PERCHLORATE ION (ClO_4^-) REMOVAL USING AN ELECTROCHEMICALLY

INDUCED CATALYTIC REACTION ON MODIFIED ACTIVATED CARBON

A Thesis

by

MEREDITH CAITLYN LANGILLE

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2006

Major Subject: Civil Engineering

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Approved by:

Chair of Committee,	Timothy Kramer
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ABSTRACT

Perchlorate Ion (ClO_4^-) Removal Using an Electrochemically Induced Catalytic

Reaction on Modified Activated Carbon. (December 2006)

Meredith Caitlyn Langille, B.S., Rensselaer Polytechnic Institute

Chair of Advisory Committee: Dr. Timothy Kramer

Perchlorate is known to adversely affect the thyroid gland functions including iodide take up, thus perchlorate should be removed from drinking water. Bituminous coal-based activated carbon (AC) has been used for perchlorate removal in past years. Virgin carbon and carbon modified by oxidation with HNO₃, NaOH and H₂O₂ were examined in this study for their ability to remove perchlorate by reduction or adsorption mechanisms. Surface functional groups formed on the modified AC (MAC) were examined with diffuse reflectance infrared spectrometry. Inhibition of perchlorate removal onto MAC by various anions (Cl^- , NO_3^- , and SO_4^{2-}) and solution pH (4.5, 7.2 and 10.5) were examined to characterize the MACs before an electrochemical reaction was performed.

Surface functional groups were increased by oxidation. Groups that were found on the carbon include, but are not limited to lactone, quinine, carboxylate, and nitrogen-oxygen groups. The effect of pH on removal of perchlorate by MAC was greatly affected by the change in the zero point charge (ZPC) induced on the carbon by modification. Virgin carbon also experienced difficulty in removing perchlorate when solution pH was above the ZPC. Anion inhibition varied with the modification process. NO_3^- inhibited perchlorate removal only by the virgin carbon. The other anions showed no major effects on the removal efficiency of perchlorate by the carbons.

Electrochemical processes did not show favorable results in removal of perchlorate. The dominant mechanism of perchlorate removal during desorption tests was adsorption onto the carbon surfaces via ion exchange.

DEDICATION

I know what I know today thanks to the helpful guidance of many people in my life. It started young with my parents and siblings, continuing through my life with Mr. Marr, BC, and those close friends who stuck with me through thick and thin. I dedicate my work to those who gave me the extra drive in my life and believed that I could do it.

ACKNOWLEDGMENTS

Chunwoo Lee was the original student worker on this proposal. His initial work and investigations led to the modification of carbon and my work. The extensive knowledge he contains and his persistence in aiding my research helped me obtain the results I present in this thesis.

Dr. Bruce Herbert was kind enough to take time out of his demanding schedule to aid me with his time and resources for determining the functional groups modified on the carbon. He also provided insightful views on why some experiments worked and some did not work.

Dr. Timothy Kramer, the chair of my committee and advisor provided his positive guidance and intellectual background to help push this project to completion on time.

Without these individuals help, there would not be the thesis you are reading today. Thank you for your time.

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CHAPTER I

INTRODUCTION

Perchlorate ion (ClO_4^-) is both a naturally occurring and a man-made anion that is most commonly associated with salts such as ammonium, sodium and potassium. Perchlorate is highly mobile in soil due to it's evenly distributed negative charge on the oxygen atoms that surround the lone chlorine atom. The repulsion forces from the negatively charged soil particles prevent perchlorate from adsorbing. Perchlorate has a low charge density causing a lowered affinity with cations, thus giving perchlorate high solubility. Manmade perchlorate is used as an ingredient in solid rocket propellants and explosives (1, 2). Naturally occurring perchlorate is found in the Atacama Desert, Chile and some parts of southern Texas. Natural perchlorate is believed to be formed atmospherically and is associated with nitrate caliche ore deposits (3).

The perchlorate ion can disrupt the thyroid gland's ability to metabolize iodide ions, interfering with the production of thyroid hormones. The function of the thyroid gland in adults is to control metabolism, whereas in children the thyroid controls proper brain development. The EPA has created an official reference dose of 0.0007 mg/kg/day (1).

Contamination of perchlorate ion is a nationwide problem, including Texas, as seen in Figure 1 (4). The threat of exposure is mainly through ingestion of drinking water, though other exposure routes include food such as lettuce and milk (1, 5). Conventional treatment processes to chemically reduce (a transfer of electrons) perchlorate ion cannot do so effectively due to a high activation energy barrier. This unique energy barrier and electron transfer process is called the *bridged electron transfer* (6, 7, 8). The successful removal and destruction of perchlorate is dependent on whether

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This thesis follows the style and format of *Environmental Science & Technology*.
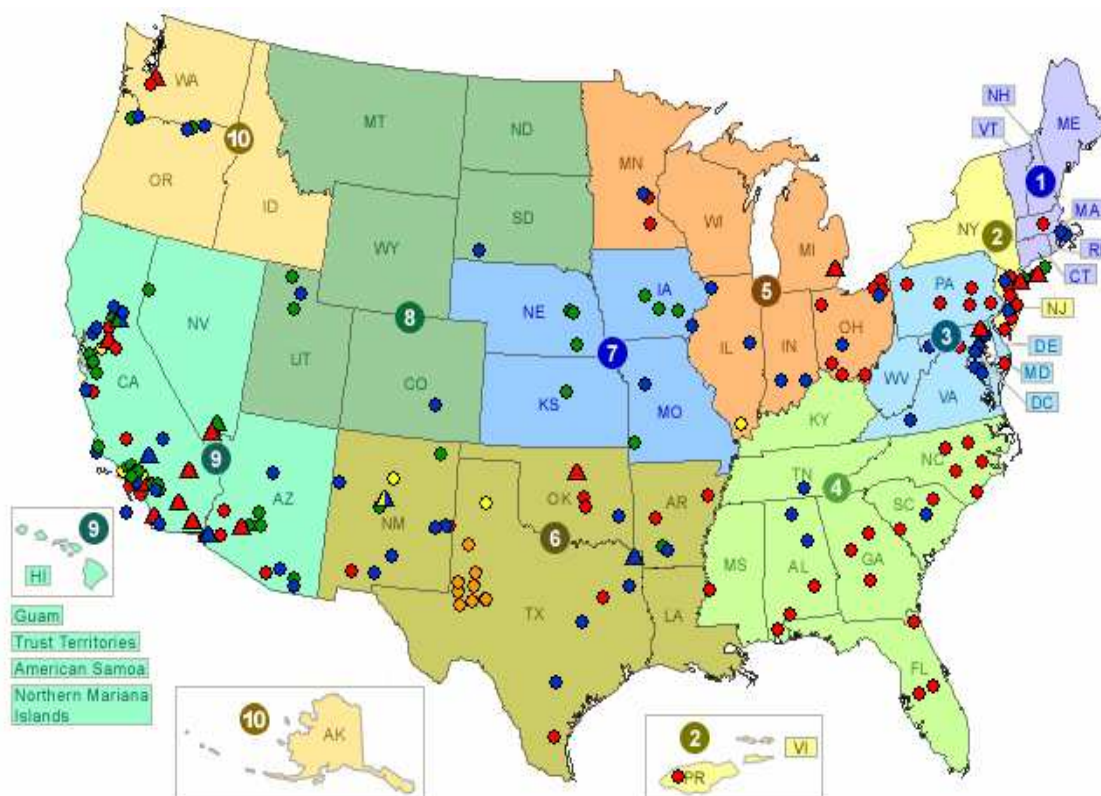
Figure 1: Perchlorate manufacturers and users as of September 23, 2004.
Source: U.S. EPA, 2004

the reductant surmounts enough energy to break the energy barrier developing a bridge complex with the perchlorate ion to transfer electrons.

Previous studies have investigated the idea of activated carbon having the catalytic potential to produce the bridged complex with hyperchlorite and chlorite (ClO^- and ClO_2^-), reducing them to the harmless chloride ion (Cl^-) (7, 8, 9, 10). It has been seen that activated carbon does not have enough energy to overcome the activation barrier of perchlorate ion (9) but the addition of an electrochemical process may over come this barrier.

The general objectives of this study were:

1. To modify a bituminous coal based activated carbon with an acid, a base and hydrogen peroxide to increase the adsorption of perchlorate from aqueous solution.

2. To identify inhibitors of the adsorption of perchlorate.

3. To investigate of the synergism between the combination of the acid, base and thermal treated activated carbons with electrochemical process.

CHAPTER II

BACKGROUND

Production of ammonium perchlorate began in the mid 1940's for military uses such as rocket and explosive propellants. Mortars, grenades, flares and solid fuel rockets commonly use perchlorate as an oxidant. The bulk of perchlorate is produced for defense activities in the aerospace industry, domestic Air Force installations as well as on military and Navy bases. General uses of perchlorate include that of pyrotechnics and fireworks, blasting agents, solid rocket fuel, matches, lubricating oils, air bags, and some types of fertilizers (1, 2, and 3).

Releases into the environment occur when improper storage or disposal is practiced. The US EPA reports that 43 states produce perchlorate. Of those 43 states, at least 26 states have contaminated soil, ground water, surface water and drinking water. Table 1 contains known perchlorate releases in Texas as of March 25, 2005 (11).

Concentrations in Table 1 range from $7\,\mu$g/L to $203\,$mg/L for ground water and $6\,\mu$g/L to 11 mg/L for surface water (11). Moreover, recent studies found perchlorate in milk and leafy vegetables (6), which indicate that many people can be exposed to perchlorate contamination and its potential health risk. Thus, some states, including Texas, have set advisory levels of perchlorate concentrations ranging from $1\,\mu$g/L to $18\,\mu$g/L. The National Research Council for the National Academies established an official reference dose concentration of 0.0007 mg/kg/day in January of 2005 (1). This is a dose that is not expected to cause adverse health effects.

Table 1: Known perchlorate releases in Texas as of March 25, 2005.

DOD Facility/Site Name	City/County	BRAC	NPL	Highest DW Conc (ppb)	Highest GW Conc (ppb)	Highest SW Conc (ppb)	Highest Soil Contam	Initial Detection Date
Lone Star Army Ammunition Plant	Texarkana	N	F	--	23	6	157 (soil) 186 (sed)	07/2001
Longhorn Army Ammunition Plant	Karnack	N	F	--	203000	11000	163000	02/1998
McGregor Naval Weapons Industrial Reserve Plant (NWIRP)	McGregor	N	N	--	91000	{6600}	{1,8000,000}	05/1998
Red River Army Depot	Texarkana	Y	N	--	7	417	{226}	11/1999
Camp Bullis	San Antonio	N	N	--	345 - DOD 424 - TCEQ	--	--	08/2001
Other Federal Emergency Facilities								
Pantex Plant (USDOE)	Amarillo	/	F	--	408	--	5000	N/A

Legend:
BRAC = Base Realignment and Closure
N (in BRAC Column) = Site is not BRAC Facility
Y (in BRAC Column) = Site is a BRAC Facility
NPL = National Priorities List
N (in NPL Column) = Site is not on the NPL
F (in NPL Column) = Site is on the Final NPL
DW Conc = Drinking Water Concentration
GW Conc = Groundwater Concentration

SW Conc = Surface Water Concentration
Soil Contam = Soil Contamination
ppb = parts per billion
Y (in Soil Contam Column) = Perchlorate has been detected in soil
-- = denotes EPA is not aware that perchlorate has been detected in that particular medium at that specific facility
[ ], { } = Data was obtained from DOD
N/A - Data is currently not available

Source: U.S. EPA, 2005

CHEMISTRY OF PERCHLORATE

Perchlorate (ClO_4^-) is a negatively charged ion (Figure 2) (12, 13). It is most commonly found associated with salts such as sodium perchlorate, $NaClO_4$, and ammonium perchlorate, NH_4ClO_4. A salt containing the perchlorate ion is readily soluble in water (1, 2, 14, 15). Perchlorate ion has a chlorine atom in the center of its tetrahedral, which is surrounded by four oxygen atoms. The negative charge associated with the perchlorate ion is evenly distributed allowing it to bind feebly to positively charged items with metallic centers (14).

Figure 2: Perchlorate anion.
Source: www.chemfinder.com, http://www.chem.purdue.edu

When perchlorate ion is associated with cationic species such as ammonium (Eqn. 1) (2), sodium, potassium or magnesium forming salts, they become powerful oxidizing agents. These salts in the aqueous phase disassociate causing the perchlorate ion to loose its strength as an oxidizing agent. Thermodynamically, perchlorate ion should oxidize water, reducing perchlorate to chloride ion (Cl⁻) in the process; however, the high activation energy barrier prevents common reductants from attacking the ion, lending to great stability of the ion in water.

$$NH_4ClO_4(s)\longrightarrow NH_4^+(aq) + ClO_4^-(aq) \tag{1}$$
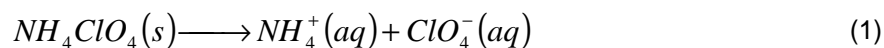
Perchlorate salts are highly inert and unreactive compounds when in the aqueous phase. It is thermodynamically possible for perchlorate to be reduced to oxygen and chloride atoms, following the reaction in Eqn. 2. However, this is not observed under ambient conditions due to its high kinetic barrier. Table 2 lists various reactions of perchlorate ion. Perchlorate ion serving as an oxidizing agent is in an aqueous solution forbiddingly slow (14, 15).

$$ClO_4^- (perchlorate) \longrightarrow ClO_3^- (chlorate) \longrightarrow ClO_2^- (chlorite) \longrightarrow$$
$$ClO^- (hypochlorite) \longrightarrow Cl^- (chloride) \qquad (2)$$
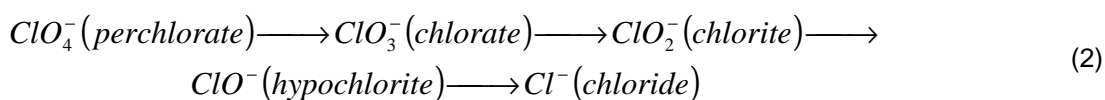
Table 2: Various methods of representing the oxidation strength of perchlorate ions.

$ClO_4^- + 2H^+ + 2e^- \longleftrightarrow ClO_3^- + H_2O$	$\Delta E^o = +1.20V$	(3)
$ClO_4^- + H_2 \longleftrightarrow ClO_3^- + H_2O$	$\Delta G^o = -232kJ$	(4)
$ClO_4^- + 8H^+ + 8e^- \longleftrightarrow Cl^- + 4H_2O$	$\Delta E^o = +1.38V$	(5)
$ClO_4^- + 8H^+ \longleftrightarrow Cl^- + 4H_2O$	$\Delta G^o = -1066kJ$	(6)
$O_2 + 4e^- + 4H^+ \longleftrightarrow 2H_2O$	$\Delta E^o = +1.27V$	(7)

Source: Espenson, J. H., 2000; Brown, G. M. and Gu, B., 2006

Comparing the potential for perchlorate (Eqn. (5)) to that of oxygen in Eqn. (7), leads to the conclusion that perchlorate is unstable in relation to the production of oxygen from water (15).

TOXICITY

Perchlorate interferes with the uptake of iodide in the thyroid gland, thus upsetting the function of the gland and decreasing hormone output (1, 2). The thyroid regulates metabolism in adults, where as in children it is essential to growth as well as metabolism. If a fetus or an infant is exposed to perchlorate by ingestion of

contaminated water or milk, critical brain development may be disrupted causing mental retardation, delayed development and potential thyroid tumors (1, 2).

The thyroid gland is unique in that it takes iodide ion from the bloodstream and converts it to organic iodide to be used as hormones that regulate metabolism. Large amounts of iodine that are used for the production of hormones accumulate in the thyroid (16). The cellular iodide pump, the mechanism responsible for this process, selects anions based on their ionic volume. Perchlorate's ionic volume (44.5) is larger than iodine (36.7). Perchlorate was once used to treat hyperthyroidism, also known as Graves' disease (1, 16, 17). Graves' Disease is found in the United States at a rate of approximately 1-2% in females (16).

The hypothalamus gland controls the secretion of hormones from the thyroid gland. Perchlorate may competitively inhibit the cellular iodide pump that transports iodine from the blood to the thyroid (17). Perchlorate finds its way out of the body through urine, with peak concentrations occurring three hours after consumption unmetabolized. Perchlorate has not been linked to cancer. In rare instances congenital hypothyroidism occurred when a severe iodine deficiency happens in utero. Cases where workers were exposed to particulate perchlorate had adsorbed and excreted perchlorate, but no adverse affects on their thyroid production were seen (16).

Perchlorate can also affect ecological receptors. Perchlorate is known to inhibit the main function of the thyroid gland in many animals. Thyroid hormones play a homologous role in many vertebrate and invertebrate taxa, thus, perchlorate has the possibility of being an endocrine disrupter in ecological species (18). Perchlorate is not lethal to earthworms, but may reduce their weight. Amphibians are the most sensitive to perchlorate exposure, affecting metamorphosis in amphibians. Long term exposure of perchlorate to fish showed thyroid gland structural perturbations (18).

Perchlorate is used to treat patients who have iodine-induced thyrotoxicosis, a syndrome that results when tissues are exposed to a high level of circulation thyroid hormones (16). Exposure pathways include ingestion, inhalation and absorption.

Inhalation and absorption are minor ways to be exposed. Factory workers where ammonia perchlorate is produced are exposed to the dust (17).

CARBON

Activated carbon has been used for water and wastewater treatment for years. The surface of activated carbon acts as an adsorbent, adsorbing compounds such as organics. Activated carbon is manufactured from natural, carbonaceous materials through several different processes, although they all follow the same basic manner of preparation. The most common materials used to produce activated carbon are those that tend to have carbon in them. These include bituminous coal, peat, lignite, petrol coke, wood, and nut shells. Each raw material produces a product that has a unique pore structure when activated. Chemical activation involves chemicals like zinc chloride being added to the raw materials at high temperatures. The carbon is then pyrolyticly heated, cooled, and the activating agent extracted. Physical activation involves a gaseous agent being exposed to the carbon at elevated temperatures in an endothermic process. As is an oxidizing step. In general, exposure time and type of agent will determine adsorption properties. Treating carbon until 40 to 50 percent burnoff will produce the most surface area, a property that is known to increase adsorption capability (19).

The structures created after activation contains turbostratic crystallites. These crystallites have parallel layers of trigonally covalent bonded carbon. The crystallite alignment is what makes the micropores in the structure as seen in Figure 3 (20). The porous nature of activated carbon is what allows it to adsorb material. A description of porosity includes: pore shape, pore size, pore volume, surface area, and their spatial distribution within the carbon particle (19).
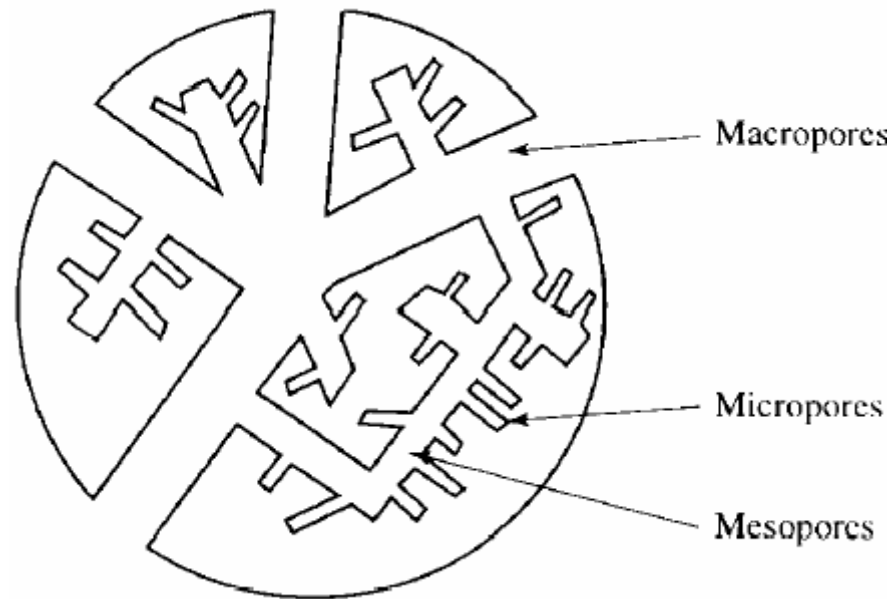
Figure 3: Activated carbon schematic.
Source: Rodriguez-Reinoso, F., 1998.

Adsorption properties are also determined by the surface functional groups on an activated carbon. Approximately 5 to 10 percent by weight of activated carbon is non-carbon elements. Surface groups are what make up the majority of the non-carbon weight. The surface groups are mostly made of oxygen, and are generated based on the activation agent reacting with the precursor material. Surface functional groups have oxygen groups dominating, with some hydrogen containing groups. Surface functional groups on carbon can display both acidic and basic properties, depending on the surface oxide present (21). Examples of functional groups are shown in Figure 4 (20).
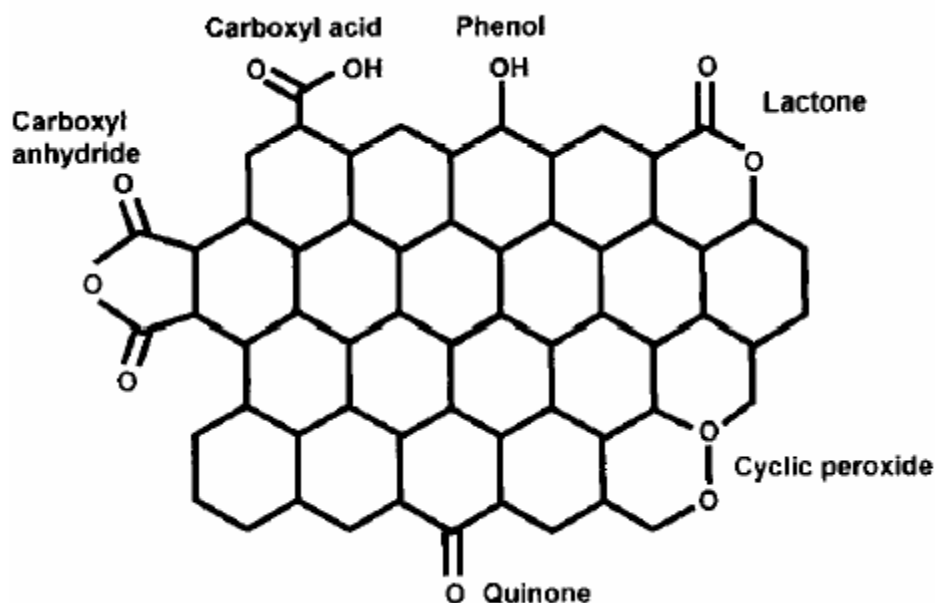
Figure 4: Examples of carbon functional groups.
Source: Source: Rodriguez-Reinoso, F., 1998.

Activated carbon has a charged surface that can either repel or attract the solute. The charge on the surface varies with the pH and the point of zero charge (PZC) is that pH at which net charge on the surface is zero. When pH values are below this value, the surface is positively charged, and vice versa when it is above the PZC value. The surface of carbon without the functional groups is hydrophobic. The addition of the oxygenated surface functional groups which are hydrophilic, reduce the hydrophobicity of the carbon (19, 21).

During adsorption from an aqueous solution, the dissolved material is transported to the solid surface by means of diffusion before it is sorbed onto the extensive inner surface. The sorption process associated with activated carbon can be chemical or physical. During physical sorption, the non-specific secondary binding mechanisms are rapid and reversible. Chemisorption is determined by the transfer or sharing of electrons and is not reversible (19).

MODIFIED CARBON

Modification of activated carbon surface area changes functional groups allowing the carbon to be tailored at removing specific chemicals. Chemical treatment with nitric acid (HNO_3), hydrogen peroxide (H_2O_2) or sodium hydroxide ($NaOH$) can all modify the functional groups that are associated with activated carbon in different ways.

Properties such as surface area, porosity, chemical inertness and oxygen surface groups present on carbon are what define its ability to be modified during preparation for catalytic activity and selectivity. If these properties are evenly distributed through out the carbon, there is a better chance for uniform distribution of large active sites per unit area. Activated carbon that has not been modified contains a porous structure with hydrogen or oxygen heteroatoms. A portion of carbon ash contains mineral matter. The micropores in carbon are created by aromatic sheets that are layered with variable gaps. Adsorption does not only occur at micropores, but also at meso- and macropores. When carbon is activated, it becomes more disordered, creating more edges and unpaired electrons. The increase in edges creates a higher inclination for oxygen chemisorption. The pH of the system delineates the surface functional groups. When the surface charge on the carbon is zero, the carbon has reached its point of zero charge. A pH below this point indicates that protonated carboxyl groups exist, or the carbon attracts anions from solution; vice versa for a pH above this point. Oxidation of carbon produces a surface that is more acidic, or a positively charged surface area that attracts negatively charged anions (20, 21, and 22).

Hydrogen Peroxide

Modification of carbon with hydrogen peroxide has been reported to result in no significant change in its properties, including surface area (23). Oxidation with hydrogen peroxide resulted in an increase in hydroxyl groups when the pH of the solution was allowed to vary, but a decrease in hydroxyl groups when pH was raised or lowered to a constant value. If the carbon was outgassed at low temperatures, the

original surface functional groups may not change, which causes mineral matter to remain present. When mineral matter is present, there is a good chance that the formation of carbon dioxide will occur upon oxidation. Gomez-Serrano *et al.* established the formation of carbon dioxide or carbon monoxide as a surface functional group if the pH was fixed at a certain value (24). Aside from hydroxyl groups being formed, C-O-C groups are also formed (24).

Nitric Acid

Nitric acid-treated carbon has the highest amount of surface-oxygen containing groups. These included carboxylic groups, carboxylic anhydride groups, lactone groups, phenol groups and carbonyl groups (21, 23, 25). Carboxylic acid is formed due to a decrease in the zero point charge. Increasing the oxidation level allows acidic groups to develop to the point where they dominate the surface charge (26).

Sodium Hydroxide

Treating activated carbon with sodium hydroxide increases the content of hydroxyl groups (25). The increase in the hydroxyl groups may be the result of a surface reaction with lactone groups. Chun and Wu (25) used NaOH to modify activated carbon. When the carbon was neutralized with alkali by Chun and Wu, it caused the laconic structures found in the virgin material, to open up and carboxylate structures to dominate.

ELECTROCHEMICAL

In order for an atom to be transferred at an electrode, electrodes that are normally covered by an oxygen, or hydroxyl, would have to be vacant for the adsorption to occur (15). A solution containing perchlorate will not react with the metal electrode that is covered with air and water creating a surface oxide, thus producing the following reactions obtained from (15).

$$[Me(I)(OH)]_a + e^- + H^+ \longrightarrow [Me(0)]_a + H_2O \qquad (8)$$

$$[Me(O)]_a + ClO_4^- \longrightarrow [Me - O - ClO_3]_a^{-*} \qquad (9)$$

$$[Me - O - ClO_3]_a^{-*} \longrightarrow [Me(I)O]_a^- + ClO_3 \qquad (10)$$

$$[Me(I)O]_a^- + H^+ \longrightarrow [Me(I)OH]_a \qquad (11)$$
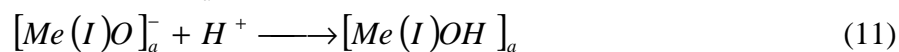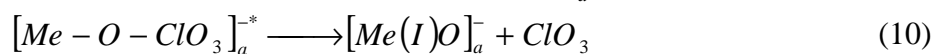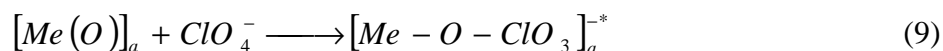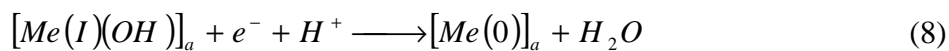
Subscript 'a' represents the species is surface stabilized and adsorbed and '*' represents an active complex. $[Me(0)]_a$ in this representation is an oxygen vacancy. This base model represents the one-electron transfer mechanism that perchlorate follows. Perchlorate is also a very poor nucleophile, therefore anion inhibition is predicted to displace it from the oxygen vacancy (15). The reaction of this cell is very slow, but when used in conjunction with an ion exchange resin (27), and a reducing agent that is generated by the electrochemical process, the ion-exchanged perchlorate can be reduced.

REMOVAL TECHNIQUES

Current technologies are limited in their ability to treat perchlorate and reach advisory levels. Methods vary from physical, chemical, and biological processes to remove perchlorate ion. Bioremediation has been used to remove perchlorate, generally with the addition of acetate and hydrogen as electron donors. Phytoremediation with plants like smartweed, watercress and the trees chinaberry, elm, willow, mulberry and hackberry have also been used. Perchlorate can accumulate in leaves because perchlorate is highly soluble and follows the water movement in the plant, with the last stop being in the leaves before transpiration (15). Degradation with plants (Eastern cottonwood, Black willow, Willow, *Ecalyptus cineria*, French tarragon and spinach) was observed by Nzengung and Wang (28) where hydroponically grown woody and aquatic plants showed a slow initial uptake and transformation (phytodegradation) of perchlorate followed by a rapid removal of perchlorate from solution (rhizodegradation) by the plant root. Depending on the plant physiology and environmental conditions, removal of perchlorate using selected woody, edible and aquatic plants is possible (28).

Recent advances have been made in the use of ion exchange in the treatment, recovery and destruction of perchlorate. Major issues associated with ion exchange include resin regeneration, secondary waste production, perchlorate destruction, slow kinetics and associated costs (29, 30). A bifunctional resin was created to have a longer quaternary ammonia group for higher selectivity, and a smaller one to improve kinetics (29, 31). Resin choice is based on the concentration of the perchlorate in solution. Selective resins could perform better than non-selective resins by orders of magnitude. At high concentrations of perchlorate, bioremediation may be a better choice due to regeneration and replacement costs of exhausted resin. When uranium is a co-contaminant it forms stable ionic species such as $UO_2(CO_3)_2^{2-}$, a highly charged anionic specie. This specie can be retained by the resin by electrostatic forces, even if uranium is present at low concentrations. As it is desirable to remove both perchlorate and uranium at the same time, having a mixed waste poses a problem. Various forms of synthetic resins can aide in sorbing U(VI), thus separating uranium from perchlorate in secondary waste segregation and minimization (29).

The high reduction potential of perchlorate makes it an ideal electron acceptor for microbial metabolism under anaerobic conditions. Numerous types of bacteria have been shown to be capable of reducing perchlorate including: *Escherichia coli, Proteus mirabilis, Rhodobacter capsulatus* and *Rhodobacter sphaeroides*. Certain environmental factors, such as trace elements, pH, salt concentration, and the presence of other electron accepters have affected the microbial reduction of perchlorate (32, 33). Neutral pH is optimal for the growth of perchlorate reducing bacteria. Salinities greater than 2 percent have inhibited reduction of perchlorate. This is a set back for resin secondary waste reduction as it is a brine. At times, addition of electron donors can cause unwanted microorganisms to become active, thereby interfering with the operation by altering the physical/chemical characteristics of the system as well as further reducing the water quality by releasing unwanted end products. This field, though, is still young. It has come a long way from where it started, but more research is needed (32).

Parette and Cannon (34) examined to adsorption of perchlorate by proportional diffusivity with bituminous granular activated carbon. The activated carbon removed perchlorate from the sample water to an extent. When competing ions were present, perchlorate removal was not as efficient. pH has an effect on the removal of perchlorate with activated carbon. As the pH decreases, the positive charge on the carbon increases. Parrette and Cannon determined that lowering the pH increased the number of bed volumes their reactor could operate before breakthrough. Iron pre-loaded carbon was able to remove perchlorate four times longer than virgin material while granular activated carbon preloaded with cationic polymer was able to extend the bed volume before breakthrough. Greene and Pitre explored the ability of granulated activated carbon and sand to remove perchlorate with the addition of an electron donor in fluidized bed reactors (35). Significant removal of perchlorate was observed when a combined electron donor of ethanol and methanol was added.

Membrane separation and ion exchange are physical methods showing potential for removing perchlorate from water, but they are not a destructive technology (2, 9). When perchlorate is not destroyed, a highly concentrated solid phase resin or liquid brine is produced. The remaining residual is now a waste that needs to be disposed.

An emerging technology uses ferric chloride and hydrochloric acid under elevated pressure and temperature to reduce perchlorate ion to innocuous chloride. The reduction (a transfer of electrons) of the ion is important to ensure regeneration and reuse of the solution (9). Titanous ion combined with several new organic ligands is able to react with perchlorate at a measurable rate (36). These methods have setbacks due to slow kinetics, high temperature and pressures that are not practical to drinking and ground water treatments. Possibilities of unknown risk to human health exist with the use of organic ligands.

METHODS FOR ANALYZYING PERCHLORATE

Due to perchlorate's strong dissociation properties, the use of gravimetry to measure it by precipitation is difficult. The first methods known for quantification of perchlorate came from gravimetry with nitron (3,5,6-triphenyl-2,3,5,6-tetraazabiclyco-[2.2.1]he-1-ene). Another way to detect perchlorate is potentiometry using ion-selective electrodes. This method has been able to detect perchlorate at concentrations as low as 10^{-5} to 10^{-2} M (2, 37).

Ion chromatography and capillary electrophoresis have detected perchlorate. Ion chromatography used with hydrogen cyanurate ions produced excellent peaks. Phthalate can be used, but long retention times of 40 minutes slow the process of analysis. The use of acetonitrile to modify the eluent dielectric constant and a solid phase reagent managed to bring the retention time to 20 minutes. Further, sodium hydroxide as the eluent greatly reduced the retention time to less than 10 minutes (2). Jackson *et al.* investigated the use of IonPac AS5 of AS11 columns, large loop injection and suppressed conductivity detection as a simple way to detect perchlorate concentrations in the range of a few micrograms per liter (38). Dissolved solids can interfere with the detection of perchlorate by interfering with the signal to the conductivity detector (39).

Capillary electrophoresis has an advantage for the use in detection of perchlorate in that it strongly retains ions such as perchlorate. In this process, ionic mobility is the most important factor, compared to chromatography, where interactions with stationary and mobile phases are important. Some slow eluters used in ion chromatography may be fast for capillary electrophoresis. This process has been used to quantify a perchlorate concentration as low as 10 µM (2).

Electrospray mass spectrometry was determined to be a viable method of detection for perchlorate and it decreases detection limit by an order of magnitude compared to ion chromatography. Total dissolved solids can interfere with the analysis of perchlorate by plating out on the heated capillary causing an error of up ton 60-70

percent (39). Capillary failure will result with turbid water, causing background noise which makes the detection of perchlorate less accurate.

CHAPTER III

EXPERIMENTAL METHODS AND MATERIALS

MODIFICATION OF ACTIVATED CARBON

Nitric Acid (21, 25)

Approximately 80 milliliters (ml) of a 5 molar (M) Nitric Acid (HNO_3) solution and 5.0 grams (g) of bituminous coal based granulated activated carbon (Norit GAC, 1240 (plus), steam activated, granulated material (~1mm)) were added to a 100 ml flask. The flask was placed on a hot plate and heated until boiling. The nitric acid and activated carbon were boiled for three hours before being sieved using a No. 20 USA Standard Testing Sieve (ASTM E-11 with an opening of 850 micrometer or 0.0331 inches). This was repeated for a total of one liter of HNO_3 before being rinsed (See: RINSING).

Sodium Hydroxide (25)

1 liter (L) of a 1 M of a NaOH solution and 5 g of AC were added to a 1 liter beaker. The solution soaked for three hours before being drained using No. 20 USA Standard Testing Sieve (ASTM E-11 with an opening of 850 micrometer or 0.0331 inches) and rinsed (See: RINSING).

Hydrogen Peroxide (21)

A solution volume of 1 liter containing 5 M H_2O_2 was added to 5 g of AC. The solution was allowed to decompose before it was drained into a No. 20 USA Standard Testing Sieve (ASTM E-11 with an opening of 850 micrometer or 0.0331 inches) and rinsed (See: RINSING).

RINSING

The drained modified activated carbons (MAC) were rinsed in the sieve with nanopure water before being placed in a tube apparatus where nanopure water was pumped continuously over the MAC for 48 hours. Once rinsing was complete, the MAC were removed and placed in a Deapatch oven and dried for 24 hours at a constant temperature of 100 degrees Fahrenheit.

DIFFUSE REFLECTANCE INFRA-RED SPECTROSCOPY

Surface functional groups of finely ground virgin activated carbon (VAC) and MAC were identified using a Nicolet Mangna IR 560 Spectrometer. Diffuse reflectance infra-red spectroscopy (DRIFTS) method was used with 2048 scans per sample. The absorbance was measured in Kubelka-Munk units at a resolution of 4 cm^{-1}. The spectra for the VAC was subtracted from of each MAC to determine what functional groups were modified by the oxidation processes. Previous background spectra of water vapor were subtracted from each sample.

CARBON pH (25)

A 0.1 M solution of $NaNO_3$ was prepared and its pH measured. 25 ml of this solution was then added to 500 milligrams (mg) of the MAC and shaken for 48 hours. The pH of the solution measured at the end of the 48 hours using a Beckman, Φ-260 pH meter. The pH measured represented the approximate (less than 2%) carbon point of zero charge based on results offered by Chen and Wu (25).

ISOTHERMS

A 100 ml graduated cylinder was used to measure 40 ml aliquots of a 1 M solution of potassium perchlorate ($KClO_4$) that were added to selected weights (0.05, 0.1, 0.2, 0.3, 0.5, 0.6, 1.0, 1.5, 2.5 g) of the MAC. The mixture was rotated for 24 hours before being sampled using a (BD) 10 ml Syringe with a Luer-Lok Tip and a Gelman Lab 25 mm Easy Pressure Syringe Filter Holder. The pH of the perchlorate solution was measured before and after the reaction, and the pH values of the mixtures were measured after sampling. Samples were analyzed for chloride and perchlorate concentration using a Dionex, DX 500 Ion Chromatograph equipped with a Dionex, AS 40 autosampler, sample loop size 25 μm, and a type AS 16 column.

BATCH ANIONS

The abilities of select anions (SO_4^{2-}, NO_3^-, and Cl^-) to inhibit perchlorate removal were determined using batch testing where 1 mM solutions of the selected sodium salts were prepared and spiked with 1 μM of $KClO_4$. 500 mg/L of MAC was added to the spiked solution and samples were taken regularly over a 6 hour period (specifically: 0, 10, 30, 60, 90, 120, 180, 240, 360 minutes) with a (BD) 10 ml Syringe Luer-Lok Tip and Gelman Lab 25 mm Easy Pressure Syringe Filter Holder. The samples were analyzed for their perchlorate concentration using a Dionex, DX 500 Ion Chromatograph equipped with a Dionex, AS 40 autosampler, sample loop size 100 μm, and a type AS 16 column.

BATCH pH

Influence of pH on the abilities of the MAC to remove ClO_4^- was measured in experiments using 1 liter of a 2 mM of phosphate buffer solution with a starting pH of 4.5. The pH was adjusted using a 1 M solution of NaOH to 7.2 and 10.5. To each reaction vessel, 1 liter of 1 μM $KClO_4$ was added along with 500 mg/L of MAC. The MAC was suspended with a stirring plate for 6 hours and samples were taken at 0, 10, 30, 60, 90, 120, 180, 240, and 360 minutes with a (BD) 10 ml Syringe Luer-Lok Tip and Gelman Lab 25 mm Easy Pressure Syringe Filter Holder. The samples were analyzed using a Dionex, DX 500 Ion Chromatograph equipped with a Dionex, AS 40 autosampler, sample loop size 100 μm, and a type AS 16 column for perchlorate concentrations.

ELECTROCHEMICAL ANALYSIS

The modified activated carbons (5 g) were packed in the electrochemical cell shown in Figure 5 and a series of batch experiments were conducted using a graphite sheet (Electronic Space Products International, 0.125"T X 0.5" X 4", Electro grade) of reticulated carbon as an electrode. The dimensions on the cell were: 1 inch wide, 1 inch long and 5 inches tall.
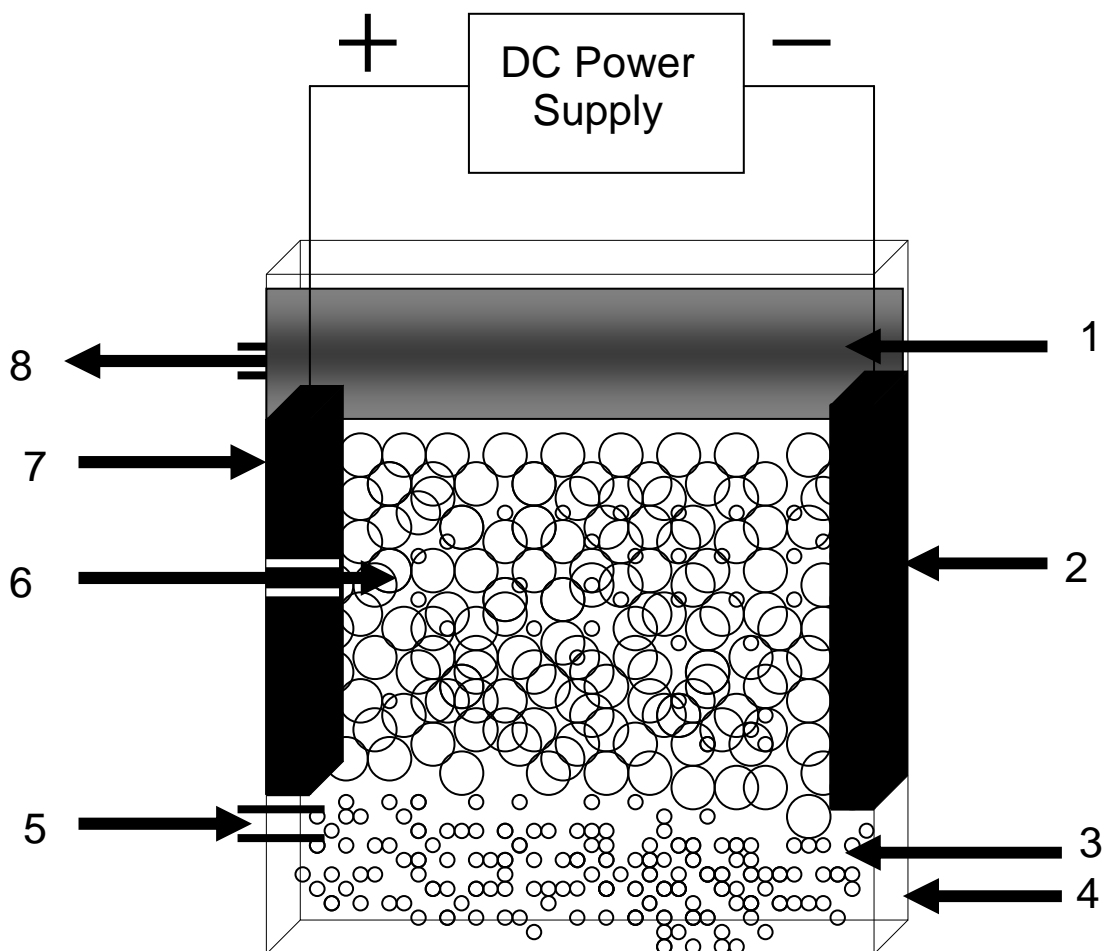
Figure 5: Schematic diagram of activated carbon combined electrochemical cell (1: Glass Wool; 2: Cathode; 3: Glass Beads; 4: Support; 5: Inlet Perchlorate Solution; 6: MAC; 7: Anode; 8: Outlet Perchlorate Solution).

Fluidized experiments measured the effects of electrical potential (voltage) and reaction time on perchlorate removal. Current was provided by a Kenwood Regulated DC Power supply at 50 and 100 mA. Perchlorate at a concentration of 1 mM and 5 mM of sodium sulfate was pumped with a MasterFlex® variable speed pump at 7 ml/min for a period of 6 hours. Perchlorate concentrations were analyzed using a Dionex, DX 500 Ion Chromatograph equipped with a Dionex, AS 40 autosampler, sample loop size 100 μm, and a type AS 16 column.

DESORPTION

After completion of the electrochemical analysis, activated carbon was removed from the electrochemical cell, placed in a separate glass beaker and washed with 5 mM and 10 mM sodium nitrate ($NaNO_3$) until the perchlorate was no longer detected in the solution. Collected wash effluent was analyzed for perchlorate and chloride ion concentrations. Results from these measurements determined whether perchlorate was being adsorbed onto the carbon or chemically reduced in the cell.

CHAPTER IV

CHARACTERISTICS OF THE SURFACE MODIFIED CARBONS

DIFFUSE REFLECTANCE INFRA-RED SPECTROSCOPY

Each MAC was analyzed by infra-red (IR) spectrometry, using the DRIFTS method. Surface functional groups were identified by IR by comparison with literature values. Table 3 (40) summarizes previously identified functional groups on activated carbon.

Table 3: IR assignments for activated carbon functional groups.

Group or functionality	Assignment regions (cm^{-1})		
	1000-1500	1500-2050	2050-3700
C-O in ethers (stretching)	1000-1300		
Alcohols	1049-1276		3200-3640
Phenolic groups:			
C-OH (stretching)	1000-1220		
O-H	1160-1200		2500-3620
Carbonates; carboxylic - carbonates	1100-1500	1590-1600	
C=C aromatic (stretching)		1585-1600	
Quinones		1550-1680	
Carboxylic acids	1120-1200	1665-1760	2500-3300
Lactones	1160-1370	1675-1790	
Carboxylic anhydrides	980-1300	1740-1880	
C-H (stretching)			2600-3000

Source: Figueiredo, J. L. et al., 1999.

In all of the samples that were oxidized, there was a significant increase in the hydroxyl groups. Overall there was an increase in functional groups due to oxidation.

HNO$_3$

Figure 6 illustrates the HNO$_3$ treated activated carbon DRIFT spectrum after it was subtracted from the MAC spectrum. Peaks were observed at 1780, 1600 and 1290 cm^{-1}.
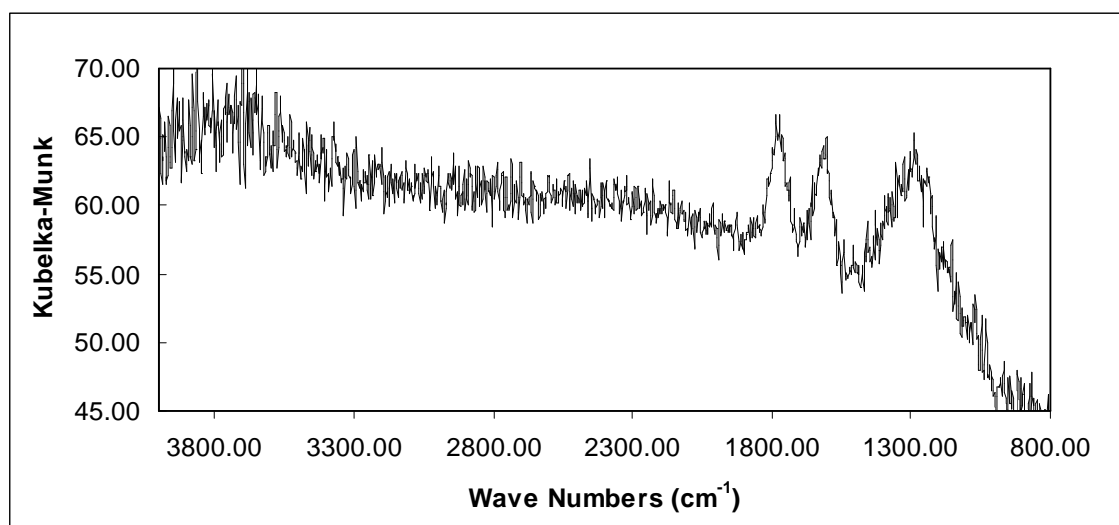
Figure 6: DRIFTS spectra recorded for HNO$_3$ MAC.

The first peak (1780 cm^{-1} wave number) has been assigned to different functional groups in the literature. Table 3 indicates that this peak might be attributable to carboxylic anhydrides (40). Sources have also attributed this peak location to a stretching vibrations of lactone (41), non-aromatic C=O stretching (41), cyclic anhydrides (42) and carboxylic acid groups (43). The most interesting change in surface functional groups was reported by Gomez-Serrano *et al.* (44) who measured a change in surface functional groups of activated carbon treated with nitric acid using Fourier transform-infrared spectroscopy. Gomez-Serrano *et al.* (44) identified the 1800-1600 cm^{-1} wave number range to be attributed to oxygen containing as well as N-O containing structures. The N-O containing structures include nitro and nitrate groups. They reported that the –NO$_2$

functional groups replace the hydrogen on the surface of the carbons. Such observations were also reported by Chen and Wu (25). They reported that HNO_3 treatment increased the number of surface functional groups such as carbonyl, carboxyl and nitrate groups suggested that oxygen and nitrogen functional groups are incorporated into the basal plane of the activated carbon during oxidation (25).

The next peak, located at 1600 cm^{-1} wave number, can be attributed to numerous groups, including carbonates, carboxylic-carbonates (1590-1600 cm^{-1}), C=C aromatic (stretching) (1585-1600 cm^{-1}) and/or quinones (1550-1680 cm^{-1}) (40, 41, 42, 43, 44). This peak may also be related to the –NO group (44).

The final noticeable peak in this spectra at 1290 cm^{-1} wave number can be related to C-O in ethers (stretching) (1000-1300 cm^{-1}), carbonates, carboxylic-carbonates (1100-1500 cm^{-1}), lactones (1160-1370 cm^{-1}) and carboxylic anhydrides (980-1300 cm^{-1}) (40). Chingombe and Wakeman (2005) (45) found, at 1240 cm^{-1} wave number, epi-oxide and phenolic structures in various environments associated with HNO_3 treatment of carbon. They also associated this wave number with C-N stretching vibrations (44).

Overall, oxidation with HNO_3 generates a significant increase in the surface functional groups on the carbon (25).

NaOH

The NaOH MAC spectrum is shown in Figure 7. There are several broad bands with possible underlying peaks observed in this spectrum. Peaks are apparent at 1625-1600 cm^{-1} and 1360 cm^{-1} wave number.
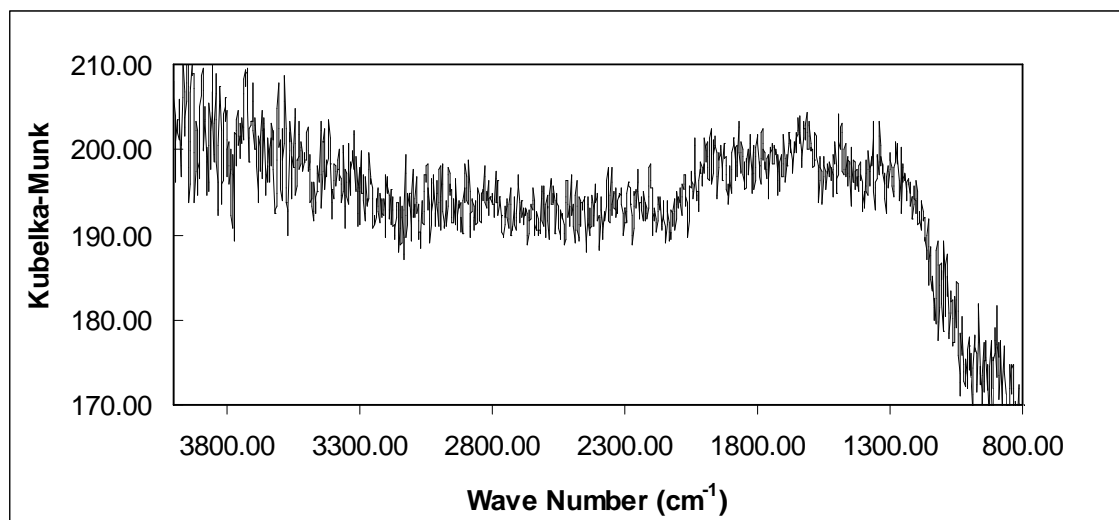
Figure 7: DRIFTS spectra recorded for NaOH MAC.

The peak at 1625-1600 cm^{-1} wave number is identified as carboxylate ion (CO_2^-) and possible C=C stretching vibrations and chelated carbonyl groups (46). The peak located at 1360 cm^{-1} wave number is related to –O-H bending vibrations (46).

H_2O_2

The H_2O_2 MAC spectrum is shown in Figure 8. Peaks of this spectrum are relatively difficult to determine. Peaks that do stand out include those at 1620 and 1400 cm^{-1} wave number. The peak located at 1620 cm^{-1} wave number corresponds to quinones (1550-1680 cm^{-1}) (40). The peak located at 1400 cm^{-1} wave number is characteristic of carbonate and carboxyl-carbonates (1100-1500 cm^{-1}) (40).
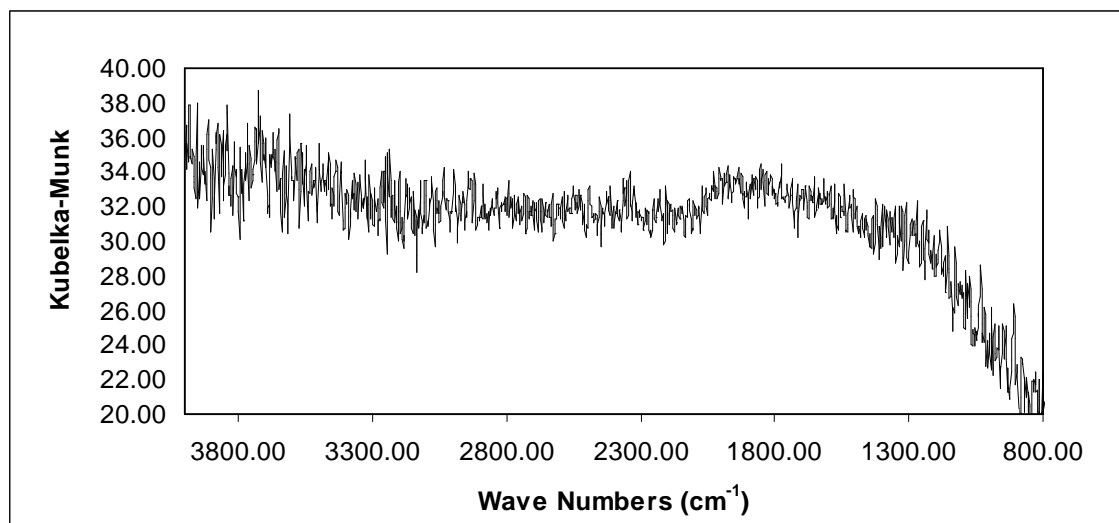
Figure 8: DRIFTS spectra recorded for H$_2$O$_2$ MAC.

CHAPTER V

SORPTIVE PROPERTIES OF MODIFIED CARBONS WITH PERCHLORATE

ISOTHERMS

Data for the isotherm tests on both the VAC and the MAC is provided in Figure 9. VAC shows a high adsorption capacity for perchlorate compared to HNO_3 MAC. The solid phase equilibrium concentration starts to level off at a very low liquid phase concentration and continues this trend as the liquid phase concentration continues to increase (Figure 9(a)-(d)) except HNO_3 MAC (Figure (9(e)-(f)). The equilibrium adsorption capacity increases dramatically as the equilibrium liquid concentration increases from zero to 2 or 4 mg/L for the all the samples except HNO_3 MAC. The HNO_3 MAC has a low concentration on perchlorate of it showing poor adsorption.

VAC data in Figure 9 (a) levels off at a solid phase concentration of about 13 mg/g. H_2O_2 MAC does not exceed a solid phase concentration of 9 mg/g which is less than the VAC value observed. VAC has a higher adsorption capacity than the H_2O_2 MAC. NaOH MAC also does not extend past 9 mg/g, showing a lower adsorption capacity than the VAC.
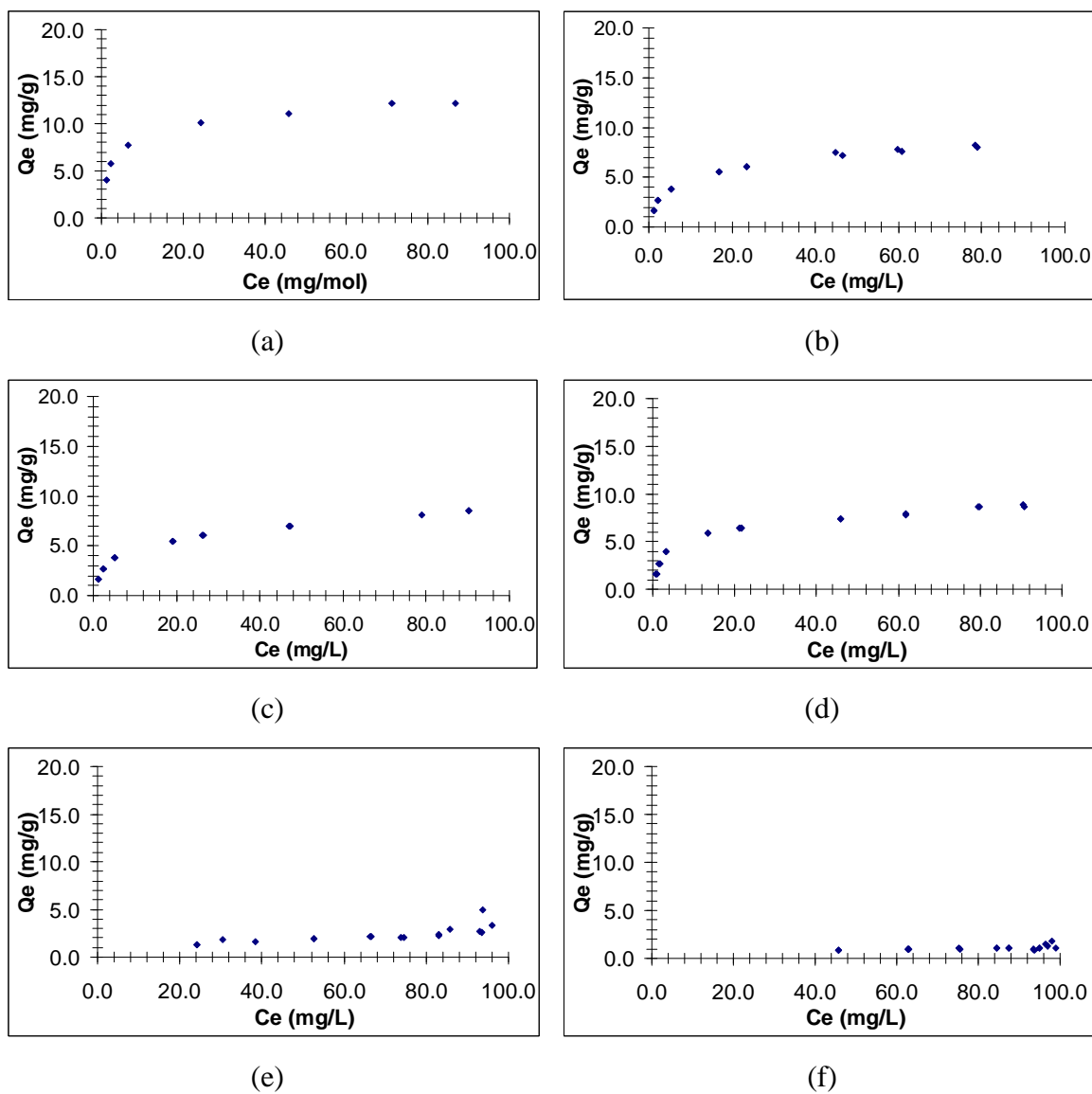
Figure 9: Isotherm data for: (a) VAC; (b) H$_2$O$_2$; (c) NaOH Batch 1; (d) NaOH Batch 2; (e) HNO$_3$ Batch 1; and (f) HNO$_3$ Batch 2.

Freundlich and Langmuir models were applied to the isotherms. The Freundlich model, as shown in Equation 12, when mathematically derived, assumes adsorption sites have different affinities for the sorbate where as the Langmuir model (Equation 13) assumes that all sites have the same affinity when mathematically obtained.

$$Q_e = k_f C_i^{1/n} \qquad\qquad (12)$$

$$Q_e = Q_0 \frac{bC_i}{1+bC_i} \qquad\qquad (13)$$

In both Equation 12 and 13, Q_e represents the number of moles (or mass) of adsorbate adsorbed per unit mass of adsorbent, C_i is the equilibrium concentration of species i in the mixture and Q_0 is the maximum saturation capacity to form a complete mono-layer on the surface. k_f is an affinity coefficient. $\frac{1}{n}$ indicates the linearity of the system and b is an equilibrium constant representing the rate of affinity of perchlorate onto the carbon to the rate off affinity of perchlorate off the carbon.

Figure 10 compares the isotherm data shown in Figure 9 (a)-(f) and their respective Freundlich and Langmuir parameters. In comparison of the experimental data with the Freundlich model for VAC (Figure 10 (a)), the experimental data started to level off at a solid phase concentration of about 13 mg/g, but the Freundlich model continued to grow, predicting that the equilibrium capacity for the VAC will continue to grow. The H_2O_2 MAC and the NaOH MAC Freundlich models (Figure 10 (b)-(d)) do not show this trend as dramatically. The Freundlich models for these carbons do start to deviate from the experimental data of which a maximum capacity is seen around 9 mg/g for the NaOH and H_2O_2 MAC, however there is not a dramatic increase in deviation as is seen in the VAC carbon. The Freundlich model, as indicated earlier, assumes adsorption sites have different affinities for the sorbent. When the experimental data fits to the Freundlich model, sorption sites would have different affinities for the perchlorate. The different affinities cause the isotherm to grow.

The Langmuir model is a model that assumes an adsorption process to be single layered and to occur on sites with the same affinity for the sorbate. The VAC carbon Langmuir model is under predicting the adsorption capacity of the carbon, as seen in

Figure 10 (a) by leveling off below the experimental data at a value of 11.13 mg/g. In Figure 10, the VAC carbon appears to be single layered and to occur on sites with the same affinity for the sorbate.
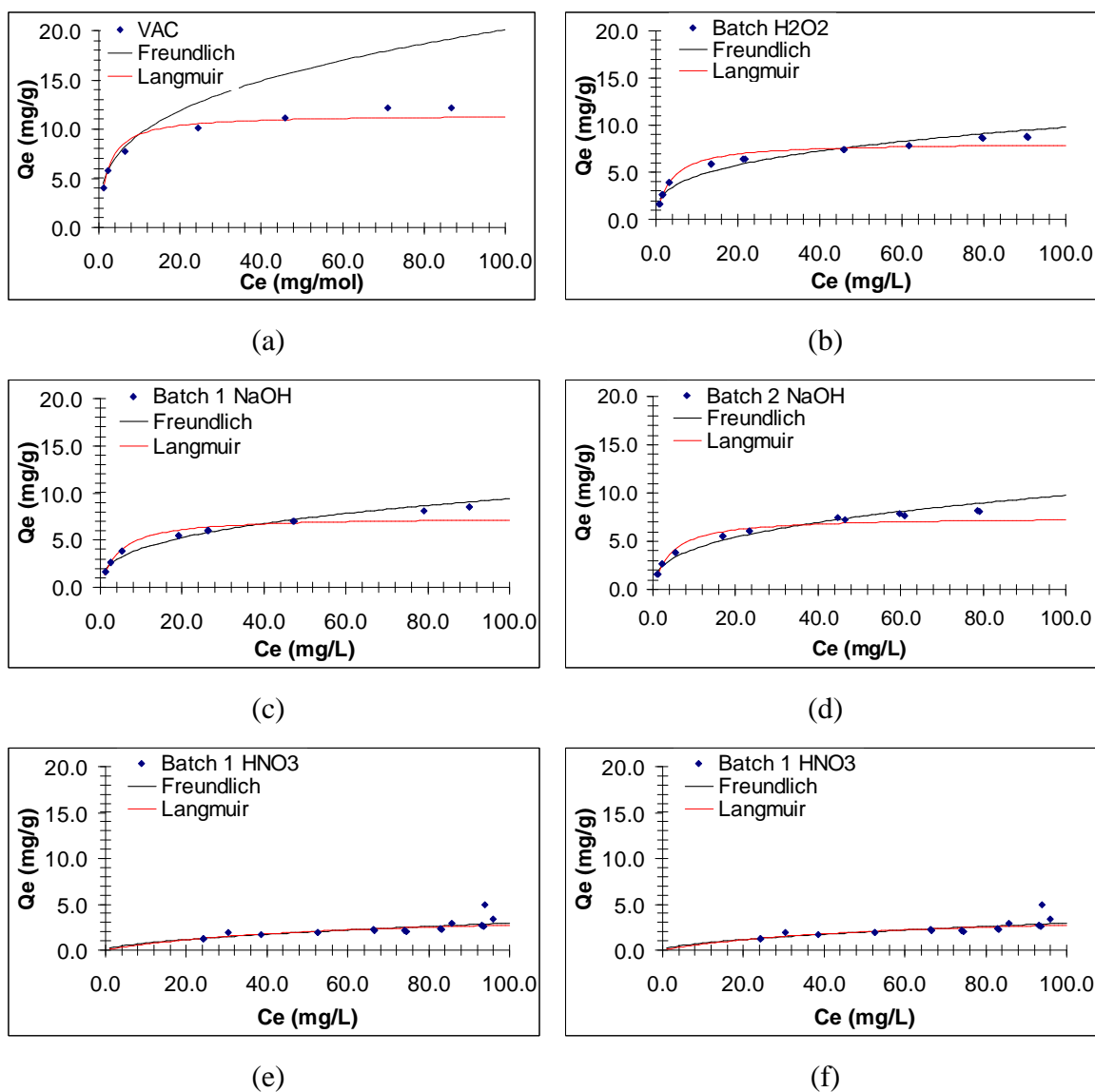
Figure 10: Isotherm data and models for: (a) VAC; (b) H$_2$O$_2$; (c) NaOH Batch 1; (d) NaOH Batch 2; (e) HNO$_3$ Batch 1; and (f) HNO$_3$ Batch 2.

Figure 10 (b)-(d) contains the Langmuir model for the NaOH and H_2O_2 MAC's. Similar to the VAC, the Langmuir model appears to under-predict the carbons sorption capacity by leveling off below the experimental data, leveling off at 8 and 8 mg/g, respectively, values that are below the 9 mg/g maximum capacity observed in Figure 10 (b)-(d). These carbons, though, like the VAC carbon, have an under-prediction, where a gap between the model and experimental data exists.

HNO$_3$ MAC models in Figure 10 (e)-(f) appear to follow the trend of the experimental data, but due to the low adsorption capacity indicated in Figure 9(e)-(f), the models cannot be clear indications of its ability to represent the data. The parameters and the sum of the squares of the residuals were obtained and are shown in Table 4 to aid the visual representation of the isotherms. The values of the parameters for the models and which model best fits the data is discussed below.

Table 4 presents the parameters for the Freundlich and Langmuir isotherms. Also shown in the table is the sum of the squares of the residuals with respect to the regression line (Equation 14), (where Q_{exp} is the Q_e calculated from the experiment and Q_{ecalc} is the Q_e calculated from the respective model) and the r^2 value with respect to the linear regression line.

$$s_r = \sum_{i=1}^{n} \left(Q_{exp} - Q_{ecalc} \right)^2 \qquad\qquad (14)$$

Table 4: Isotherm model parameters.

	Freundlich				Langmuir			
Carbon	1/n	K_f	r^2	Sr	b	Qo	r^2	Sr
VAC	0.24	4.46	0.96	109.36	0.47	11.47	0.98	3.09
H_2O_2	0.33	2.17	0.95	4.96	0.29	8.14	1.00	4.81
NaOH								
Batch 1	0.36	1.79	0.97	2.02	0.22	7.48	0.99	6.24
Batch 2	0.37	1.80	0.97	2.95	0.23	7.52	0.99	4.41
HNO_3								
Batch 1	0.58	0.20	0.67	5.71	0.02	4.24	0.80	6.48
Batch 2	0.34	0.24	0.22	0.70	0.04	1.41	0.24	17.93

Where a high value of Sr in Table 4 represents a poor model prediction for the respective models, the Sr value for the VAC is 109.36 for the Freundlich model which is much larger than 3.09 for the Langmuir model. The Freundlich Sr value calculated for VAC supports the visual evidence seen in Figure 10 (a) where the model over predicts the experimental data. The H_2O_2 MAC in Table 4 has a Sr value of 4.96 for the Freundlich model, which is slightly larger than the Sr value for the Langmuir model of 4.81. Thus the Langmuir model best predicts the VAC and H_2O_2 MAC carbon, assuming that all sites have the same affinity. The Sr values for the two batches of NaOH from Table 4 are 2.02 and 2.95 for the Freundlich model and 6.24 and 4.41 for the Langmuir. The HNO_3 MAC Sr values for the two batches are 5.70 and 0.70 for the Freundlich model and 6.48 and 17.93 for the Langmuir. The Freundlich model best predicts the NaOH and HNO_3 MAC carbon because the Sr values for the Freundlich models are less than the Langmuir models, thus assuming that the adsorption sites have different affinities for the sorbate. The HNO_3 MAC Sr values are not replicated like the NaOH MAC values are, showing a lack in depth to the experiment.

Q_0 is the maximum saturation capacity to form a complete mono-layer on the surface at the isotherm temperature. The VAC has the largest value for this term in Table 4 for the Langmuir isotherm. Due to the Sr value, the Langmuir model also best represents the VAC. The Q_0 value is in mg/g, therefore VAC has a maximum saturation

capacity of 11.47 mg/g of perchlorate. H_2O_2 MAC has the next largest value of Q_0, 8.14 mg/g and is best represented by the Langmuir model due to the Sr value. The remaining carbons have smaller values, but due to their Sr value, the Freundlich model best represents the experimental value for those carbons (HNO_3 and NaOH) modified.

b is an equilibrium constant representing the rate of affinity of perchlorate onto the carbon to the rate off affinity of perchlorate off the carbon for the Langmuir isotherm. The higher the value of b, the faster the equilibrium is reached. The highest value of b is seen in the VAC data, with a value of 0.47. H_2O_2 and NaOH MAC have values for b that are relatively close to each other. These MAC reach equilibrium at relatively the same rate, which is evident in Figure 10 (b)-(d). The HNO_3 MAC has the lowest value of b, 0.02-0.04. As seen in Figure 10 (e)-(f), HNO_3 MAC performs the worst.

k_f in the Freundlich model is an affinity coefficient. The higher the value of k_f the more affinity perchlorate will have to sorb onto the activated carbon, or a higher Q_e. k_f values can only be compared if $\dfrac{1}{n}$, the measure of linearity, are close. The VAC carbon and the H_2O_2 MAC have values of $\dfrac{1}{n}$ that are close (0.24 and 0.33, respectively), but the k_f value for the VAC is 4.46 and 2.17 (L/g) for the H_2O_2 MAC. The higher value of k_f for the VAC carbon supports its experimental data in Figure 10 (a) where the carbon has a higher affinity for the perchlorate. The NaOH MAC has a close $\dfrac{1}{n}$ value (0.36-0.37) to the H_2O_2 MAC. NaOH MAC's k_f is lower than H_2O_2 MAC with a value of 1.79 and 1.80 for the two separate batches. NaOH MAC has a lower affinity to sorb perchlorate than does H_2O_2 MAC. HNO_3 MAC has $\dfrac{1}{n}$ values for the two separate batch reactions that cannot be compared to each other. The second batch isotherm has a $\dfrac{1}{n}$ value of 0.34. This value is comparable to the other carbons. The k_f for HNO_3

MAC is 0.24, the lowest k_f for all the carbons, thus indicating the lowest affinity to sorb perchlorate.

It is uncertain as to why the HNO$_3$ MAC performed poorly. Tests were conducted numerous times with the same results. Modification methods used to modify the VAC with HNO$_3$ may have been too strong, thus reducing its ability to adsorb perchlorate. The surface area of the VAC may have been destroyed to an extent that reduced its surface area, decreasing its ability to remove perchlorate. The pH of the perchlorate before the isotherms were conducted was in the range of 5-7. After the isotherms were conducted, pH values for the HNO$_3$ MAC were measured to be 3.15. NaOH MAC pH was 9, and H$_2$O$_2$ MAC ranged from 5.19 to 6.22. The VAC carbon pH after the isotherm was conducted reached a value of 8-9. The influence of pH on perchlorate removal will be discussed in a later section.

Periera *et al.* (23) studied the impact of the surface modification of activated carbon on the adsorption of different dyes, observing that the carbon treated with HNO$_3$ was unable to remove anionic dyes compared to cationic dyes. Experimental data in Figures 9 (e)-(f), 10 (e)-(f) and Table 4 shows that carbon treated with HNO$_3$ was unable to remove an anionic constituent (perchlorate). Modification of the surface charge on HNO$_3$ MAC may be the predominate mechanism that may be affecting the results for the HNO$_3$ MAC and the other modified carbons. This is discussed further in a separate section (see: THE INFLUENCE OF SOLUTION pH).

THE INFLUENCE OF SOLUTION pH

Batch tests were conducted to evaluate the impact of pH on perchlorate adsorption. Figure 11 illustrates the results found. Raw data for these experiments are located in Appendix A.

A parameter that is easily controlled in an adsorption process is the solution pH. Modifying the pH causes the adsorbent surface properties to change within the solution. The distribution of the adsorbent around the surface is determined by both the pH of the

solution and the resulting surface charge of the pH-dependent surface. As discussed in Chapter II, the charge of the surface is determined by the concentration of the charge determining ion on the surface.

(a)

(b)

(c)
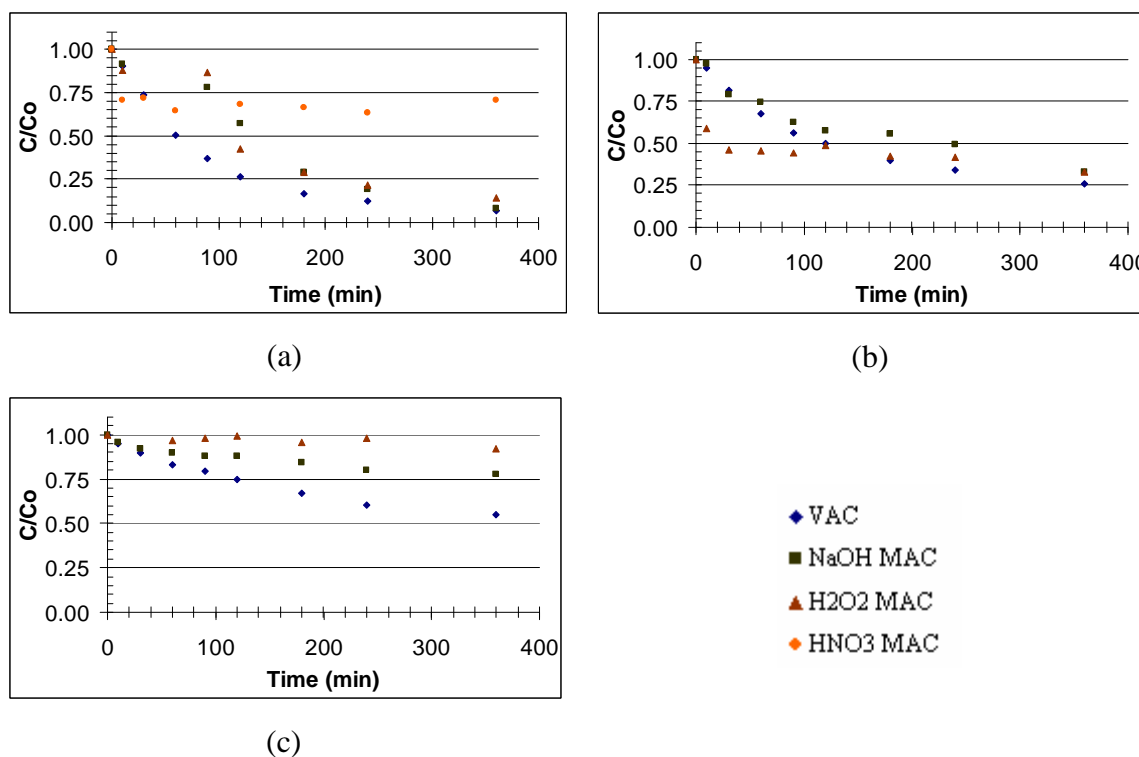
Figure 11: Batch pH tests for: (a) pH = 4.5; (b) pH = 7.2; (c) pH = 10.5.

Batch pH test for a pH of 4.5 saw a range of removal of perchlorate. HNO_3 MAC removed only 29% of perchlorate; H_2O_2 MAC removed 86% and NaOH MAC removed 92%. The VAC performed the best at this pH by removing 93% of the perchlorate.

The batch test at pH 7.2 showed lower removal than pH of 4.5. The VAC performed the best again, but with only 74% removal. The NaOH and H_2O_2 MAC both removed 67%. Due to the HNO_3 MAC's poor performance, the data is not reported. It

became evident during adsorption reactions that a side reaction was occurring. Perchlorate concentrations would first decrease in the analyzed data, but soon increase greater than the initial concentration. All experiments using HNO_3 were ceased for pH inhibition experiments with HNO_3 MAC.

The tests at pH 10.5 showed removals that were worse than those at pH of 7.2. The VAC, once again, out performed the other carbons with 45% removal. NaOH MAC had 23% removal and H_2O_2 MAC removed 8%.

At low values of pH, the surface of the carbons is surrounded by positively charged H^+ ions, induces a positive charge on the surface, increasing its affinity for the perchlorate ion in solution. VAC showed a greater ability to remove perchlorate at the three separate ranges of pH. The VAC's ability to remove perchlorate better than the MAC may be due to the pH of the solutions containing the MAC. Tests performed to determine the pH of the suspensions with MAC found them to be 2.43 for HNO_3 MAC, 10.25 for NaOH MAC and pH 7.3 for H_2O_2 MAC. Modifying the solutions pH can interfere with the carbon's ability to remove perchlorate if the solution is at a different pH. The modification process has induced a pH on the carbon by modifying the surface functional groups that affect acidity. The carbon pH can indicate (with a 2% error) the pH at which PZC (point of zero charge) is reached (25). HNO_3 treatment decreases the carbon's pH to a value of 2.43. A pH solution above this value (such as the ones used in the experiment) will cause the surface charge on the HNO_3 MAC to be negative, repelling the perchlorate in solution. The pH for NaOH MAC was determined to be 10.25 and 10.06 for VAC. A pH value below the values for these carbons will cause the surface to be positively charged, allowing adsorption of perchlorate. NaOH MAC and the VAC carbon were still able to remove perchlorate at pH 10.5 due to the 2% error in determining the carbon pH (which is subsequently related to the carbon's PZC (25).

Noh and Schwarz (26) concluded in their study that HNO_3 treatment of GAC lowers its PZC value. Any pH above this value will create a negatively charged surface which would repel a negatively charged ion such as perchlorate. Noh and Schwarz reported without nitric acid treatment, the PZC was 10. The PZC steadily decreased

from 10 to 3.5 as the concentration of nitric acid used during treatment increased from 0.0 M to 2.0 M. The HNO_3 MAC in this experiment was treated with 2 mM. The experimental data for pH measured in suspensions of the HNO_3 MAC does not coincide with literature because it is much less than Noh and Schwarz's values. It is believed that the oxidation treatment that the HNO_3 MAC underwent was strong enough to reduce the PZC sufficiently so that the surface charge of the carbon would be negative. The nitric acid used in this experiment may have degraded over time causing calculations for molarity to be incorrect. The PZC for the surface of the HNO_3 MAC is below the pH of the solution, thus creating a negatively charged surface, which repels the negatively charged perchlorate.

A study conducted by Faria *et al.* (21) observed the effects of HNO_3 and H_2O_2 treatment on activated carbon as measured by their ability to adsorb three different types of dye (acidic, reactive and basic). They concluded that the presence of oxygen containing functional groups reduces the ability of the carbons to adsorb anionic species from solution. There is an electrostatic repulsion between the negative surface charge and the anions of the dyes in solution. These reduced effects describe H_2O_2 MAC's performance in the pH and isotherm tests.

The ability of VAC to remove more perchlorate at a lower pH is due to a positive charge that is induced on its surface as the pH is lowered. Figure 11 (a)-(c) illustrates that as the solution became more basic, VAC's, as well as the MAC's, ability to remove perchlorate decreased and the surface charge became more negative (34).

THE INFLUENCE OF BACKGROUND ANIONS ON PERCHLORATE SORPTION

  Batch tests were conducted to determine if anions in solution would inhibit the removal of perchlorate. Trends that are evident in Figure 12 (a)-(c) are discussed with raw experimental data located in Appendix A.

(a)   (b)

(c)
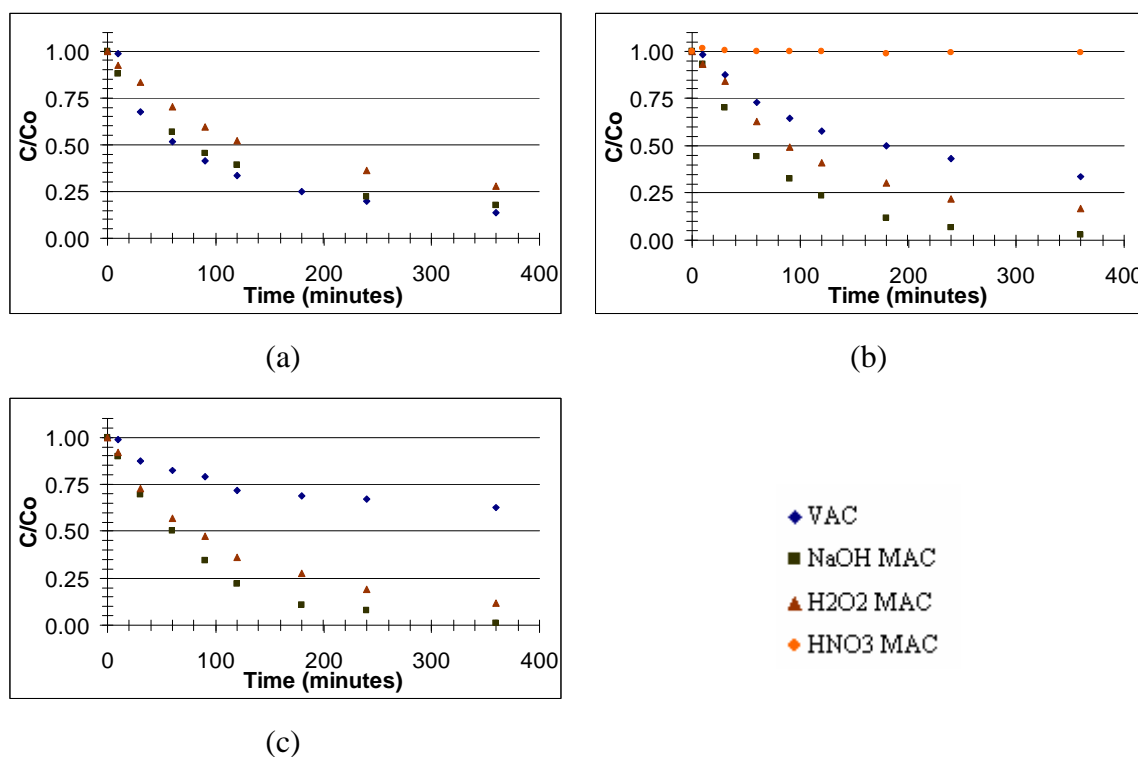
Figure 12: Batch anion tests of 1 mM for: (a) Cl$^-$; (b) SO$_4$$^{2-}$; (c) NO$_3^-$.

  The NaOH MAC performed the best in the batch tests with SO_4^{2-}, reaching approximately 97% removal in 6 hours, followed by H$_2$O$_2$ MAC with 83% removal. VAC was only able to remove 66% of the perchlorate. HNO$_3$ MAC performed poorly in this test and showed no response or removal over the given time period. Overall, the sulfate ion in solution with perchlorate did not interfere with adsorption due to its strong performance with removal of perchlorate with sulfate ions in solution.

Figure 12 shows the removal of perchlorate when NO_3^- is present in the system. NaOH and H_2O_2 MAC outperformed VAC in this test. The modified carbon, with the exception of HNO_3, was able to remove greater than 80% of the perchlorate when in solution with nitrate, compared with the VAC that removed less than 40% of the perchlorate. The VAC was inhibited by the presence of nitrate in solution. NaOH and H_2O_2 MAC were not inhibited by the nitrate anion being in solution.

Removal of perchlorate in the presence of chloride (Cl^-) was measured and the results are shown in Figure 12(a) for VAC. The VAC was able to outperform the NaOH and H_2O_2 MAC. Chloride anion in solution did not inhibit the removal of perchlorate by any of the carbon samples, with the exception of the HNO_3 treated sample. H_2O_2 and NaOH MAC as well as the VAC were able to remove more than 60% of perchlorate in solution in the presence of chloride anion.

HNO_3 MAC performed poorly in the presence of chloride. HNO_3 MAC's poor performance might have been foreseen, based on the results with VAC. The VAC carbon sample significantly out performed in the NO_3^- inhibition experiment. A possible explanation for this behavior might be that there is some functional group on the VAC that inhibits adsorption of perchlorate and is not modified when treated with HNO_3. No literature on anion inhibition for perchlorate adsorption onto carbon is available to the author's knowledge.

CHAPTER VI

ELECTROCHEMICAL BEHAVIOR OF MODIFIED CARBON AND

PERCHLORATE

ELECTROCHEMICAL BEHAVIOR

Separate tests were preformed on the MAC and VAC at 50 mA and 100 mA in a fluidized bed reactor illustrated in Figure 5. Figure 13 contains the data collected for the two separate currents.

Figure 13 shows that at both 50 and 100 mA, the VAC carbon was able to remove more perchlorate than with the MAC. The reaction conducted at 50 mA removed a little more than 25% the perchlorate for the NaOH and H_2O_2 MAC where as the VAC removed a little more than 50%. These numbers are less than the removal seen in the anion influence batch tests. The reaction with 100 mA current shows a slight increase in removal from the 50 mA tests for the NaOH and H_2O_2 MAC, but approximately the same removal percentage for the VAC.

(a)   (b)
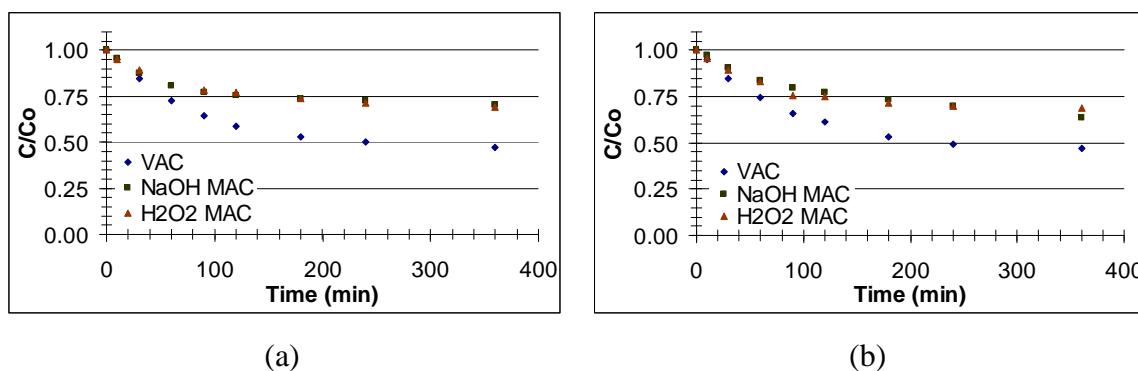
Figure 13: Electrochemical reactions with: (a) 50 mA and (b) 100 mA.

Figure 14 compares the data for all the carbons at both 50 mA and 100 mA. This figure shows that a change in voltage had little effect on the removal efficiency of the

carbons. Raw data for the experiment at both 50 mA and 100 mA can be found in Appendix A.
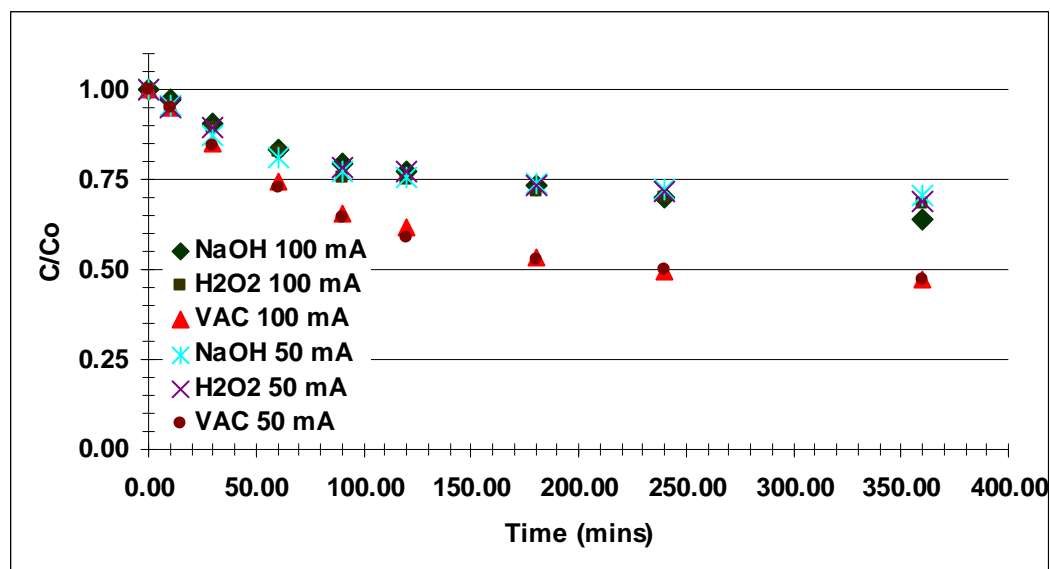
Figure 14: Comparison of 50 mA and 100 mA voltage source data.

DESORPTION

Desorption tests were performed with all the carbon samples used in the electrochemical process. Table 5 provides data for the percent of perchlorate removed by desorption tests for each individual carbon samples analyzed. The initial concentration is the concentration of perchlorate measured at time zero during the electrochemical experiment. Final concentration is the concentration measured at time equal to 6 hours. The concentration adsorbed represents the initial concentration minus the final concentration. The desorbed concentration is the mass balance concentration calculated after desorption tests were preformed. The percent desorbed is the desorbed concentration divided by the total adsorbed concentration.

Table 5: Percent of perchlorate desorbed from the carbon used in the electrochemical analysis.

Sample	Initial Concentration	Final Concentration	Concentration Adsorbed	Desorbed Concentration	% Desorbed
NaOH 50 mA	98.19	69.06	29.13	24.94	86.00
NaOH 100 mA	98.38	62.73	35.65	30.67	86.00
H_2O_2 50 mA	98.95	68.35	30.61	26.05	85.00
H_2O_2 100 mA	98.37	67.37	31.00	27.55	89.00
VAC 50 mA	97.54	45.80	51.74	37.27	72.00
VAC 100 mA	102.57	48.38	54.19	37.72	70.00

The desorption data indicates whether the perchlorate was adsorbed or reduced to chloride ion during the electrochemical process. The NaOH MAC and H_2O_2 MAC samples desorbed no more than 90% of the perchlorate that was initially sorbed by the carbon during the electrochemical experiment. VAC shows signs of low desorption recovery of the perchlorate concentration that was adsorbed. The VAC at 50 mA desorbed 72% of the perchlorate adsorbed versus the VAC 100 mA desorbed 70% adsorbed.

Based on the desorption data in Table 5, the adsorption process can be identified as the main mechanism of perchlorate removal over the reduction of perchlorate. Brown *et al* (47) reported approximately 100% perchlorate recovery in desorption tests and they suggest the main removal mechanism is ion exchange. However, desorption data in Table 5 shows only 70-80% recovery of perchlorate. This is less recovery than what Brown *et al.* (47) observed, who suggested the main mechanism of perchlorate removal to be ion exchange, but electrochemical reduction cannot be ruled out. Electrochemical reduction can be occurring, but adsorption is the main mechanism of removal.

Brown (7) conducted a study were the reduction of perchlorate was attempted at an active titanium surface. The reduction of a perchlorate ion at an electrode surface is an unusual occurrence, but a titanium electrode was able to reduce perchlorate as reported in Brown's (7) study.

Complete recovery (100%) of the perchlorate sorbed onto the carbon may not be possible due to the pores on the surface tightly holding onto the perchlorate. The sodium

nitrate used to desorb the perchlorate may not be able to reach into the inner pores with in the carbon to effectively remove the perchlorate that has been adsorbed onto the carbon. The loss in perchlorate may also indicate that reduction is occurring, however more research is needed to accurately conclude this.

CHAPTER VII

CONCLUSIONS

There are two variables that are changed when oxidizing carbon: the surface area and the functional groups. The functional groups can be modified (such as the case with the HNO_3 MAC) or increased (as was seen in the NaOH and H_2O_2 MACs) with oxidation. The surface area can either be increased or decreased based on the strength of the oxidation method.

Total sorption capcity is proportional to the total number of functional groups on the carbon surface. In Figure 10, the isotherm tests where the VAC out performed the MAC, all that was in solution was perchlorate and the cation that it was associated with in the solid state. When a competitive anion was added to the solution (Cl^-, SO_4^{2-}, or NO_3^-), competitive sorption was observed. In competitive sorption, high energy is needed at the surface site to selectively sorb the chemical of concern to the surface. During the electrochemical analysis, high surface area is needed to adsorb the perchlorate onto the surface. The data indicates that the oxidation processes used to modify the carbon changed the functional groups by increasing their density, but due to the strong oxidation process, the surface area was decreased, thus making the carbon ineffective in sorption tests. Pereira *et al.* (23) reported a decrease in micropore volume following oxidation with nitric acid. A decrease in the micropore volume would cause a decrease in the surface area. Further research conducted in this field that would find a less invasive oxidation process that can modify the surface functional groups while not decreasing the surface area would be beneficial.

Poor performance of HNO_3 MAC was evident throughout the experiments. HNO_3 MAC's poor performance may be due to the functional groups modified. DRIFT analysis showed that the HNO_3 MAC had a distinct separate peak from the other MAC's. This peak, identified as being –NO functional group, may be what is inhibiting the adsorption of perchlorate. The –NO functional group may have already been present on the VAC and the modification process with nitrate acid increasing its presence.

VAC performed poorly in the presence of anions, while the NaOH and H_2O_2 MAC were not inhibited by NO_3^- being in solution. HNO_3 MAC was observed to remove perchlorate when the experiment started, but as more perchlorate was adsorbed onto the surface, some chemical that was on the surface of the carbon was being removed. The unknown chemical's peak would come out at the same time as the perchlorate peak in the analysis, thus showing an increase in perchlorate concentration over time that was greater than the initial concentration. Until the unknown chemical can be identified, the surface oxidation treatment of nitrate acid is not recommended.

Experiments to determine the effect of pH on perchlorate removal by the carbons showed that removal is based on the pH of the system and the induced charge on the surface due to changes in the pH. When the carbon was modified, the pH values of suspensions of the carbon were also modified, thus changing the surface charge of the carbon due to a pH being above or below the carbon's PZC. The pH in a suspension of HNO_3 MAC's was pH 2.36. The suspension values for all other carbons were above 4.5. A pH above pH 2.36 would induce a net negative charge on the surface of the carbon, which would repel a negatively charged ion (25).

Overall, this study has provided information about perchlorate removal with activated carbon and an electrochemical process. Carbon surfaces were oxidized to increase removal of perchlorate. Perchlorate removal was evident in equilibrium adsorption tests with VAC carbon and MAC carbon. pH plays an important role in removal of perchlorate, especially at high pH values. In the presence of anions at constant pH, more perchlorate was removed by MAC than by VAC. However more perchlorate was removed by VAC in the electrochemical experiments at the two separate currents investigated.

LITERATURE CITED

1 US EPA, Perchlorate. Accessed June 15, 2006. http://www.epa.gov/fedfac/documents/perchlorate.htm.

2 Urbansky, E. T. Perchlorate chemistry: Implications for analysis and remediation. *Bioremed. Jour.***1998**, *2*, 81-95.

3 Jackson, W., A; Anderson, T.; Harvey, G.; Orris, G.; Rajagopalan, S.; Kang, N. In *Perchlorate: Environmental Occurance, Interactions and Treatment*; Gu, B., Coates, J. D., Eds.; Springer Science + Business Media, Inc.: New York, 2006, pp 49-66.

4 UA EPA, National Perchlorate Detections as of September 23, 2004. Accessed June 15, 2006. http://www.epa.gov/fedfac/documents/perchlorate_map/nationalmap.htm.

5 Kirk, A. B.; Smith, E. E.; Tian, K.; Anderson, T. A.; Dasgupta, P.K. Perchlorate in milk. *Environ. Sci. Tech*. **2003**, *37*, 4979-4981.

6 Earley, J. E.; Tofan, D. C.; Amadei, G. A. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 89-98.

7 Brown, G. M. The reduction of chlorate and perchlorate ions at an active titanium electrode. *J. Electroanal Chem.* **1986**, *198*, 319-330.

8 Wasberg, M.; Horà nyi, G. The reduction of ClO_4^- ions on Rh electrodes. *J. Electroannal Chem.* **1995**, *385*, 63-70.

9 Gu, B.; Dong, W.; Brown, G. M.; Cole, D.R. Complete degradation of perchlorate in ferric chloride and hydrochloric acid under controlled temperature and pressure. *Environ. Sci. Technol*. **2003**, *37*, 2291-2295.

10 Almeida, C. M. V. B.; Giannetti, B. F.; Rabockai, T. Electrochemical study of perchlorate reduction at tin electrodes. *J. Electroannal Chem*. **1997**, *422*, 185-189.

11 US EPA, Known Perchlorate Releases in the U.S., March 25, 2005. Accessed June 15, 2006. http://www.epa.gov/fedfac/pdf/detect0305.pdf.

12 Database & Internet Searching. Perchlorate Structure. Accessed June 15, 2006. http://www.chemfinder.com.

13 Picture of Perchlorate Ion. Accessed June 15, 2006. http://www.chem.purdue.edu/gchelp/molecules/clo4.gif.

14 Espenson, J. H. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 1-8.

15   Brown, G. M.; Gu, B.; In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Eds.; Springer Science+Business Media, Inc: New York, 2006, pp 17-47.

16   Clark, J. J. J., In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 15-29.

17   Mattie, D. R.; Strawson, J.; Zhao, J. In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Eds.; Springer Science+Business Media, Inc: New York, 2006, pp 169-196.

18   Smith, P. N. In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Eds.; Springer Science+Business Media, Inc: New York, 2006, pp 153-169.

19   Sontheimer, H.; Crittenden, J. C.; Summers R. S. *Activated Carbon for Water Treatment:* AWWA Research Foundation: Denver, 1988, pp 51-105.

20   Rodriguez-Reinoso, F. The role of carbon materials in heterogeneous catalysis. *Carbon*. **36**, *1998*, 159-175.

21   Faria, P.C.C.; Orfao, J.J.M.; Pereira, M.F.R. Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Research*. **38**, *2004,* 2043-2052.

22   Bohem, H.P. Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon*. **32**, *1994*, 759-769.

23   Pereira, M. F. R., Soares, S., Orfao, J.J.M., Figueiredo, J.L. Adsorption of dyes on activated carbons: influence of surface chemical groups. *Carbon.* **41**, *2003*, 811-821.

24   Gomez-Serrano, V., Acedo-Ramos, M.' Lopez-Peinado, A. J., Valenzuela-Calohorro, C. Oxidation of activated carbon by hydrogen peroxide. Study of surface functional groups by FT-i.r. *Fuel*. **73**, *1994*, 387-395.

25   Chen, J. P., Wu, S. Acid/Base-treated activated carbons: Characterization of functional groups and metal adsorptive properties. *Langmuir*. **20**, *2004*, 2233-2242.

26   Noh, Jo. S., Schwarz, J. A. Effect of HNO_3 treatment on the surface acidity of activated carbons. *Carbon*. **28**, *1990*, 675-682.

27   Gu, B.; Bonnesen, P. V.; Sloop, F. V.; Brown, G. M. In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Eds.; Springer Science+Business Media, Inc: New York, 2006, pp 373-388.

28   Nzengung, V. A. and Wang, C. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 219-230.

29 Brown, G. M.; Gu, B.; In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Ed.; Springer Science+Business Media, Inc: New York, 2006, pp 209-252.

30 Batista, J. R.; Mcgarvey, F. X.; Vieira, A. R. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 135-146.

31 Tripp, A. R. and Clifford, D. A. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 123-134.

32 Coates, J. D. and Achenbach, L. A. In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Ed.; Springer Science+Business Media, Inc: New York, 2006, pp 279-296.

33 Giblin, T. L.; Herman, D. C.; Frankenberger, W. T. Jr. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 199-212.

34 Parrette, R. and Cannon, F. S. In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Ed.; Springer Science+Business Media, Inc: New York, 2006, pp 343-372.

35 Greene, M.R. and Pitre, M. P. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 241-256.

36 Lui, B.; Wagner, P. A.; Earley, J. E. Reduction of perchlorate ion by (N-(Hydroxyethyl)ethylenediaminetriacetato)aquotitanium(III). *Inorg. Chem.* **23**, *1984*, 3418-3420.

37 Mosier-Boss, P.A. In *Perchlorate: Environmental Occurrence, Interactions and Treatment*. Gu, B.; Coates, J. D., Eds.; Springer Science+Business Media, Inc: New York, 2006, pp 111-151.

38 Jackson, P.E; Gokhale, S.; Rohrer, J. S. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000 pp 37-44.

39 Clewell, R. A.; Chaudhuri, S.; Dickson, S.; Cassaday, R. S.; Wallner, W.N.; Eldridge, J. E.; and Mattie, D. R. In *Perchlorate in the Environment*. Urbansky, E. T., Ed.; Kluwer Academic/Plenum Publishers: New York, 2000, pp 45-58.

40 Figueiredo, J. L., Pereira, M. F. R., Freitas, M. M. A., Orfao, J. J. M. Modification of the surface chemistry of activated carbons. *Carbon*. **37**, *1999*, 1379-1389.

41 Moreno-Castilla, C., Lopez-Ramon, M. V., Carrasco-Marin, F. Changes in surface chemistry of activated carbons by wet oxidation. *Carbon*. **38**, *2000*,

1995-2001.

42 Fanning, P. E., Vannice, M. A. A DRIFTS study of the formation of surface groups on carbon by oxidation. *Carbon*. **31**, *1993*, 721-730.

43 Vinke, P., Van der Eijk, M., Verbree, M., Voskamp, A. F., Van Bekkum, H. Modification of the surfaces of a gas-activated carbon and a chemically activated carbon with nitric acid, hypochlorite and ammonia. *Carbon*. **32**, *1994*, 675-686.

44 Gomez-Serrano, V.; Acedo-Ramos, M.; Lopez-Peinado, A.J.; Valenzuela-Calahorro, C. Mass and surface changes of activated carbon treated with nitric acid. Thermal behaviors of the sample. *Thermochimica Acta*. **176***, 1991*, 129.

45 Chingombe, P., Saha, B., Wakeman, R.J. Surface modification and characterisation of a coal-based activated carbon. *Carbon*. **43**, *2005*, 3132-3142.

46 Ishizaki, C., Marti, I. Surface oxide structures on a commercial activated carbon. *Carbon*. **19**, *1981*, 409-412.

47 Brown, C. B.; Snoeyink, V. L.; Kirisits, M. J. Abiotic and biotic perchlorate removal in an activated carbon filter. *AWWA Journal.***94**, *2002*, 70-79.

APPENDIX A

Table A- 1: Raw Data for Batch pH Tests.

4.5					
	Time	Coal % removal	NaOH MAC	H_2O_2 MAC	HNO_3 MAC
	0	1.00	1.00	1.00	1.00
	10	0.91	0.92	0.88	0.71
	30	0.74	--	--	0.72
	60	0.50	--	--	0.65
	90	0.37	0.78	0.86	
	120	0.26	0.57	0.42	0.68
	180	0.17	0.29	0.29	0.66
	240	0.12	0.19	0.21	0.63
	360	0.07	0.08	0.14	0.71

7.2					
	Time	Coal % removal	NaOH MAC	H_2O_2 MAC	HNO_3 MAC
	0	1.00	1.00	1.00	1.00
	10	0.95	0.98	0.59	0.98
	30	0.81	0.79	0.46	1.00
	60	0.68	0.75	0.46	1.08
	90	0.56	0.63	0.44	1.04
	120	0.50	0.57	0.48	1.23
	180	0.40	0.55	0.42	1.18
	240	0.34	0.49	0.42	1.36
	360	0.26	0.33	0.33	1.18

10.5				
	Time	Coal % removal	NaOH MAC	H_2O_2 MAC
	0	1.00	1.00	1.00
	10	0.95	0.95	--
	30	0.89	0.92	--
	60	0.83	0.90	0.97
	90	0.80	0.88	0.98
	120	0.75	0.88	0.99
	180	0.67	0.84	0.96
	240	0.60	0.80	0.98
	360	0.55	0.77	0.92

Table A- 2: Raw Data for Batch Anions.

Cl⁻					
	Time	Coal % removal	NaOH MAC	H_2O_2 MAC	HNO_3 MAC
	0	1.00	1.00	1.00	1.00
	10	0.99	0.88	0.93	0.92
	30	0.67	--	0.84	0.88
	60	0.52	0.57	0.70	0.86
	90	0.41	0.45	0.59	0.91
	120	0.33	0.39	0.52	0.84
	180	0.25	--	--	--
	240	0.20	0.22	0.36	0.86
	360	0.14	0.18	0.28	0.87

SO_4^{2-}					
	Time	Coal % removal	NaOH MAC	H_2O_2 MAC	HNO_3 MAC
	0	1.00	1.00	1.00	1.00
	10	0.98	0.93	0.93	1.01
	30	0.88	0.70	0.84	1.01
	60	0.73	0.44	0.63	1.00
	90	0.65	0.32	0.49	1.00
	120	0.58	0.24	0.41	1.00
	180	0.50	0.12	0.30	0.99
	240	0.43	0.07	0.22	0.99
	360	0.34	0.03	0.17	0.99

NO_3^-					
	Time	Coal % removal	NaOH MAC	H_2O_2 MAC	HNO_3 MAC
	0	1.00	1.00	1.00	1.00
	10	0.99	0.90	0.92	0.96
	30	0.87	0.70	0.73	0.83
	60	0.82	0.50	0.57	0.83
	90	0.79	0.34	0.47	0.71
	120	0.72	0.22	0.36	0.72
	180	0.69	0.11	0.28	0.84
	240	0.67	0.08	0.19	1.07
	360	0.63	0.01	0.12	1.13

Table A- 1: Raw Data for the Electrochemical Reactions.

	Time	Coal % removal	NaOH MAC	H$_2$O$_2$ MAC
Background electrolyte – 5 mM Na2SO4				
50	m Amp			
	Time	Coal % removal	NaOH MAC	H$_2$O$_2$ MAC
	0	1.00	1.00	1.00
	10	0.95	0.95	0.95
	30	0.85	0.87	0.89
	60	0.73	0.81	--
	90	0.65	0.77	0.78
	120	0.59	0.76	0.77
	180	0.53	0.74	0.73
	240	0.50	0.72	0.71
	360	0.47	0.70	0.69
100	m Amp			
	Time	Coal % removal	NaOH MAC	H$_2$O$_2$ MAC
	0	1.00	1.00	1.00
	10	0.95	0.97	0.96
	30	0.85	0.90	0.89
	60	0.74	0.84	0.83
	90	0.66	0.80	0.76
	120	0.62	0.77	0.75
	180	0.53	0.73	0.72
	240	0.49	0.70	0.70
	360	0.47	0.64	0.68

VITA

Meredith Caitlyn Langille received her Bachelor of Science degree in environmental engineering from Rensselaer Polytechnic Institute located in Troy, NY in May of 2005. She entered the Civil Engineering Department of Texas A&M University in September of 2005 and received her Master of Science in December of 2006. Her research interests include fate and transport and remediation of hazardous materials in the environment.

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