the adsorption performance, various efforts have been made to improve the affinity towards specific contaminants by chemical modification. Acidic treatment is the most popular way to introduce functional groups to improve the heavy metal adsorption. Huang et al. \cite{49} treated activated carbon with nitric acid, which showed improved adsorption capacity up to 16.1 mg/g at pH 4.0 and an initial concentration of 25 ppm.

There are very few reports on low concentration of Cr(VI) removal. Pillay et al\cite{54} studied the Multi-walled carbon nanotubes (MWCNT) for Cr(VI) removal at ppb levels. The study showed that MWCNT can adsorb up to 98\% of Cr(VI) at initial concentration of 100 ppb. Another paper by Yue et al\cite{55} studied Cr(VI) removal by Activated Carbon Pellet (Pellet-600) with high mesopore content. The study showed that 176 mg of Pellet-600 is able to remove 4ppm of 200 ml Cr(VI) down to 2 ppb.

The dominant mechanism for Cr(VI) adsorption by activated carbon includes three steps: 1) surface attraction, 2) surface reduction from Cr(VI) to Cr(III) \cite{56} and 3) adsorption of Cr(III) \cite{7}. Since in water Cr(VI) is an anion in form of CrO$_4^{2-}$ or HCrO$_4^-$, sorption of Cr(VI) only happens at low pH when the surface is positively charged\cite{57}. A spectrum of functional groups such as hydroxyl and ketone on the surface of activated carbon is capable of reducing Cr(VI) to Cr(III) \cite{7}.

While the merits of the activated carbon system have been noted, activated carbon also suffers from several problems: Cr(VI) adsorption has to be carried out at low pH, which implies the usage of large amount of acid chemicals and is not applicable for POU treatment; the surface of an untreated activated carbon is non-
polar and hydrophobic, and therefore the equilibrium is attained very slowly due to slow pore diffusion of Cr(VI) ions[58]; The geometric size of GACs are very big on the level of mm, which limits the mass transfer and thus kinetics. An AC system with permanently positive charged surface and small mass transfer distance is necessary for POU applications.

2.2.4 Others

There are also several other technologies which have also been studied.

Precipitation such as chemical precipitation [57] and electrochemical precipitation [8] is used primarily for wastewater treatment. These techniques are only effective for high concentration of chromium, and the disposal of residual Cr(VI) from incomplete removal and sludge is still a challenge.

There are also numerous studies on low-cost adsorbents, such as chitosan have very good capacity up to 100 mg/g, which is a very competitive process [7]. However, they also suffer from problems including high pH dependence and slow kinetics due to nonporous structure which limits POU applications [7].

Most of the literature for Cr(VI) removal is on wastewater system, where it is present at ~100 or ~1000 ppm; more studies are needed to focus on drinking water, where Cr(VI) presents at ppb to a few ppm level [54, 55]. Kinetics and selectivity are the two limiting factors when applied the current technology for POU applications.

2.3 Novel Activated Carbon Fiber System

In order to improve the mass transfer and adsorption rates, a novel family of chemically activated carbon fibers by using low-cost glass fibers as substrate (CAF) have been developed by the Economy group [59-66]. CAF offers a number of
advantages over GACs: lower activation temperature < 450 °C; very low cost ($1-2/lb) due to use of glass fiber as a core substrate; excellent wear characteristics; and most importantly, the ~7 µm diameter of CAFs greatly improves contact efficiency and thus greater adsorption rates compared with mm size of GACs. CAFs are very effective in removing trace level of organic contaminants in drinking water down to below 1 ppb, such as BTEX (benene, toluene, ethylbenzene and p-xylene)[66], TCE (trichloroethylene), atrazine, half mustard and humic acid[61], etc.

Besides, a hybrid cation exchange/activated carbon fiber system was also developed based on CAFs by Economy [67, 68]. This novel hybrid activated carbon/cation exchanger (HACCX) material was prepared by sulfonation of phenolic based activated carbon coated on glass fibers to introduce strong –SO₄H⁻ and weak -COOH and -OH functional group. HACCX combines cation exchange functional groups in a micropore structure of activated carbon fibers, which shows excellent adsorption properties towards cation heavy metals such as Cs⁺, Sr²⁺, etc.[68].

In parallel to the opportunities for the of HACCX system, there remains the need for an hybrid anion exchange/activated carbon fiber system, which potentially can address anion contaminants problems in drinking water effectively, especially for anion heavy metals, such as Cr(VI), As(III), etc.

2.4 Vision for the Hybrid Materials

Motivated by the gaps between the needs to remove trace Cr(VI) down to ppb level for POU applications and lag behind state-of-the-art technology, the current study is intended to design a novel materials system with rapid kinetics and great selectivity; In light of the success of heavy metal removal by cation exchangeable activated carbon fiber system [68], a concept of novel anion exchangeable activated
carbon system is proposed and explored in this work for Cr(VI) like anion removal. If successfully made, this hybrid activated carbon/anion exchange (HACAX) materials potentially should display the properties indicated below:

- High surface area to provide more functional sites and improve mass transfer in small scale;
- Positively charged sites in natural pH to attract Cr(VI) electrostatically without changing pH of natural water;
- Surface reducing functional group to convert Cr(VI) to low toxic Cr(III) at the same time of adsorption process;
- Fiber form with a diameter of 7 µm with glass fiber core to improve mass transfer in larger scale as substrate without introducing massive pressure drop.

With all these properties, HACAX combined the advantages of AC and IXR plus enhanced kinetics in multi-scale, and hence could more effective for Cr(VI) removal. It is very important to synthesis such a hybrid material and examines it.

To the author’s knowledge, there is no literature on introducing strong base functional group onto activated carbon yet. The conventional approach to introduce permanent positive charge surface, similar to the synthesis of an anion exchange resin, is to add a chloromethyl group to activated carbon, and then introduce trialkylamine to form positively charged amines; it should be noted that it is very difficult to introduce a chloromethyl group to the rigid carbon structure.

One possible way to have the quarterized amines on activated carbon is through direct N-methylation of a special nitrogen-containing activated carbon. If nitrogen incorporates in the activated carbon in form of pyridine or pyridine-like structures, quarterized amines could be formed by direct N-methylation. As a popular
precursor for carbon fibers used today, PAN (polyacrylonitrile) could also be used as precursor for activated carbon fiber with very high nitrogen content[69, 70]. The mechanism of the heat treatment of PAN has been studied extensively, and the most accepted mechanism from polymer to carbon is cyclization to form ladder polymer structure followed by graphitization where ladder structures start to fuse together, as shown in Figure 2.4.

As for CAFs, Yue et al.[62] studied the CAFs using PAN (polyacrylonitrile) as precursor by XPS, and found out the about half of the nitrogen was in pyridine form, as shown in Figure 2.5. Both papers implied that the presence of pyridine-like structure and thus the methylation reactions could possibly introduce the quarterized amines to the surface, as shown in Figure 2.6, which is the basis for the current work.

Figure 2.4 Proposed Mechanism for PAN during stabilization (left) and Carbonlization (right)[69].
Figure 2.5 XPS N s spectra of PAN powder, stabilized PAN and activated PAN on fiberglass

![Graph showing XPS N s spectra of PAN powder, stabilized PAN and activated PAN on fiberglass.](image)

Figure 2.6 Proposed mechanism to synthesis Hybrid Activated Carbon/Anion Exchange Materials

![Graph showing the proposed mechanism to synthesis Hybrid Activated Carbon/Anion Exchange Materials.](image)

2.5 References


EWG, EWG-commissioned testing for hexavalent chromium in tap water from 35 cities.


Hawthorne, M., High levels of chromium found in Chicago-area tap water, in Chicago Tribune 2010: Chicago.

Koch, W., Study: Tap water in U.S. cities has probable carcinogen, in USA TODAY 2010.


CHAPTER 3
EXPERIMENTAL

There are two objectives of the experiment of design: 1) explore the synthesis of anion exchange/activated carbon fibers (HACAX), and 2) study the Cr(VI) removal performance of this novel HACAX.

3.1 Chemicals and Reagents

Polyacrylonitrile (PAN) ((C₃H₃N)n, Mₜ ~ 150,000, Aldrich Co. Cat. 181315) and Zinc Chloride (ZnCl₂, Reagent grade, ≥ 98% Sigma Cat. 208086) was used for the synthesis of an activated carbon coating on a substrate fiber (Craneglass 230, 0.015 nominal, fiber diameter of 6.5 μm). This was a nonwoven glass fiber mat with 7% PVA (polyvinyl alcohol) binder made by Crane&Co. Iodomethane (CH₃I, ≥ 99%, Sigma-Aldrich, Cat. I8507) was used for the methylation reaction. Potassium Dichromate (ACS reagent, ≥ 99.0% Sigma-Aldrich, Cat. 207802) was used as a stock solution of hexavalent chromium, and 1,5-Diphenylcarbazide (DPC) (ACS Reagent, Sigma-Aldrich, Cat. 259225) was used as the color reagent. Methanol (Fisher Chemical, Cat. A454-1) was HPLC grade for dissolving color reagent. All reagents are used without further purification.
3.2 Preparation of HACAX

3.2.1 Preparation of PAN-based Activated Carbon Fiber

PAN based Activated Carbon Fiber (PANCAF) was prepared using a patented approach developed in Economy’s Group with minor modifications[1]. Polyacrylonitrile (PAN) was dissolved in DMF at 60 °C, then ZnCl₂ was added to make a viscous solution with weight ratio PAN: ZnCl₂: DMF = 6.52:19:173.7. After all solids dissolved in the solution, a glass fiber mat (Crane 230, Crane Co.) was dip-coated into the above mixture. The coated fiber was then dip-washed with 5%wt ZnCl₂ aqueous solution to make a uniform coating without losing ZnCl₂. The mat was dried in the hood overnight at room temperature, and then was put in a furnace at 200°C for 10 hours in air. After that, the mat was activated in flowing N₂ by heating it to 450°C at ~ 30°C/min and then isothermed for 30 mins. After cooling in flowing N₂ for 3 hrs, carbonized fiber mat was washed with 0.5 M HCl, then rinsed with DI water, then washed with 0.5 M NaOH and DI water rinsed again. The sample was then dried in the hood at room temperature overnight, then dried in 110 °C in the oven for 1 hr, and transferred to a vacuum oven and dried further at 110 °C under vacuum overnight to remove residual moisture and HCl. The final product, namely PAN-based Chemically Activated Carbon Fiber (PANCAF) was stored for further use.

3.2.2 Anion Exchange Functionality of Activated Carbon Fibers

Anion Exchangeable Activated Carbon Fibers were prepared by PANCAF methylation. PANCAF mat was cut into small pieces, and mixed into solutions with NaI, CH₃I and NMP with ratio PANCAF: NaI: CH₃I: NMP = 0.6g: 0.6g: 1.6ml: 10ml. Methylation reaction is carried out in a sealed 50 ml flask at 20, 50, 70, 90 °C for 2 hrs. After stop the heating and cool down the solution, the solid samples were
filtered and washed several times with ethanol and DI water to remove the residual chemicals attached on the fiber. The sample was stored in DI water for further tests and characterization.

3.3 HACAX Characterization

3.3.1 Ion Exchange Properties

Ion exchange capacity was measured by putting ~ 50 mg HACAX samples in 1M NaNO₃ solution shaking for 1 day, and then using an iodide selective electrode to measure iodide concentration in solution. Ion exchange kinetics of HACAX was measured by putting small pieces of 70 mg of HACAX into 200 ml 1M NaNO₃ solution with violent 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 Purolite A400 was used under the same conditions. Iodide concentration was analyzed by iodide ISE electrode (double-junction, BNC, Cole-Parmer, Cat. No. EW-27502-23) with detection limit from 6 ppb to 127,000 ppm. The ion exchange reaction is shown in Figure 3.1.

![Figure 3.1 Ion Exchange of Iodide vs. NO₃⁻](image)

3.3.2 BET

Brunauer-Emmett-Tell (BET) Surface Area and micropore and mesopore volumes of HACAX and PANCAF were measured by Quantachrome Autosorb-1 apparatus. All samples were degassed at 200°C until the outgassing pressure change was below 5µHg/min before analysis. N₂ is used to measure the surface area and pore
volume at 77 K. BET equation was used to calculate the surface area using P/P₀ange 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.

3.3.3 TGA

The coating content of HACAX was measured using TGA (Hi-Res TA
Instruments 2950 Thermogravimetric Analyzer) by burning off the carbon coating at
800°C in air.

3.3.4 XPS

X-ray photoelectron spectroscopy (XPS) (Physical Electronics PHI Model
5400) data was acquired for surface analysis of PANCAF, HACAX and Cr(VI)
loaded HACAX. XPS data acquisition was performed using an achromatic Mg Kα
(1253.6 eV) x-ray source operated at 300 W. Survey scans were accumulated from 0-
1100 eV. High-resolution scans were performed with the pass energy adjusted to
35.75 eV. The inside pressure of the vacuum chamber was maintained at
approximately 10⁻⁹ Torr during the experiments. The binding energy was calibrated
with Carbon 1s peak with 284.5 eV.

A non-linear least squares curve fitting program (XPSPEAK version 4.1)
program with a symmetric Gaussian-Lorentzian sum function and Shirley background
subtraction was used to deconvolute the XPS peaks.

3.3.5 SEM

SEM images were obtained using a Hitachi S-4700 with mixed field emission
with a 10 kV or 12 kV accelerating voltage. PANCAF and HACAX samples were
attached on an aluminum sample holder using a carbon tape. The sample were coated using a gold palladium plasma spray.

### 3.4 Cr(VI) Adsorption Test

#### 3.4.1 Cr(VI) Solution Preparation

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). By dilution of stock solution, test solutions and standard solutions were made by diluting the 1000 ppm stock solution. In the whole procedure, pH was not adjusted.

#### 3.4.2 Adsorption Isotherm

The adsorption isotherm was studied in Cr(VI) aqueous solution at room temperature. Initial Cr(VI) solutions were prepared by diluting 1000 ppm stock solution into different concentrations in DI water. 15 mg of HACAX sample was weighed and put into these solutions for 6 days, and then 3 ml solution, or after appropriate dilution if necessary, was analyzed for Cr(VI) concentration. The following equation was used to calculate the removal capacity

\[
Q = \frac{(C_0 - C_e) \times V \times 10^{-3}}{m} \tag{3-1}
\]

where \(Q\) is removal 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 \(m\) is the dry weight of HACAX sample (g).

#### 3.4.3 Adsorption Kinetics

Adsorption kinetics was studied in aqueous solution at room temperature in 250 ml flask with magnetic stirring. Initial Cr(VI) concentration is 4 ppm, and ~150 mg HACAX sample was put into 200 ml solution mixed with a magnetic stir bar. The
solution was sampled at pre-set time points. 1 ml or 10 ml solution was sampled at each time point for Cr(VI) concentration analysis depending on the concentration estimation of solution. Several of other adsorbents, such as ACF, GAC-F400, Pellet-600 in the literature is also used as comparison under the same condition.

3.4.4 Sample Concentration Analysis

The concentration of Cr(VI) was measured by UV-Vis Spectroscopy at $\lambda=540$ nm via photometric diphenylcarbohydrazide method [2, 3]. Color reagent was prepared by dissolving 125 mg of 1,5-diphenylcarbohydrazide into 25 ml HPLC-grade methanol, then 125 ml 5.5% H$_2$SO$_4$ (made by dissolving 14 ml 98% H$_2$SO$_4$ in DI water) was added and diluted into 250 ml solution with DI water. Before UV-Vis Spectroscopy measurement, a 3ml sample solution (or diluted sample ) and 1 ml color reagent was mixed well and put into 3.5 ml polystyrene disposable cuvette. Standard solutions were prepared at concentrations of 0, 5, 10, 20, 40, 80, 120, 400, 600, 800, 1000 ppb for calibration. After mixing with color reagent, the sample was measured within 2 hrs to ensure a precise result.

In order to study the mechanism of adsorption of Cr(VI) and possible transition from Cr(VI) to Cr(III), total chromium concentration is measured by ICP (Inductively Coupled Plasma, OES Optima 2000 DV by Perkin Elmer) in the Microanalysis Lab in the School of Chemical Science at UIUC.

3.5 References


CHAPTER 4
RESULTS AND DISCUSSION

In the first part of this chapter, properties of HACAX will be discussed. First, ion exchange properties of HACAX were measured and discussed; then the physical and chemical properties of HACAX are discussed. After that, the mechanism of functionalizing ion exchange onto activated carbon is proposed.

The second part will discuss the Cr(VI) removal performance of HACAX material. First, the result of adsorption kinetics and isotherm is presented and discussed; then the characterization of HACAX is discussed and based on this, a mechanism for adsorption of Cr(VI) is proposed.

4.1 Ion Exchange Properties

4.1.1 Ion Exchange Adsorption

Different reaction temperature gives different yields: As the equilibrium test shown in Figure 4.1, the anion exchange capacity of HACAX material is range from 0.38 to 0.52 meq/g, with the highest reaction yield at 70 °C. The highest ion exchange capacity is 1.5 mmol/g based on coating. This is the first time of such materials ever been made; also, it is a reasonable capacity even compared with polystyrene based anion exchange resins ~ 2.5 mmol/g.
As for kinetics, Figure 4.2 shows the ion exchange adsorption of $\text{NO}_3^-$ onto HACAX compared with PANCAF. This graph shows that before methylation, there is nearly no ion exchange reaction; after methylation, HACAX can exchange out iodide ions and thus adsorb nitrate ions at very fast rates. The results show that PAN-based activated carbon fibers has been well functionalized with strong base anion exchange group, which represent the first report in the literature to the author’s knowledge.
Kinetics comparison between HACAX and Purolite A400 was also made on a log time scale. It shows HACAX has faster kinetics compared with polystyrene based ion exchange resins. The reason for the fast kinetics is most likely due to the fiber form of the material which could enhance particle and film diffusion of anions. After 10 mins, the relatively lower capacity of HACAX limits its exchange rate.
4.1.2 Morphology and Porous Structures

It is very important to understand how the carbon materials coated on glass fiber. As shown in Figure 4.4, there are two patterns for active materials coating onto glass fiber: uniform carbon coating on glass fiber and non-uniform bridging between fibers.

![SEM image of HACAX: two pattern of coatings](image)

Surface area and pore volume including microporous and mesoporous volume of PANCAF and HACAX are listed in Table 4.1. After modification, HACAX surface areas increased slightly from 982 m$^2$/g to 1045 m$^2$/g based on coating materials; mesopore content of HACAX increased greatly from 7% to 54%. According to Yue et al.’s[1] study, higher mesopores content is favorable for the removal of Cr(VI) from water.
Table 4.1 Normalized surface area and pore volumes of PANCAF and HACAX

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Areaa</th>
<th>Volume</th>
<th>Volume Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET m²/g</td>
<td>DR Micropore ml/g</td>
<td>Mesopore ml/g</td>
</tr>
<tr>
<td>PANCAF</td>
<td>982</td>
<td>0.51</td>
<td>0.036</td>
</tr>
<tr>
<td>HACAX</td>
<td>1045</td>
<td>0.49</td>
<td>0.59</td>
</tr>
</tbody>
</table>

*Note: all data are normalized based on the coating by TGA measurement.

The increased mesopore content could be further proven by use of SEM. Compared with PANCAF (Figure 4.5 left), HACAX (Figure 4.5 right) shows more porous structure in sub-microns scale and nano-scale, which suggested the increased mesopore content of HACAX.

4.1.3 Mechanism

According to the literature on heat treatment of PAN fiber and XPS studies and adsorption property tested in this work, the following Figure 4.6 shows the proposed mechanism of formation of anion exchange activated carbons.
4.2 Cr(VI) Removal by Hybrid Materials

4.2.1 Cr(VI) Adsorption Kinetics

Cr(VI) removal by PANCAF and HACAX vs. adsorption time is shown in Figure 4.7. Most of activated carbon materials, including commercially available Granular Activated Carbon F400, high performance activated carbon fiber like ACF, PVA-300, and PAN based CAF are not able to remove Cr(VI) down to EPA level at a reasonable time. The Pellet-600 and HACAX show superior activity for Cr(VI) removal. Compare with other adsorbents on the same weight level, Pellet-600 and HACAX demonstrates fast kinetics and the ability to bring Cr(VI) level from 4 ppm
down to 1 ppb.

![Graph](image)

**Figure 4.7** Cr(VI) removal by HACAX and various adsorbents vs. adsorption time Note: Data of Pellet 600, GAC F400, ACF-10 were provided by Z. Yue.

Between the best two adsorbents Pellet-600 and HACAX, the HACAX materials not only could remove Cr(VI) down to ppb levels (and potentially even lower level, which is limited by the detection limit), but also with faster kinetics. Time needed for removing Cr(VI) down to 2 ppb is 50 hrs and 145 hrs for HACAX and Pellet-600, respectively. Furthermore, a better comparison on kinetics is shown in Figure 4.8 starting with a Cr(VI) concentration of 4 ppm. It shows that within 30 mins, HACAX can remove ~90% of Cr(VI) compared with just 40% removal by Pellet-600. There are two reasons for the improved kinetics by HACAX: The anion exchange functionality provides a positively charged surface which facilitates the adsorption by electrostatic force. Fiber form of HACAX with 7 µm-in-diameter greatly increase the particle and film diffusion of Cr(VI) from bulk solution to
adsorbent surface, which also improves the adsorption rates. Moreover, HACAX also showed superior performance on kinetics even compared with Purolite A400, as shown below. HACAX is able to remove twice more of Cr(VI) than Purolite A400 within 10 mins.

![Figure 4.8 Kinetic Comparison between HACAX, Purolite A400 and Pellet-600](image)

4.2.2 Cr(VI) Adsorption Equilibrium

The adsorption isotherms for the various materials are shown in Figure 4.9. This graph shows that at most of concentration range, HACAX materials have better adsorption capacity; this advantage is more obvious at low residual concentration, which is orders of magnitude more adsorption capacity. This means that HACAX is a good adsorbent at low level of Cr(VI) such as drinking water treatment.
There are basically two well established types of adsorption isotherms: Langmuir adsorption isotherm and Freundlich adsorption isotherm. These two models were applied here to this novel IXAC in order to find out the mechanism of adsorption.

### 4.2.2.1 Langmuir isotherm

Langmuir adsorption isotherm describes a scenario where: adsorbent surface is homogenous; all adsorption sites have equal adsorbate affinity with monolayer coverage[2]. The Langmuir equation is

$$ Q_e = \frac{q^* b c_e}{1 + b c_e} \quad 4-1 $$

The linear form of the Langmuir equation is

$$ \frac{c_e}{q_e} = \frac{1}{q^* b} + \frac{1}{q^*} c_e \quad 4-2 $$
Where $Q_e$ is the amount of adsorbate adsorbed (mg/g), $C_e$ is equilibrium concentration (mg/L or ppm), $Q^0$ is monolayer adsorption capacity (mg/g), and $b$ is the constant related to free adsorption energy.

Langmuir plot is shown in Figure 4.10:

![Langmuir Fit of IXAC Isotherm](image)

**4.2.2.2 Freundlich isotherm**

This isotherm developed by Freundlich in 1909 is an empirical expression which describes the equilibrium on heterogeneous surfaces without necessarily monolayer capacity.

The Freundlich equation is

$$Q_e = K C_e^{1/n}$$

with the linear form described as:

$$\log Q_e = \log K + \frac{1}{n} \log C_e$$
Where $Q_e$ is the adsorbed amount per adsorbent weight (mg/g), $C_e$ is the equilibrium concentration (mg/L or ppm), $K$ is a constant indicating adsorption capacity (mg/g) and $1/n$ indicates the intensity of adsorption. The fit of Freundlich is shown below.

![Figure 4.11 Freundlich isotherm](image)

Summary of parameters and constants are in Table 4.2.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_0$</td>
<td>33.11</td>
<td>0.7872</td>
</tr>
<tr>
<td>$b$</td>
<td>0.00049</td>
<td>2.8019</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9887</td>
<td>0.8959</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td></td>
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</tr>
</tbody>
</table>

From $R^2$, we can find that the Langmuir equation gives a better description of the adsorption data. The values of $Q_0$ and $b$ were determined from the figure, namely, 33.11 mg/g and 0.00049 l/mg, respectively. $R_L < 1$ shows that this is a favorable adsorption.
4.2.3 Cr(VI) Reduction and Characterization

In kinetic study, besides Cr(VI) concentration was measured by UV-Vis, total Cr was also measured by ICP-MS. It turns out that after most of the Cr(VI) adsorbed and accumulated onto the surface of activated carbon, there are Cr(III) coming out and existing in the solution, as shown in Figure 4.12.

![Figure 4.12 Conversion from Cr(VI) to Cr (III) by Hybrid Materials](image)

XPS study of Carbon 1s showed that there was 14% decrease in the signal for C-H and C-C peak and a corresponding increase of C=O peak, as shown in Figure 4.13. This might suggest that activated carbon surface has been oxidized, and Cr(VI) been reduced by surface functional groups. The reduction of Cr(VI) to Cr (III) is helpful for POU application since it not only converts toxic to beneficial Cr (III) to below 100 ppb and thus facilitate more adsorption of Cr(VI), but also prevents the leaking out of Cr(VI) as more background ions flow through.
4.2.4 Mechanism of adsorption

According to the XPS study, the literature review[3] and adsorption measurements of changes for Cr(VI) and Cr (III), the following electrostatic attraction – accumulation – surface reduction – repulsion mechanism for the Cr(VI) removal by novel hybrid materials is proposed:

1. multi-scale mass transfer of Cr(VI) is facilitated from bulk to surface by the 7 μm diameter of the fiber, presence of a macro-porous structure and high mesopore content;
2. attracted through electrostatic force by surface positive charged functional pyridium-like structure group and accumulated in the pores;
3. reductions of Cr(VI) by nearby surface functional group to positively charged Cr(III);
4. Cr(III) is repelled by positive charge group nearby into bulk solution.

4.3 Summary and Future Work

At this time Cr(VI) has been identified as a carcinogen. Hence, an effective POU system is urgently needed to bring trace Cr(VI) from ppm down to ppb levels.

In this study, we have successfully synthesized the first hybrid activated carbon/anion exchange material. Compared with current state-of-the-art technology, HACAX demonstrated a superior performance to rapidly remove Cr(VI) down to ppb levels. Unlike earlier data on the activated carbon system described in the literature, HACAX is able to work at natural pH with several orders of magnitude faster kinetics; HACAX has faster adsorption rates and mechanisms to convert toxic Cr(VI) to nutrients Cr(III). Besides, fabricating the hybrid material in the fiber form using glass fiber as the substrate provides easy, cost-effective preparation, ease of handling and higher throughput without introducing big pressure drop, which are very important factors for considering a POU filter system.

Currently the author continues working on characterization such as FTIR, Zeta Potential and thermal stability to study the general basic properties of HACAX. In future the following works will also be explored:

Optimize the synthesis route, including temperature, time, methylating reagent and catalysts to get the most process-feasible way for system scale-up;

Use Ion Chromography (IC) for Cr(VI) measurement to lower the detection limit and study the performance around or below 1 ppb.
Explore other applications of these hybrid materials for phenol [4, 5], perchlorate[6], and arsenic removal [7] in drinking water. Another important area is for catalysis[8], since potentially HACAX have better thermal stability compare with anion exchange resins.

4.4 References


