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Abstract

Stormwater is an increasing global threat to water quality in water bodies. Urbanization is expanding, and so is the amount of impermeable surfaces that prevents water seepage into the ground. This is disturbing the natural water cycle and is leading to increased surface runoff. Waters that receives this runoff are exposed to rapid shock concentrations of pollutants. Nitrate is such a pollutant. High concentrations of nitrate lead to several adverse effects on human health and nature, like methaemoglobinaemia in infants and eutrophication of water bodies.

In this study, batch experiments were performed on synthetic stormwater with commercial activated carbon added to investigate the sorption of nitrate. Synthetic stormwater samples contained various concentrations of nitrate-nitrogen. The activated carbon used as sorbents were Hydrodarco 3000 and the Sub-bituminous CR830A . Sampling was performed at specific time intervals and analyzed by an ion chromatograph for anion concentrations. Freundlich and Langmuir adsorption models were investigated for their prediction to explain the experimental data.

Between 49 - 95% of the nitrate-nitrogen was removed from the samples to which the sub-bituminous carbon was added, with an average percent removal of 75%. Adsorption capacity was determined to be between 11.662 - 2363.814 mg/kg. None of the adsorption models were found suitable. Samples with added Hydrodarco carbon had an nitrate-nitrogen removal between 31 - 93 % , and the average percent removal was 67%. Adsorption capacity was found to be between 32.547 - 5192.875 mg/kg. The Freundlich isotherm was found to be the most suitable model.

Adsorption occurring in this study were found to be quick, where equilibrium was reached rapidly after activated carbon was added to the synthetic stormwater samples. Sulfate release was observed at high amounts in equilibrium samples containing activated carbon.

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Abbreviations

RAL = Research Analytical Laboratory

F.W.=Formula Weight

IC= Ion Chromatograph

RPM = Revolutions Per Minute

AC = Activated Carbon

PAC = Powered Activated Carbon

GAC = Granular Activated Carbon

WHO = World Health Organisation

US EPA = United States Environmental Protection Agency

CC = Calibration Curve

NPDES = The National Pollutant Discharge Elimination System

CWA = Clean Water Act

1. Introduction

Stormwater is an increasing risk to the water quality in water bodies. Areas with a growing population are particularly vulnerable, due to urbanization. Miles of highways and other impermeable surfaces are disturbing the natural water drainage system which results in increased runoff. The impact of this is that waters close to urban areas are exposed to rapid first flushes with high pollutant concentrations (Han et al., 2006, U.S.EPA, 2008).

One of the biggest concerns is the increase of nitrate in the receiving waters. High nitrate concentrations have contributed to negative effects on human health and on the environment. Common treatment methods for nitrate removal include several physicochemical and biological processes, but few of them have been found effective for application to stormwater treatment systems. However, adsorption has potential as a possible treatment method to remove nitrate (Ahmadzadeh Tofighy and Mohammadi, 2012).

The goal of this thesis is to investigate sorption of nitrates from synthetic stormwater using activated carbon as a sorbent. Two types of commercial activated carbon were evaluated in isotherm experiments. The assignment was provided by John S. Gulliver and William A. Arnold at the University in Minnesota, and is a cooperation with the University in Stavanger, as arranged by my faculty supervisor Torleiv Bilstad. Experimental work was performed at a laboratory in the Saint Paul campus in Minnesota 16.01.12-14.04.12. Analysis, evaluation and the final reporting were completed in Stavanger. This research is a part of a larger project to develop treatment methods for removal of several pollutants from stormwater. My advisors John S. Gulliver, William A. Arnold and Andrew J. Erickson continue to work on this project and will take my research and results further.

2. Theory

This chapter presents the issue of nitrate, its origin, and the problems connected to stormwater and urbanization. Possible treatment methods are summarized, where the focus is directed to adsorption by activated carbon.

2.1 Stormwater pollution

One major cause for pollution of waters is stormwater runoff, which occurs during and after precipitation events and snow melt where water flows over impermeable surfaces and does not seep into the ground. Examples of impermeable surfaces are highways, parking lots, streets and roofs on buildings (U.S.EPA, 2008). Pollutant materials accumulated during dry periods are transported to waters by the runoff from these surfaces (i.e., surface runoff)(Akan and Houghtalen, 2003).

Stormwater from urban runoff remains one of the biggest challenges when it comes to pollution control in modern time. The runoff is a major reason for poor water quality across the U.S. (U.S.EPA, 2008). The magnitude of the problem is not yet quantified, and treatment methods are still in the development phase (Han et al., 2006). The problem is expected to expand as a result of population growth and the resulting increase in urbanization. This emerging urbanization leads to formation of more impervious surfaces, affecting the water movement over and below the ground surface. Before urbanization, natural systems had higher infiltration rates, which added to the groundwater and soil moisture. When stormwater flows rapidly over the land, the receiving waters are subjected to shock concentrations of pollutant materials (Figure 2-1)(U.S.EPA, 2008).
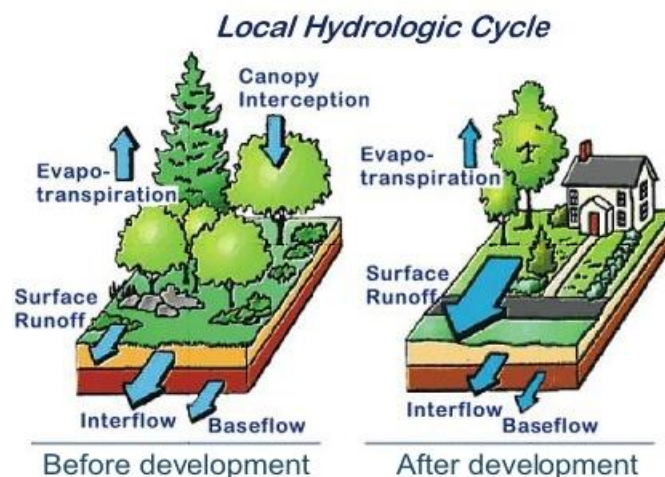
Figure 2-1: Illustration of the hydrological pathways in a watershed before and after urbanization. The size of the arrows indicates the amount of the various elements in water cycle(U.S.EPA, 2008)

The National Pollutant Discharge Elimination System (NPDES) program under Clean Water Act (CWA) has the main responsibility for controlling the water quality in the U.S. The purpose of the program was to decrease the pollution from industrial wastewater and sewage discharges from municipalities. These sources were determined as the main causes of impaired water quality, and were easily handled considering their origins from known locations. Stormwater was added as a source for impaired water quality in 1987 to a stormwater control program in the NPDES program. In 1990 and 1999, the Environmental Protection Agency (EPA) established stormwater rules, known as Phase I and Phase II.

Regulations and laws to control stormwater have occurred over the last 25 years. The awareness, however, of the negative effect of stormwater on water quality has been known for a long time. The long delay for development and management in urban areas are now facing problems due to conflicts between new incomplete stormwater laws and the state with its local laws (U.S.EPA, 2008). Ideally, regulations for stormwater would include direct controls and monitoring on developed land. There should also be strict regulations on runoff water quality and quantity of it, together with regulations on products which are impairing the water quality, such as fertilizers (U.S.EPA, 2008).

2.2   Nitrogen problems

Various forms of nitrogen present in waters can cause adverse effects. Nitrate promotes growth of algae and can lead to eutrophication of water bodies, especially in estuaries and oceanic water bodies. Degradation of algae consume large amounts of oxygen which can lead to an anaerobic environments and be harmful for the biota (Akan and Houghtalen, 2003).

Nitrate is hazardous to infants and pregnant women due to the risk of methaemoglobinaemia , also called the "blue-baby syndrome". Reduction of nitrate to nitrite in the stomach of infants occurs, where nitrite will bind to haemoglobin and form methaemoglobin in the red bloodcells (equation 2-1). Metaemoglobin binds up oxygen and prevents oxygen transport. When the levels of it exceed 10 %, there is risk for cyanosis (blue-baby syndrome) where the infants are suffocated. Most of the nitrate in the body will oxidize to nitrate, but there will be residual that can react with the haemoglobin. The risk is greater for bottle-fed-infants than adults and children, due to the infants body weight and limited ability to produce repairing enzymes. In studies reported by the World Health Organization (WHO), 97% of the cases where symptoms of cyanosis were observed occurred in infants that were mostly under 3 months old, and the nitrate concentration in the water was over 44.3 mg/L. Methaemoglobinaemia is normally seen as a result of high nitrate concentrations in drinking water, even though it has been found in infants that are related to high nitrate consumption from vegetables.

High nitrate levels in drinking water is clearly an essential risk factor for infants (Bhatnagar and Sillanpää, 2011, Shrimali and Singh, 2001, WHO, 2011).

$$Haemoglobin\ (Fe^{2+}) \xrightarrow{NO_2^-} Methaemoglobin \qquad \text{2-1}$$
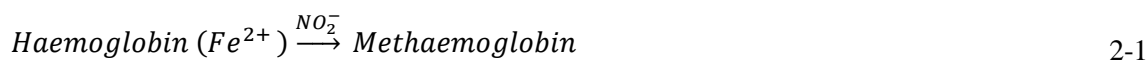
In drinking water, nitrate may cause different types of cancer in humans who are exposed to high amounts. Nitrite can potentially react with dimethyl amine and form the carcinogenic dimethyl nitrosamine(2-2)(Bhatnagar and Sillanpää, 2011) (WHO, 2011)(Shrimali and Singh, 2001).

2-2
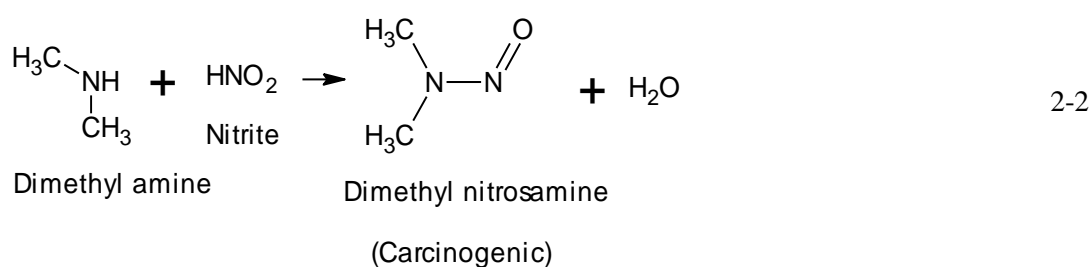
Connections exists between nitrate intake and several disorders and adverse effects, however there is still a lack of compelling evidence (WHO, 2011). In humans, water contaminated with nitrate has been related to outbreaks of infectious diseases, childhood diabetes and decrease iodine uptake, but the current studies are incomplete. Other studies indicates that high nitrate uptake can lead to abortion in animals such as cattle (WHO, 2011, Bhatnagar and Sillanpää, 2011, Shrimali and Singh, 2001).

WHO has given guideline values for safe amount of nitrate and nitrite in the drinking water to protect bottle-fed infants from methaemoglobinaemia. Nitrate should not exceed 50 mg/L (NO_3^-) or 11 mg/L nitrate-nitrogen (NO_3^--N). Nitrite should not exceed 3 mg/L (NO_2^-) or 0.9 mg/L nitrite-nitrogen (NO_2^--N). Nitrate levels in drinking water in most countries are below 10 mg/L; however, it can increase over 50 mg/L in well water. The nitrite level is normally below a few mg/L. Basis for these guidelines are studies of bottle-fed-infants. There were no reports on infants with methaemoglobinaemia in areas where the nitrate ion concentration were below 50 mg/L in the drinking water. Due to the possible occurrence of nitrate and nitrite at the same time in drinking water, the weighted total concentrations should not exceed 1 as described by equation 2-3 (WHO, 2011).

$$\frac{NO_3^-}{50} + \frac{NO_2^-}{3} \leq 1 \qquad \text{2-3}$$

2.3 Origin of nitrate

Nitrate is a natural part of the environment and the nitrogen cycle. In oxygenated water systems it is the stable form of nitrogen. In all plants, nitrate can be found at different concentrations, and the nitrate itself is an essential nutrient for the plant. However, nitrate can pollute surface waters and ground waters, especially areas with agricultural activity nearby where there is excessive use of fertilizers. Other sources for nitrate are animal waste, sewer lines, land discharges from wastewater and atmospheric deposition (U.S.EPA, 2012, Shrimali and Singh, 2001, WHO, 2011, Bhatnagar and Sillanpää, 2011). Nitrate has a relatively high solubility and does not bind readily to soil, which makes it susceptible to leaching and a wide spread contaminant (Bhatnagar and Sillanpää, 2011). A common scenario for nitrate formation is the process occurring with urine from animal waste, which contains nitrogen as urea ($(NH_2)_2CO$). Degradation of this product results in formation of ammonia which can be oxidized to nitrite and nitrate by the aerobic process of nitrification. The process is mediated by bacteria such as *Nitrosomonas* and *Nitrobacter*, as shown in the equations 2-4 and 2-5. Oxygen consumption during these processes may have a harmful effect on the environment if the levels of oxygen consumed are sufficiently high.

$$2NH_3 + 3O_2 \xrightarrow{Nitrosomonas} 2NO_2^- + 2H^+ + 2H_2O \qquad \text{2-4}$$

$$2NO_2^- + O_2\,S \xrightarrow{Nitrobacter} 2NO_3^- \qquad \text{2-5}$$
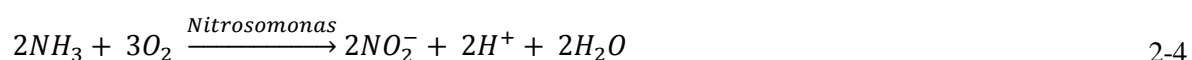
At the same time, nitrite and nitrate can be converted to nitrogen gas and nitrogen monoxide during the denitrification process mediated by denitrifying bacteria under anaerobic conditions (equation 2-6) (Shrimali and Singh, 2001).

$$\frac{NO_2^-}{NO_3^-} \xrightarrow{Denitrifiers} N_2 + N_2O \qquad \text{2-6}$$
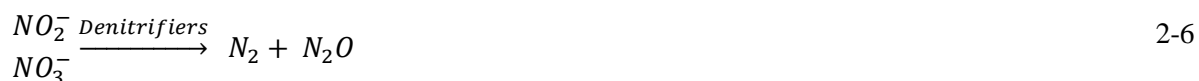
2.4　Removal of nitrate

WHO recommends biological denitrification for nitrogen removal from surface waters and ion exchange for nitrate removal from ground waters. Chlorination should be used for removal of nitrite by forming nitrate. Biological denitrification and ion exchange have the potential to provide concentrations below 5 mg/L nitrate and chlorination has the ability to provide concentrations down to 0.1 mg/L nitrite (WHO, 2011).

There are several advantages to biological denitrification. It is cost-effective and friendly to the environment. The final product is harmless nitrogen gas if enough oxygen is available. However, the process is slow, for wastewater in particular due to low temperatures and large concentrations of nitrate (Demiral and Gündüzoğlu, 2010). Other conventional alternatives for removal of nitrate are chemical processes such as ion exchange, electrodialysis and reverse osmosis (Demiral and Gündüzoğlu, 2010, Shrimali and Singh, 2001). These are inefficient processes to focus on, due to high operational costs and disposal problems of by-products (Shrimali and Singh, 2001, Bhatnagar et al., 2010).

Nitrate removal from water by adsorption has received increased attention recently. The main reasons are low to medium material cost, simple design, and easy operation. Advantages of this process are the possibilities for removal of different types of pollutants, both inorganic and organic, and post-treatments are normally not necessary. The process has been found effective in the removal of several anions, such as fluoride, nitrate, bromate and perchlorate, under the usage of different adsorption materials(Bhatnagar and Sillanpää, 2011). Choosing the right material is important for an optimal adsorption of the specific pollutant(Bhatnagar and Sillanpää, 2011).

Activated carbon appears to be a universal sorbent for pollutants, especially organic compounds. When it comes to its adsorption of nitrate, however, few results have been published. Earlier studies on activated carbon have shown poor adsorption of anionic pollutants, such as nitrate (Bhatnagar and Sillanpää, 2011). However, some studies have shown otherwise. One study wanted to focus on the effect acid treatment had on carbon cloth for adsorption of NO_2^- and NO_3^-. Protonation of surface -OH groups were used to produce positive sites on the carbon cloth, which resulted in a greater adsorption of anions (Afkhami et al., 2007). This process has been used commercially to produce acid washed activated carbon for treatment of unwanted negatively charged pollutants (Norit, 2012, Carbon-Resources, 2010).

2.5   Adsorption

Adsorption is the process where a component in the liquid phase is transferred to the solid phase. The substance removed from the liquid phase in the interface is the adsorbate. The adsorbate accumulates on the adsorbent which is a solid, liquid or gas phase. One type of adsorbent is activated carbon, which is discussed below (Metcalf & Eddy et al., 2003).

2.5.1 *Adsorption basics*

Adsorption can be described in four fundamental steps;

   (1) Bulk solution transport: movement of the substance (adsorbate) to the boundary layer, normally by advection.
   (2) Film diffusion transport: Substance is transported to the pores by diffusion through the film.
   (3) Pore transport: Substance is transported through the pores to be adsorbed. This is done by diffusion through the pore liquid, diffusion at the surface, or both.
   (4) Adsorption: The substance is attached to the adsorbent. Adsorption occurs at an available site at the outer surface or in the pores

Pores sizes are divided into macropores (>25 nm), mesopores (>1 and <25 nm) and micropores (< 1 nm). Adsorption in the macropores and mesopores are considered insignificant due to their small total surface area compared to the micropores.

Forces involved during adsorption may be coulombic-unlike charges, point charge and a dipole, dipole-dipole interactions, point charge neutral species, London or van der Waals forces, covalent bonding with reaction and hydrogen bonding (Metcalf & Eddy et al., 2003).

It is difficult to distinguish between physical adsorption (at solid surface) and chemical absorption (in the solid matrix). The "sorption" expression is therefore often used to describe a particles attachment to a solid (Brezonik and Arnold, 2011)(Metcalf & Eddy et al., 2003).

Equilibrium and the sorbent capacity is reached when the rate of sorption equals the rate of desorption. In theory, the carbons capacity for uptake of a specific pollutant can be determined via its adsorption isotherm (Metcalf & Eddy et al., 2003).

2.5.2 *Surface charges*

There are various surfaces involved in boundary layers located in aquatic systems. They can be divided in two main groups; hydrophilic and hydrophobic. Hydrophilic surfaces consist of mineral solids (like hydrous oxides of Fe and Al), carbonate, aluminosilicate clays, and sulfide minerals. These have an abundance of polar or ionizable sites at the surface and are well equipped with electronegative atoms. Hydrophobic surfaces, however, have minimal polar sites and consist of detritus (natural organic matter), which originate from biofilms, microbial cells, decomposing microorganisms and "black-carbon" formed from incomplete combustion. Ionizable functional groups on microbiological cells and detritus can act as hydrophilic sites so formation of bonds with ionic solutes is possible. This includes also the black carbon particles which are similar to commercial activated carbon.

Surface charge originates in two major ways: 1) by isomorphic substitution in the crystalline lattice of the solid, which is a permanent charge, and 2) a variable surface charge occurring on the surface of a solid in the form of ionizable functional groups.

In isomorphic substitution, positive charge is reduced in hydrous oxides by a metal center with less charge than the major metal center. This results in a negative charge. Ionizable functional groups include oxide and hydroxide, carboxylic acid (R-COOH), amino (R-NH2), phosphate (R-OPO(OH)2), thiol (R-SH), and some other acid-base groups. Their charge depends of their degree of protolysis, and the pH of the medium.

One source for surface charges is surface complexion reactions, where reactions between ionizable functional groups and ligands create the charge; this is known as specific adsorption. Another source for surface charges is when charged solutes are sorbed to an already uncharged surface, this could be the sorption of an surfactant molecule with a hydrophobic tail and an ionic functional group (Brezonik and Arnold, 2011).

2.6   Adsorption isotherm

The amount of uptake of an adsorbate depends on the adsorbate characteristics and concentration together with the temperature. In an adsorption isotherm, the quantity of adsorbed material is compared with the concentration of the material at equilibrium during constant temperature. Experimental work is required to develop the isotherm. A scenario can be various concentrations of adsorbate in a fixed volume which are exposed to a specific concentration of adsorbent. The concentrations of the adsorbate are measured at the start and the end of the test period and used in

equation 2-7 to determine the adsorbent phase concentration which is used later to create the isotherms.

$$q_e = \frac{(C_o - C_e)V}{m}$$
$$\text{2-7}$$

q_e = Adsorbent phase concentration after equilibrium, mg adsorbate/ g adsorbent

C_o = Initial concentration of adsorbate, mg/L

C_e = Final equilibrium concentration of adsorbate after absorption has occurred, mg/L

V = Volume of liquid in the bottle, L

m= mass of adsorbent, g

(Metcalf & Eddy et al., 2003)

Fitting experimental data to the different isotherm models makes it possible to find a suitable model, which later can be used in for design purposes (Demiral and Gündüzoğlu, 2010).

2.6.1 *Freundlich isotherm*

In water- and wastewater treatment, the Freundlich isotherm is an empirical relation that is the most commonly used for activated carbon (equation 2-8). There is a wide spectrum of Freundlich capacity factors for different materials, which is why the factor needs to be determined for each material (Metcalf & Eddy et al., 2003). Experimental data that fit the Freundlich isotherm can indicate heterogeneity of the adsorbent surface(Öztürk and Bektaş, 2004).

$$\frac{x}{m} = K_f C_e^{1/n}$$
$$\text{2-8}$$

x/m = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbare/g activated carbon

K_f = Freundlich capacity factor, (mg absorbate/ g activated carbon)(L water/mg adsorbate)1/n

C_e= equilibrium concentration of adsorbate in solution after adsorption, mg/L

1/n = Freundlich intensity parameter

If n=1, the equation is equivalent to a linear isotherm. The constants can be determined by plotting log x/m versus log C_e via the transformation of equation 2-8 into equation 2-9 (Metcalf & Eddy et al., 2003):

$$\log\left(\frac{x}{m}\right) = \log K_f + \frac{1}{n} log C_e \qquad\qquad 2\text{-}9$$

2.6.2 *Langmuir isotherm*

Assumptions made for the Langmuir isotherm (2-10) include:

(1) The adsorbent surface has a specific number of available sites with identical energy levels.

(2) The adsorption process has to be reversible where the rate of adsorption equals the rate of desorption when equilibrium is reached. Adsorption rate is proportional to the distinction between quantity adsorbed and quantity that actually can be adsorbed for a specific concentration, which is zero at equilibrium.

The advantage of the Langmuir isotherm is that sorption capacity can be transferred between different experimental systems, such as batch and column studies. However, the assumptions made are not necessarily correct for the specific system studied.

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \qquad\qquad 2\text{-}10$$

x/m = mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorb ate/g activated carbon

a, b = empirical constants

C_e = equilibrium concentration of adsorbate in solution after adsorption, mg/L

The constants a and b can be determined by plotting 1/(x/m) vs. 1/C_e with the usage of 2-11, a rewritten form of 2-10(Metcalf & Eddy et al., 2003).

$$\frac{1}{\left(\frac{x}{m}\right)} = \frac{1}{abC_e} + \frac{1}{a} \qquad\qquad 2\text{-}11$$

2.7 Activated carbon

To prepare activated carbon, char from organic materials has to be made. Such materials can be coconut, almond, walnut hulls, wood, bone, coal etc. The char-producing process is a pyrolysis process where the base material has to be heated up to a red heat (right below 700°C) to drive off the hydrocarbons, but with an inadequate amount of oxygen to sustain combustion. The char particle is then exposed to gases such as steam and CO_2 which are oxidizing. This happens under high temperatures between 800 - 900°C. The char particle is now activated and a porous structure with a large internal surface area is developed as result of the gases. Many surface variations are possible, due to different initial materials and preparation procedures. The activated carbon can be divided and into the two classes; powered activated carbon (PAC) and granular activated carbon (GAC) after its size and adsorption capacity. PAC has a diameter <0.074 mm and GAC has a diameter >0.1 mm (Metcalf & Eddy et al., 2003).

2.7.1 *Hydrodarco 3000*

One of the adsorbents used in this study is the acid washed granular activated carbon Hydrodarco 3000 from Norit. The carbon is made during high temperature steam activation of lignite coal. Characteristics like the wide distribution of pore sizes and large pore volumes gives a high adsorption rate and a large capacity for handling dissolved organic compounds. The specifications make the Hydrodarco 3000 excellent for removal of certain pollutants from water (Table 2-1)(Norit, 2012).

Table 2-1: Technical specifications about Hydrodarco 3000(Norit, 2012)

Specifications	Hydrodarco 3000 M1783
Mesh size(US standard sieve):	
Greater than 8	5% maximum
Less than 30	5% maximum
Molasses decolorizing efficiency	85 minimum
Iodine number, mg/g	500 minimum
Abrasion resistance (AWWA), %/mm	70 minimum
Moisture, % as packed	8 maximum
Dust, %	0.7-0.9
Typical properties:	
Tannin value, mg/L	150
pH, water extract	4.5
Apparent density, vibrating feed, g/mL	0.38
Bed density, backwashed and drained, Ib/ft³	21.5
Food Chemical Codex	Passes

*Bulk density/Apparent = used to find the weight of a fixed volume in g/ml or pounds per cubic foot for the activated carbon

**Total Ash content = amount of mineral matter in the activated carbon, like Mg, Ca, Si and Fe.

***Hardness number/Abrasion = the ability of powered or granular activated carbon to resist abrasion during operation

****Particle size= Have an effect on the rate of the pollutant adsorption or catalytic activity(Norit, 2012).

2.7.2 *Sub-bituminous CR830A*

The other adsorbent used in this study is the granular activated carbon CR830A from Carbon Resources, which is a low density sub-bituminous carbon produced under a high temperature steam process for activation. The surface area is large with an wide distribution of pore sizes and large volumes. Further information is provided in Table 2-2 (Carbon-Resources, 2010).

Table 2-2: Technical specifications Sub-bituminous CR830A(Carbon-Resources, 2010)

Specifications	Sub-bituminous CR830A
Mesh size(US standard sieve):	8x30
Greater than 8	5% maximum
Less than 30	5% maximum
Iodine number (mg/g)	950 minimum
Molasses Number	300 typical
Hardness number	88 typical
Moisture (as packed)	5% maximum
Apparent density (g/cc)	0.35 - 0.37 typical
Bulk density (Ibs/CF)	22-24
Water Soluble Ash	0.25% typical
pH	8-8.5 typical

*Bulk density/Apparent = used to find the weight of a fixed volume in g/ml or pounds per cubic foot for the activated carbon

**Total Ash content = amount of mineral matter in the activated carbon, like Mg, Ca, Si and Fe.

***Hardness number/Abrasion = the ability of powered or granular activated carbon to resist abrasion during operation

****Particle size= Have an effect on the rate of the pollutant adsorption or catalytic activity(Norit, 2012).

2.8 Earlier research

In a study where nitrate was removed from aqueous solutions with activated carbon prepared from sugar beet bagasse, they concluded that initial pH value (varied between pH 3 - 10.15) did not have significant affect on the nitrate removal, however, an increase in temperature increased the adsorption capacity. Temperature was increased from 25 - 45°C, and adsorption capacity increased from 9.14 - 27.55 mg/g. Initial nitrate concentrations in the study varied between 10-200 mg/L (Demiral and Gündüzoğlu, 2010). Nitrate removal by using carbon nanotube sheets compared with activated carbon was tested in another study. This resulted in an adsorption uptake around 13 mg/g for the activated carbon, while the best nanotube sheets had an adsorption uptake around 32 mg/g. The final concentrations in the study were measured after 50 hours, and compared with the initial nitrate concentration of 200 mg/l . Temperature was around 25 °C and pH around 7 (Ahmadzadeh Tofighy and Mohammadi). Adsorption of nitrate and nitrite by acid treated carbon cloth was tested in a study with the initial concentration of nitrate and nitrite at 115 mg/L, pH was around 7 and the experiment collected data in a time period at 60 min., which is the time to reach equilibrium. Adsorption on carbon cloth treated with distilled water decreased concentration by 8.7 % (nitrate) and 3.7% (nitrite). Acid treated carbon cloth however, decreased concentration by 29.5% (nitrate) and 12.9% (nitrite). The adsorption capacities were measured to be 23.6 mg/g (nitrate) and 2.3 mg/g (nitrite) on distilled water treated carbon cloth and 125.9 mg/g (nitrate) and 46.5 mg/g (nitrite) on acid treated carbon cloth (Afkhami et al., 2007).

3. Methods and Materials

Batch studies were performed with synthetic stormwater and two types of activated carbon used as adsorbents: sub-bituminous and hydrodarco. The synthetic stormwater had a variable concentration of NO_3-N added. Samples were collected at specific time intervals and the experimental work was performed 05.02.12 - 23.03.12 and analyzed for anion concentrations. See Appendix Table 7-1 for more detailed information about the sampling.

3.1 Materials

Sodium nitrate ($NaNO_3$ formula weight (F.W.) = 84.99 g/mol), Sodium Chloride (NaCl F.W. = 58.44 g/mol) and Magnesium Carbonate ($MgCO_3$ F.W. = 84.31 g/mol) were provided by Fisher Scientific. The following chemicals were from Sigma-Aldrich: Sodium bicarbonate ($NaHCO_3$ 99.7-100.3 %, F.W. = 84.01 g/mol), sodium sulfate (Na_2SO_4 F.W. = 142.04 g/mol) and hydrochloric acid (HCl 37%, F.W. = 36.46 g/mol). Mallinckrodt Chemicals supplied Magnesium Chloride 6 hydrate (crystal, $MgCl_2*6H_2O$, F.W. = 203.30 g/mol) and sodium hydroxide (NaOH F.W. = 40 g/mol). Ultrapure water (18.2 MΩ·cm) was provided from Milli-Q purification system by Millipore. Hydordarco 3000 M-1783 carbon was provided by Norit and Sub-Bituminous carbon CR830A was provided by Carbon Resources. All solutions in this study were made with ultrapure water. Pipettes were used when solutions needed to be diluted. Standards were refrigerated. HCl solution, eluent, and regenerant concentrate were stored at room temperature (~25°C).

3.2 Equipment

Acrodisc syringe filters 32 mm with 0.45 µm super membrane were provided by Pall Corporation, and 5 ml (6ml) syringes were obtained from Norm-Ject syringes. An Accumet Portable AP62 pH/mV meter was from Fisher Scientific and 8103BNUWP Orion Ross glass probe was supplied by Thermo Scientific. Analytical balance Model AL 204 was provided by Mettler Toledo. A 100 µl-1000 µl pipette was obtained from Eppendorf. Acura 825 5 µl-50 µl pipette was supplied from Socorex. Gilson 50µl -200 µl and 200 µl-1000 µl pipettes were from Pipetman. The stirrer/hot plate provided by Corning was used during production of regenerant and eluent. A stirrer obtained from Fischer Scientific was used during pH adjustment . Orbital shaker Model 3520 (at 150 RPM) was from LAB-Line and used in Experiments 1-2. Experiments 3-10 used an unmarked orbital shaker table due to larger bottle capacity, which was run at the "low stir" speed capacity. Ion chromatograph (IC); a 761

compact IC was provided by Metrohm ion analysis including a 6.2832.000 suppressor rotor and a MetrosepAsupp 5.150/4.06 mm 6.1006520 column.

3.3   Isotherm experiments

Two different commercial forms of activated carbon, hydrodarco and sub-bituminous, were evaluated in isotherm experiments. The main purposes were to observe how much nitrate the activated carbon adsorbed and understand the adsorption processes.

Synthetic stormwater was made similar to natural stormwater runoff (Pitt et al., 2005) with pH 7.4, hardness 39 mg/L as $CaCO_3$, alkalinity 150 - 169.5 mg/L as $CaCO_3$, and specific NO_3-N concentrations (Table 3-2). Triplicate 500 mL bottles with caps for each initial nitrate concentration were used for both of the adsorbents. Triplicate sets of blanks per batch (Appendix Table 7-1) were used as quality control. Table 3-1 lists the different samples tested in this study. A "blank" refers to a sample where only buffer solution and nitrate are added without any adsorbent. A triplicate set of adsorbent blanks were also tested in Experiment 2. An "adsorbent blank" refers to a sample where only buffer solution and adsorbent are added. The purpose is to observe the reaction of the adsorbents without any nitrate present.

Buffer solution was made of magnesium carbonate and sodium bicarbonate in Experiment 1. However, it was changed to magnesium chloride and sodium bicarbonate in the rest of the experiments. Hardness was verified at the University of Minnesota Research Analytical Laboratory (RAL). Two samples were sent for testing (#1 used in ex. 5.6.7 and #2 used in ex.8.9.10). RAL measured a total hardness at 40.4 mg/l as $CaCO_3$ in #1, and 41.7 mg/L as $CaCO_3$ in #2 (target hardness = 39 mg/L as $CaCO_3$).

Table 3-1: Sample content and labelling

Samples	Content	Label name
Blanks	Buffer + Nitrate	B*
Blanks with Sub-bituminous**	Buffer + Adsorbent	SB*
Blanks with hydrodarco**	Buffer + Adsorbent	HB*
Sub-bituminous	Buffer + Adsorbent + Nitrate	S*
Hydordarco	Buffer + Adsorbent + Nitrate	H*

 * Label name is the name used during sampling and in the raw data in Appendix, it contains also a number from 1-3 due to parallels (example B1, B2 or B3). Some samples are duplicates and are marked with a "b" in addition

** Only tested once in Experiment 2. They are marked with label name and 0 mg/L initial nitrate-nitrogen concentration in the result and discussion part. Like S(0mg/L)Blank or H(0 mg/L)Blank

Table 3-2: Initial nitrate concentrations used in the experiments; target concentrations

Sample	Experiment	Initial NO$_3$-N mg/L
Blanks		
	1	0.1
	2-10	2.5
Sub-Bituminous		
	1	0.271
	2	0.542
	3	1.083
	4	2.167
	5	4.333
	6	6.771
	7	8.666
	8	13.541
	9	20.312
	10	27.082
Hydrodarco		
	1	0.589
	2	1.178
	3	2.357
	4	4.714
	5	9.427
	6	14.73
	7	18.885
	8	29.461
	9	44.191
	10	58.922

*Average values used in results and discussion are marked with label name together with initial nitrate-nitrogen concentration, like S(0.271 mg/L) or H(58.922 mg/L)

** Adsorbent blanks are not presented in this table due to no nitrate-nitrogen content

pH was adjusted with 0.2 M hydrochloric acid using a pH-meter that was calibrated with pH standards at 4, 7 and 10. Concentrations of NO_3-N ranged from 0.271 - 27.082 mg/L for the sub-bituminous samples and 0.589 - 58.922 mg/L for the hydrodarco samples (Table 3-2). The blanks in Experiment 1 had a nitrate concentration of 0.1 mg/L. This was changed to 2.5 mg/L in Experiment 2-10, to be more representative as a control concentration. The desired NO_3-N concentrations were made from a 7.0005 g/L $NaNO_3$ standard solution.

Initial samples of ~4 mL were collected from the bottles with a syringe and filtered through a 0.45 μm syringe filter where ~3 mL were added in vials, sealed with parafilm and stored in the freezer. New syringes were used every time to prevent cross contamination between samples. Filters were occasionally reused where 1 ml ultrapure water was flushed through to prevent cross contamination. 5 grams of each adsorbent were added to separate bottles after initial samples were collected. The formation of bubbles was observed immediately after the adsorbent was added.

Figure 3-1: Batch experiment; Orbital shaker table and samples from Experiment 8-10.

The bottles were placed on an orbital shaker table (Figure 3-1) at room temperature (~21°C), and samples were collected at specific time intervals: initial (before adsorbent added), 0 hour (2 - 3 min. after adsorbent added), 24 hour, 48 hour, 72 hour, and 96 hour using the same procedure described earlier with initial samples. 1 - 2 duplicate samples for each batch were collected. All samples were stored in the freezer until they were analyzed. The sampling time at 0 hour, varied between 2 - 45 min because of the amount of bottles per batch changed (Appendix Table 7-1). Samples from blanks were collected first, then the samples were collected according to nitrate concentration, from low to high. They were collected in the same order each time.

3.4   Analytical methods

Samples were analyzed for anions by ion chromatography according to the standard method; " 4110 Determination of anions by ion chromatography, 4110A introduction, 4110B Ion chromatography with chemical suppression of eluent conductivity (Eaton et al., 1995)". In Experiment 1, 0.02M regenerant solution was diluted from 1M sulfuric acid and the eluent solution was diluted 1:100 from the concentrate solution of 100mM $NaHCO_3$ and 320 mM Na_2CO_3. Both eluent and regenerant were made and degassed before they were used according to the standard method. Due to equipment failure and limited timeframe, only the results for adsorbent blanks, initials, and 96-hour samples are reported here from Experiment 2-10.

3.5   Calibration curve

A calibration curve (CC) was made to convert the data output from Area uS/cm*sec into mg/L. Standards contained NO_3-N, Cl^-, and SO_4^{2-} with the concentrations of 0.01, 0.05, 0.1, 0.2, 0.5, 1, 2.5, 5, 10, 20, 40 and 60 mg/L in Experiment 1. These concentrations were made from a standard with 4.9455 g/L NaCl, 18.1985 g/L $NaNO_3$ and 4.436 g/L Na_2SO_4. Standards in Duluth contained NO_3^-, Cl^- and SO_4^{2-} with the concentrations 0.08, 0.8, 1.26, 12.6, 25.2, 40 and 60 mg/L in Experiment 2-10. A misunderstanding led to a CC made for NO_3^- and not NO_3-N, which resulted some in results exceeding the CC range. Some of the samples were then diluted 5x and 10x and run again to correct for this. The 0.05, 0.1, 0.2, 1, 2.5 and 5 mg/L standard from Experiment 1 were run in Duluth with the other samples to verify that both IC machines produced similar results.

4. Results and Discussion

Experiments presented in this study are shown in Table 4-1, except the blanks, due to no adsorbent added . There was not enough time to get results from Experiment 3 and 5.

Table 4-1: Sample ID

Sample ID

Experiment	Sub-bituminous	Hydrodarco
1	S(0.271 mg/L)	H(0.589 mg/L)
2	S(0.542 mg/L)	H(1.178 mg/L)
4	S(2.167 mg/L)	H(4.714 mg/L)
6	S(6.771 mg/L)	H(14.730 mg/L)
7	S(8.666 mg/L)	H(18.855 mg/L)
8	S(13.541 mg/L)	H(29.461 mg/L)
9	S(20.312 mg/L)	H(44.191 mg/L)
10	S(27.082 mg/L)	H(58.922 mg/L)
2*	S(0 mg/L)Blank	H(0 mg/L)Blank

4.1 Experiment 1

The results from Experiment 1 shown in the figures below are more complete than the data from the other experiments, and contain data from all the time intervals in the sampling period.

4.1.1 *Calculation of data output*

Output from the IC (uS/cm*sec) was converted to mg/L. This was done by determining the slope of the trend line by plotting known concentrations from standards against the data output in uS/cm*sec (Figure 4-1,Figure 4-2, Figure 4-3). The slope was then multiplied with the IC data to get the concentration in mg/L. The most linear data called "partial data" were used to create the trend lines.
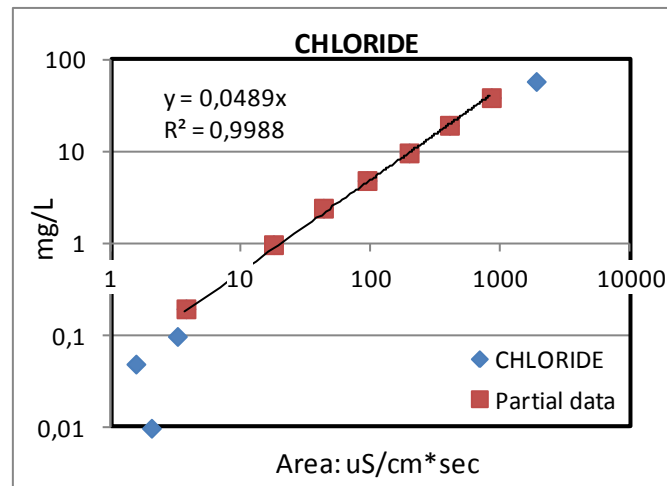
Figure 4-1: Chloride data trend line for slope determination

Data output for chloride is mostly on a straight line in Figure 4-1 with few deviations. The deviation around 0.01 mg/L is possibly a result of the IC machine's limitations to read small concentrations. The slope was determined to be 0.0489 mg/L chloride per uS/cm*sec.
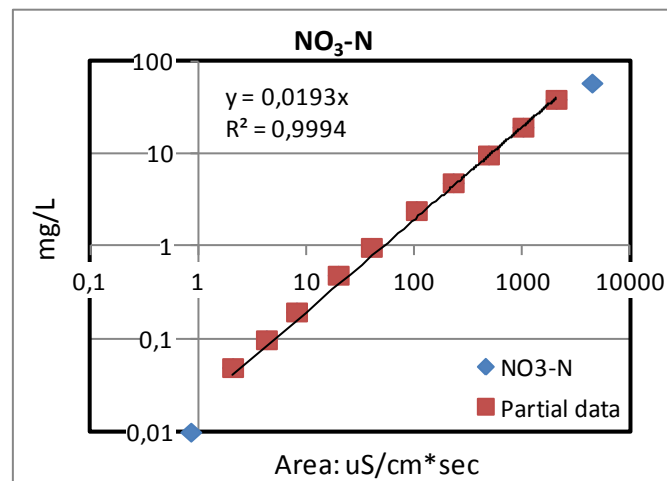
Figure 4-2: Nitrate-nitrogen data trend line for slope determination

Low deviations in the data output for nitrate-nitrogen in Figure 4-2 result in a reliable trend line. One particular deviation in Figure 4-2 at 0.01 mg/L differs from the others, but this is in the region of high IC uncertainty. The slope was determined to be 0.0193 mg/L nitrate-nitrogen per uS/cm*sec.
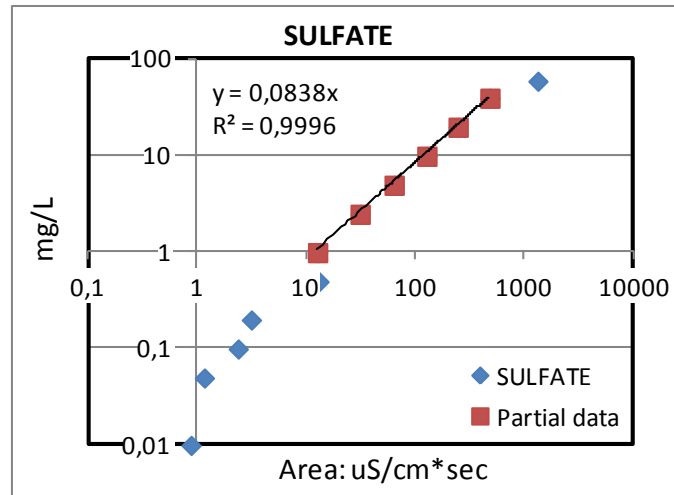
Figure 4-3: Sulfate data trend line for slope determination

Most of the data for sulfate in Figure 4-3 are close to form a straight line for sulfate in Figure 4-3. However, 6 of these data were more straight lined than the others and therefore were used to make a trend line. The particular deviation at 0.01 mg/L is probably due to the IC machines limitations to read small concentrations . The slope was determined to be 0.0838 mg/L sulfate per uS/cm*sec.

4.1.2 *Adsorption kinetics*

Blanks with no adsorbent added are compared with the adsorbent samples in this sub-chapter.
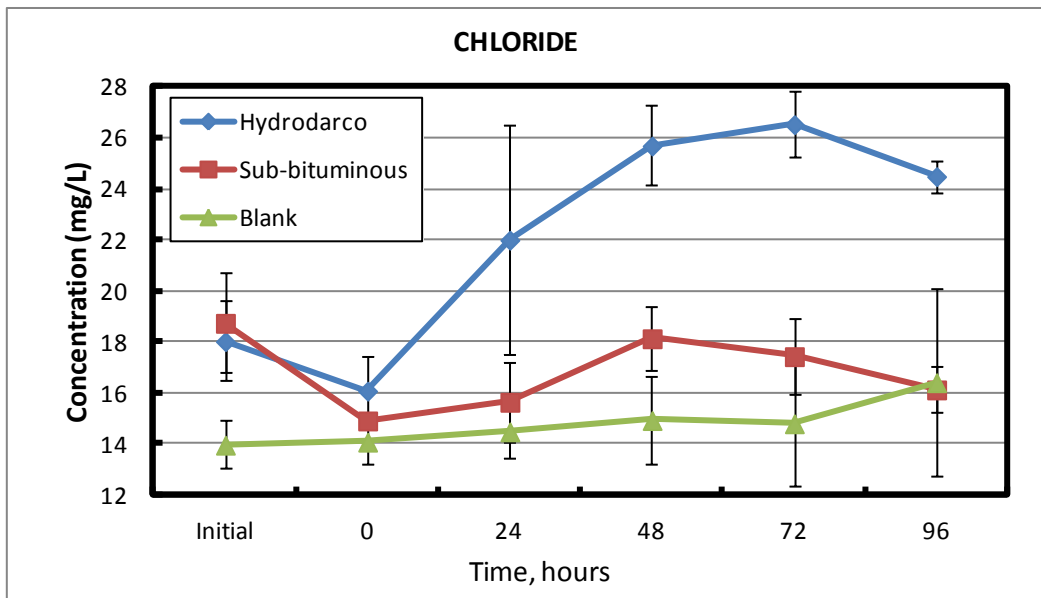
Figure 4-4: Chloride concentration at specific time intervals (error bars = 1 standard deviation)

Figure 4-4 shows a high chloride concentration during the experiment, which is expected due to pH adjustment with HCl. The amount of it in the water should be approximately the same during the

whole experiment. The observed increase of concentration in hydrodarco samples is probably an instrumental error as a result of concentrations beyond the range of the IC machine. Standard deviations observed as shown by the error bars between the different data are wide. The average chloride content varies between 16.08 - 26.54 mg/L for hydrodarco samples, 14.91 - 18.74 mg/L for sub-bituminous samples and 13.96 - 16.41 mg/L for blanks respectively.
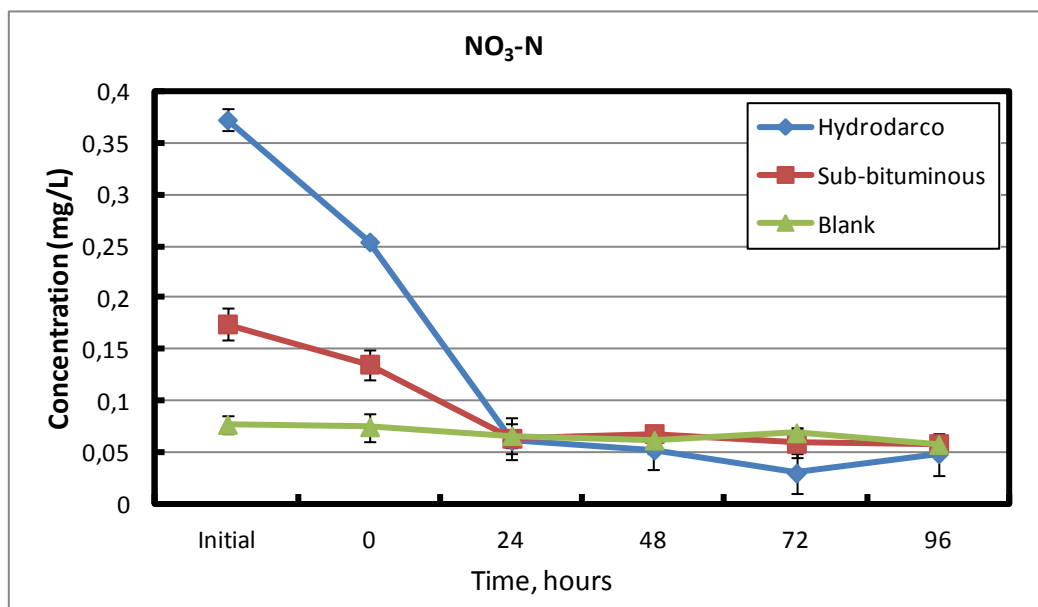
Figure 4-5: Nitrate-nitrogen reduction at specific time intervals (error bars = 1 standard deviation)

Nitrate-nitrogen becomes markedly decreased from initial- to the 24 hour sample. Reduction of nitrate occurred rapidly after activated carbon was added. The equilibrium concentration, known as when rate of sorption equals the rate of desorption, is most likely reached right after the 0 hour sample was taken due to the reduction was already halfway completed. Nitrate-nitrogen concentration decreased from 0.174 mg/L to 0.058 mg/L in the sub-bituminous sample, a reduction of 67%. In the hydrodarco sample, nitrate-nitrogen was reduced from 0.373 mg/L to 0.0480 mg/L, a reduction of 87%.
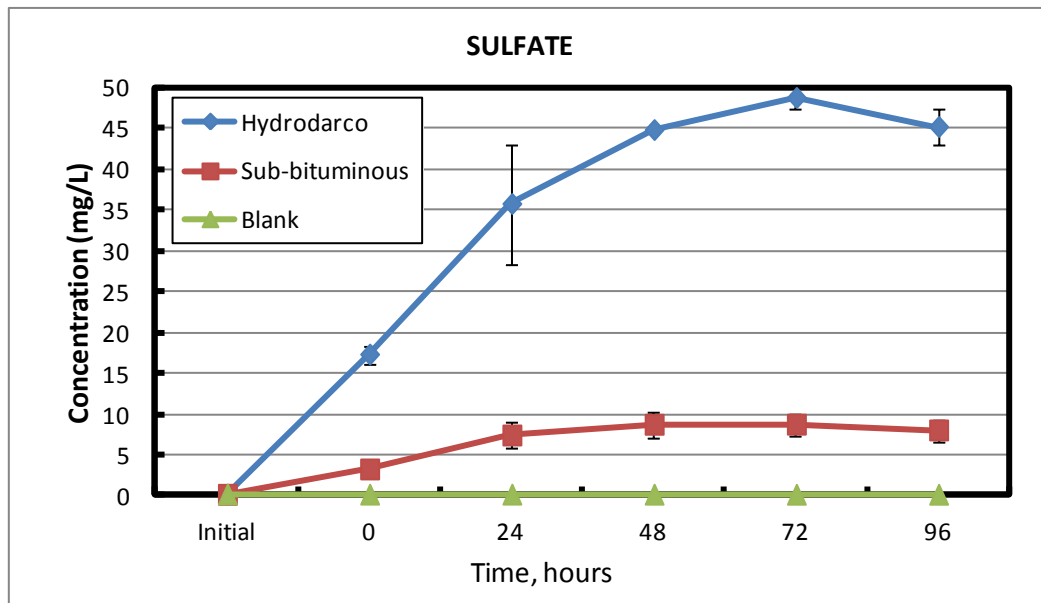
Figure 4-6: Sulfate concentration after specific time intervals (error bars = 1 standard deviation)

Sulfate concentration presented in Figure 4-6 increases from the initial sample to the 24 hour samples containing sub-bituminous and hydrodarco. Concentration of sulfate in the sub-bituminous sample stabilized after the 24 hour sample and likely reached equilibrium right after the 0 hour sample was taken. The amount of sulfate in the Hydrodarco sample is first stabilized around the 48 hour sample. This could be instrumental error, but also note that there are high deviations in 24 hour samples (appendix Table 7-4) which indicates that the 24 hour sample concentration may actually be similar to the 48 hour sample and thus equilibrium. In the sub-bituminous sample sulfate is increased from 0.091- to 7.984 mg/L, an increase of 8708%. Sulfate is increased from 0.111- to 45.207 mg/L in the hydrodarco sample, which is equivalent to an increase of 40615%. The sulfate concentration in the samples have likely been released from the activated carbon added.

4.2 Experiment 1 - 10

Only data collected from initial- and equilibrium samples in Experiment 1-10 are presented in the next sub-chapters. Data output from Experiment 2-10 were transformed in Nate Johnson's Laboratory in Duluth, Minnesota, USA to mg/L by determining the slope of a trend line as described under the section earlier called Experiment 1. In Experiment 2 - 10 some sample vials were broken, and some samples were not readable for the IC. This resulted in that some data were not available. Therefore, the average data plotted in the figures below are determined by 1-3 parallel samples, see overview in the Appendix. Ideally, 3 parallels samples are preferable since they give a more reliable estimate of the actual concentrations in the samples. Experimental data that differs from the normal expectations may

be explained by the fact that some data originates from samples that were run with broken glass in the bottom, or were one of the samples that were diluted before running because of a wrong CC range. Contamination of samples or instrumental error are also possibilities. Samples from Experiment 1 were run with a different IC machine than Experiment 2-10, which should be considered during data analysis. However, standards from Experiment 1 were analyzed by both IC machine in and output concentrations seemed to be the similar (Appendix

Table 7-14). Chloride concentrations are expected to differ between Experiment 1 and Experiment 2-10 due to the change in chemicals used to make the another buffer solution.

4.2.1 *Sub-bituminous results*
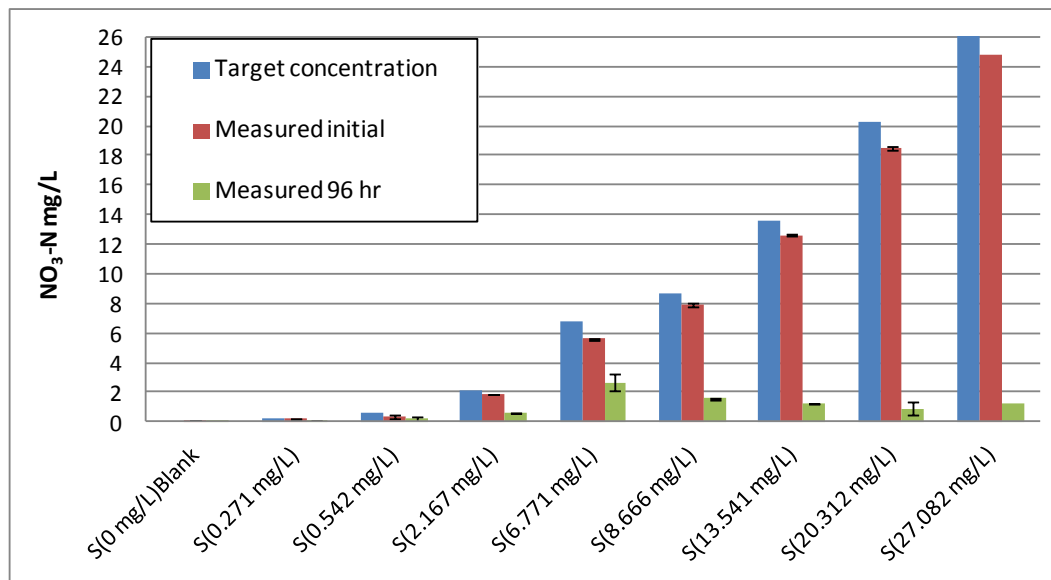
Figure 4-7: Measured initial nitrate-nitrogen concentrations compared to equilibrium and target concentrations

Figure 4-7 shows that the target sample values (Table 3-2) are higher than the actual initial values measured. Ideally, these values should have been the same. The equilibrium values display a clear decrease of nitrate-nitrogen concentration in the samples. The initial concentration of NO_3-N in the solution doesn't seem to affect the equilibrium concentration of nitrate-nitrogen when mixed with activated carbon. Normally, the highest initial NO_3-N concentration should have provided the highest equilibrium concentration. Therefore, this may indicate error values in some of the samples.
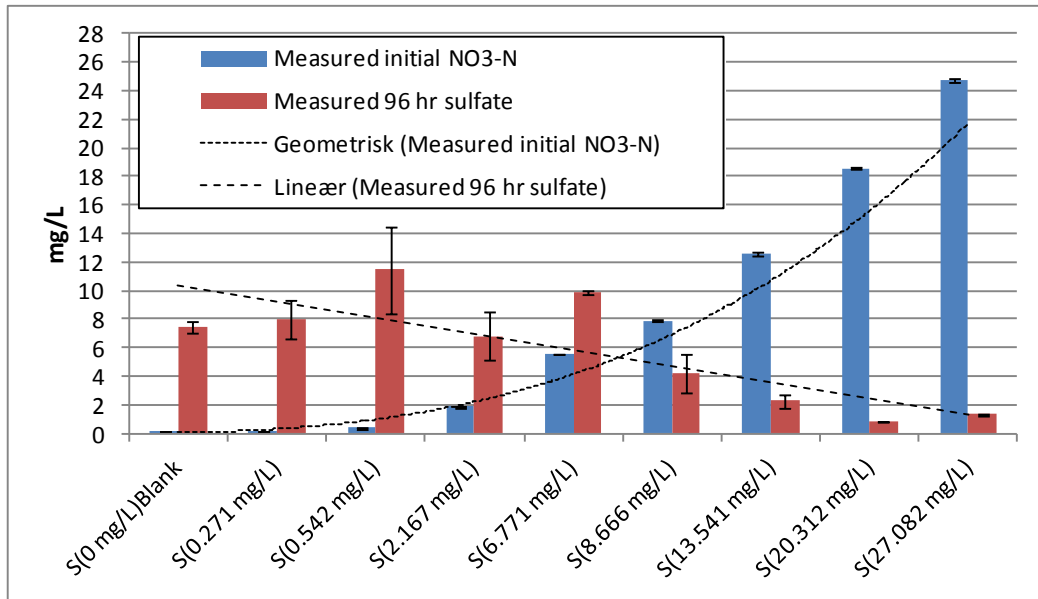
Figure 4-8: Sulfate values at equilibrium vs. initial nitrate-nitrogen values

Sulfate seems to be released from the sub-bituminous carbon when nitrate is sorbed as shown in Figure 4-8. Measured initial sulfate concentrations are below 0.7 mg/L (Appendix Table 7-15). No explanation has been determined for the decreased sulfate concentration in some of the measures with high initial NO_3-N concentrations. Sulfate is clearly produced in the S(0 mg/L) Blank, which might indicate that sulfate is only dependent on activated carbon present and not the interaction between nitrate content in the synthetic stormwater and the activated carbon. However, an initial concentration of 0.101 mg/L NO_3-N was measured in this blank, but this can be explained by a contamination of used IC vials or the 500 mL sample bottles, or maybe an IC error.
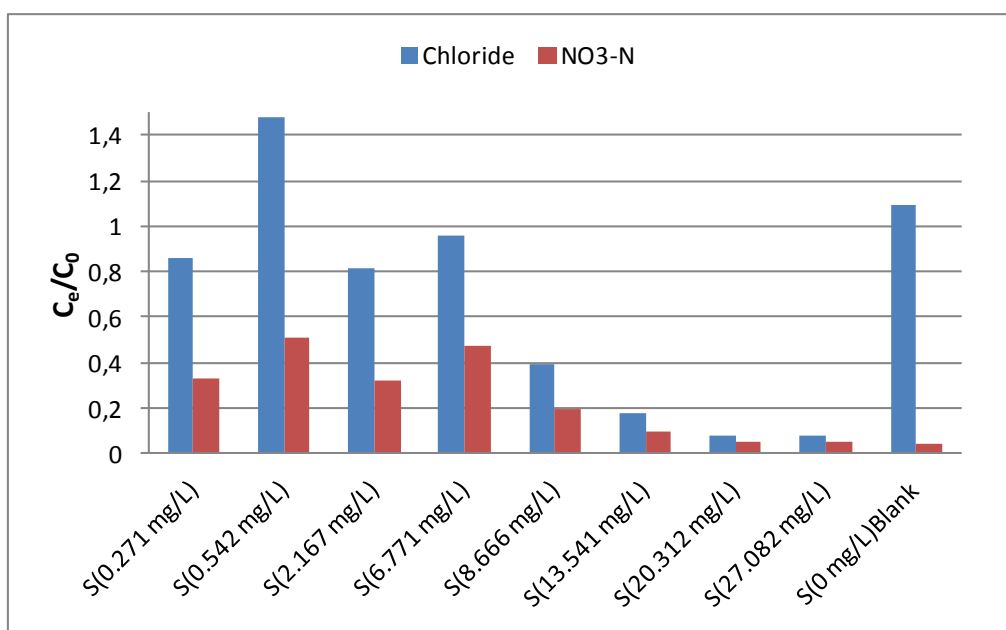
Figure 4-9: Chloride and NO_3-N equilibrium concentration (C_e) divided by initial concentration (C_0)

Equilibrium sulfate concentrations in the sub-bituminous samples are to high compared to initial sulfate concentration and can't be presented with chloride and nitrate-nitrogen concentrations in Figure 4-9 and Figure 4-10.
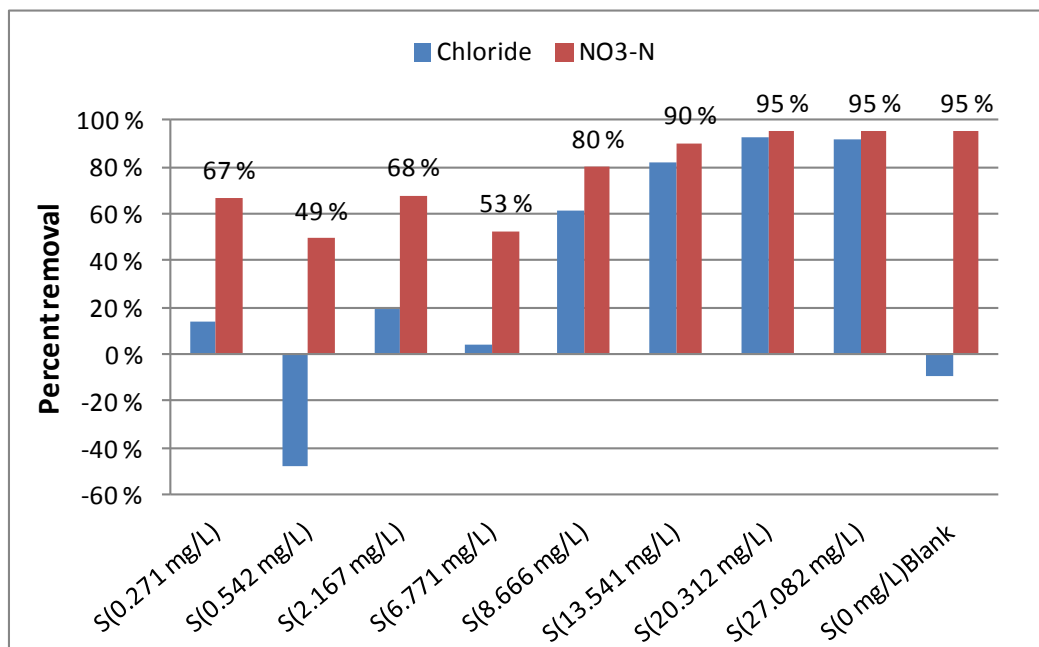
Figure 4-10: Percent removal of nitrate-nitrogen and chloride

Nitrate-nitrogen removals in the sub-bituminous samples are between 49 - 95% as shown in Figure 4-10 with an average percent removal of 75%. The presence of chloride is expected due to chloride content in the buffer solution, but also by the addition of HCl during pH adjustment.

4.2.2 *Hydrodarco results*
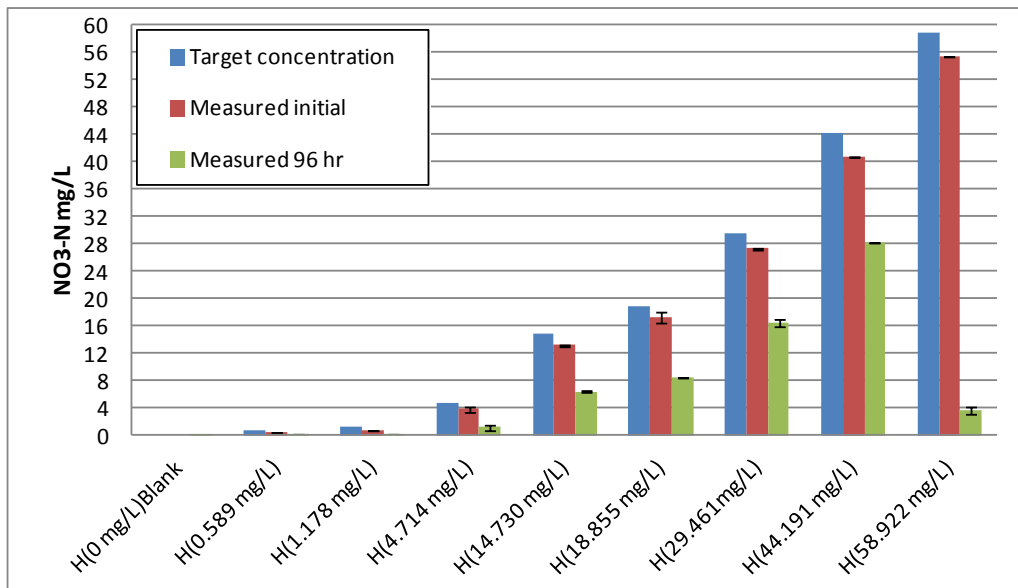
Figure 4-11: Initial values of nitrate-nitrogen compared with equilibrium- and sample ID values

Target sample values in the hydrodarco samples (Figure 4-11) are higher than the actual initial values, but these are expected to be equal. Reasons for this deviation could be instrumental error or inaccurate preparation of samples. The concentration of nitrate-nitrogen in the equilibrium samples seems to be dependent on the initial concentration of nitrate-nitrogen represented in the solution. Measured equilibrium concentration from sample H(58.922 mg/L) differs from the others as shown in Figure 4-11 and Figure 4-12. One of the 2 parallels which are representing the H(58.922 mg/L) sample (Appendix Table 7-13) originates from one of the sample glass containers that was broken during the transit to Duluth. However, the samples were run anyway with glass still in the bottom, which may have caused this deviation.
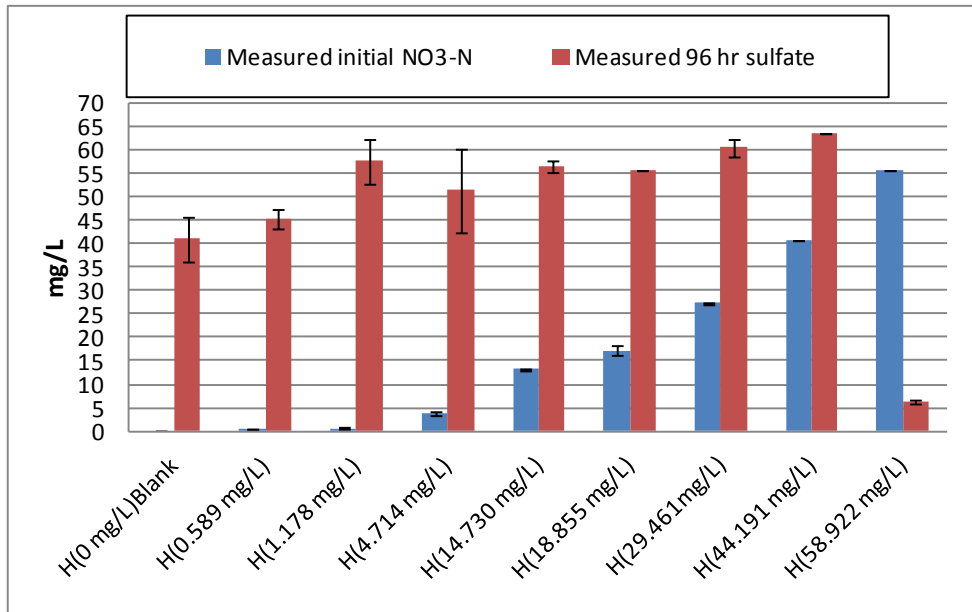
Figure 4-12: Initial nitrate-nitrogen values vs. sulfate values at equilibrium

High amounts of sulfate are clearly released in the Hydrodarco samples with different concentrations of nitrate-nitrogen as shown in Figure 4-12. Measured initial sulfate concentrations are below 0.7 mg/L (Appendix Table 7-15). The equilibrium H(0 mg/L) sample shows a high release of sulfate, similar to the sulfate concentrations in the other samples containing nitrate-nitrogen. This indicate a connection between sulfate release and the presence of Hydrodarco carbon, where initial nitrate-nitrogen content is negligible.
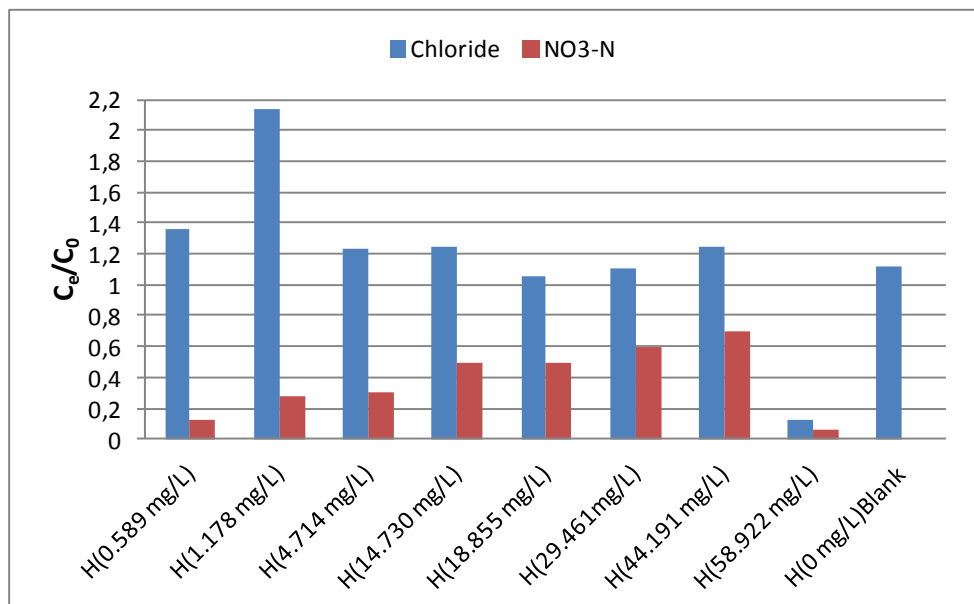
Figure 4-13: Chloride and NO$_3$-N equilibrium concentration (Ce) divided by initial concentration (C$_0$)

Equilibrium sulfate concentrations in the Hydrodarco samples are to high compared to initial sulfate concentration and can't be presented with chloride and nitrate-nitrogen concentrations in Figure 4-13 and Figure 4-14.
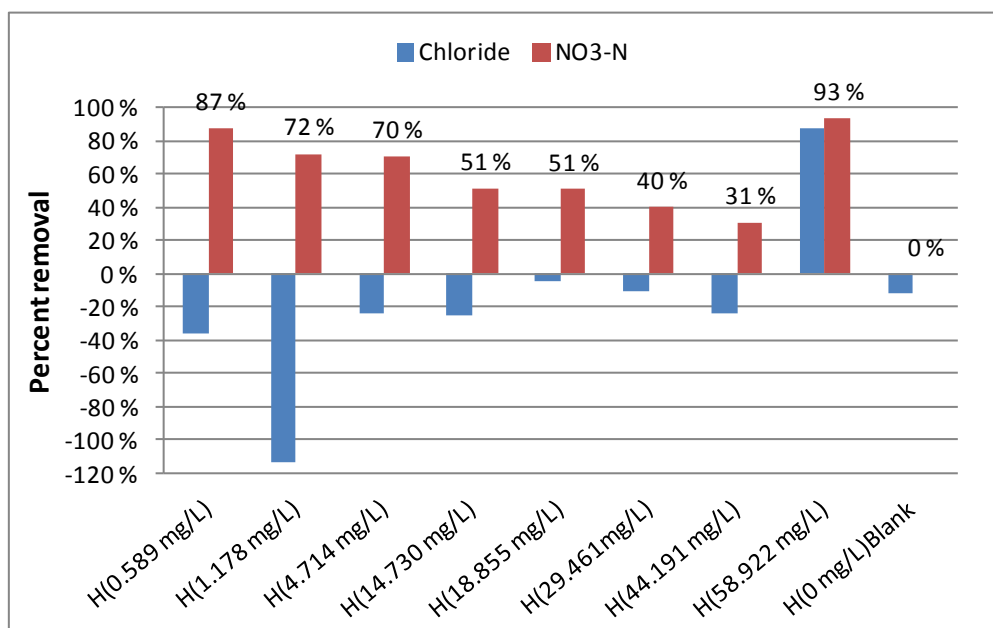
Figure 4-14: Percent removal of chloride and nitrate-nitrogen

The removal of nitrate-nitrogen in the Hydrodarco samples is between 31-93%, as shown in Figure 4-14, with an average percent removal of 62%. However data from sample H(58.922 mg/L) are suspect. Initial nitrate-nitrogen data is missing in the H(0 mg/L) Blank, so the 0% removal listed above is incorrect. Chloride is also present at different concentration in all the samples, probably because of chloride content in the buffer solution and HCl added during pH adjustment. No logical pattern of chloride content is observed.

4.3 Adsorption isotherms

Experimental data for nitrate-nitrogen adsorption by the two adsorbents were analyzed using models of the Freundlich and Langmuir isotherms.

4.3.1 *Sub-Bituminous*

Table 4-2: Adsorption capacity of nitrate-nitrogen by Sub-bituminous

Sample ID	Adsorption capacity mg/ kg (q_e)	Adsorption capacity* mg/ g (q_e)
S(0.271 mg/L)	11.662	0.012
S(0.542 mg/L)	18.690	0.019
S(2.167 mg/L)	128.834	0.129
S(6.771 mg/L)	294.446	0.294
S(8.666 mg/L)	633.753	0.634
S(13.541 mg/L)	1134.876	1.135
S(20.312 mg/L)	1764.868	1.765
S(27.082 mg/L)	2363.814	2.364

*Adsorption capacity is also illustrated in mg/g so it will be easier to compare the results with earlier research

Adsorption capacity were determined to be between 11.662 - 2363.814 mg/kg in the S(0.271 mg/L) - S(27.082 mg/L) samples as shown in Table 4-2.

Freundlich

$y = 1,333x + 2,6591$
$R^2 = 0,6851$

Log (q_e) vs Log (C_e)
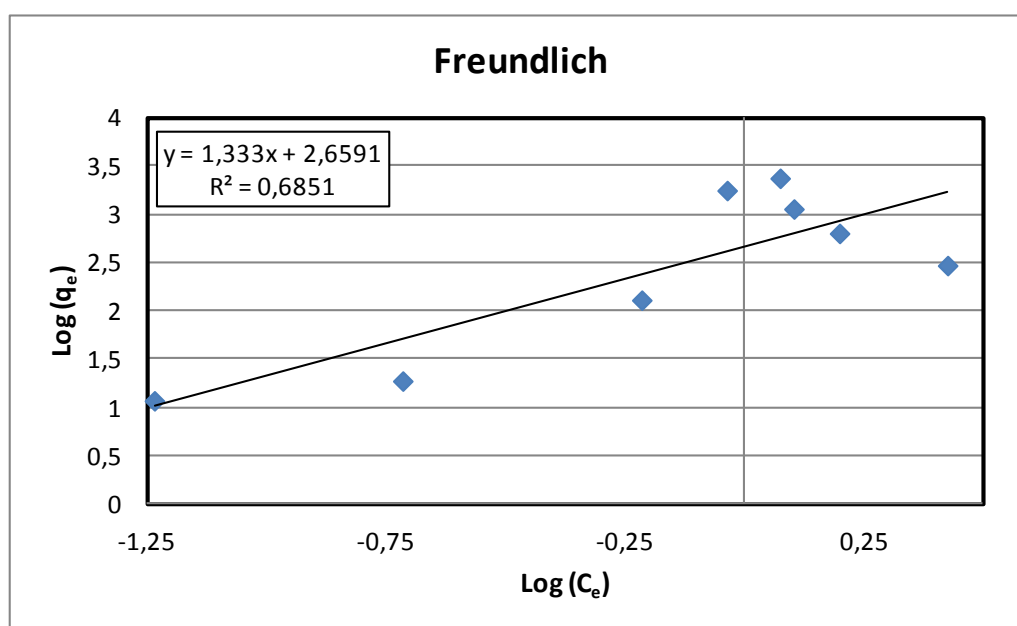
Figure 4-15: Determination of constants for Freundlich isotherm
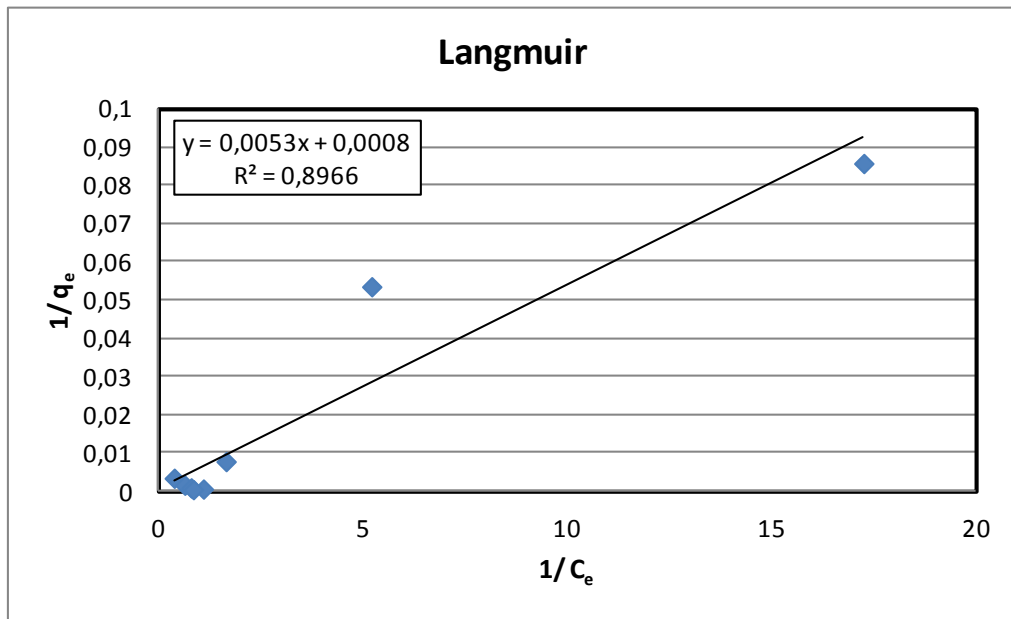
Figure 4-16: Determination of constants for Langmuir isotherm

Figure 4-15 and Figure 4-16 were used to determined the constants to make the isotherms in Figure 4-17. Several deviating data in Figure 4-15 makes the correlation constant (R^2) to differ from 1, mainly S(8.666 mg/L), S(13.541 mg/L), S(20.312 mg/L) and S(27.082 mg/L), which have abnormal equilibrium concentrations (C_e)(Figure 4-7 or Appendix Table 7-15). The samples with highest initial nitrate-nitrogen concentration should have given the highest C_e, but this is not the case for these samples. Plotted data will therefore deviate from a linear curve. Sample S(0.542 mg/l) differ in Figure 4-16, and is the main reason for a R^2 unequal to 1.
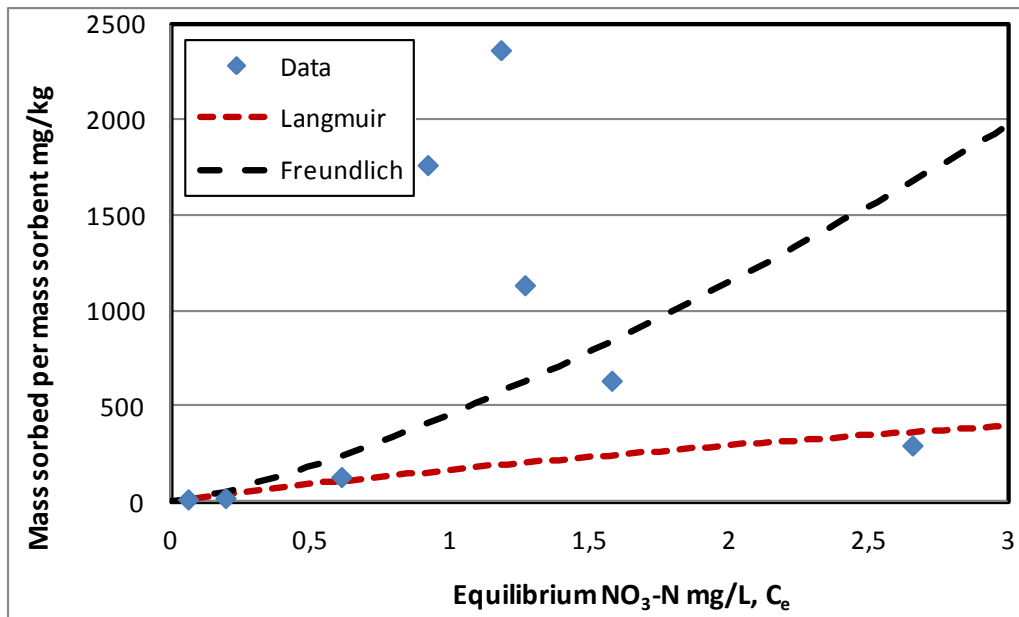
Figure 4-17: Langmuir and Freundlich isotherm plotted together with data from sub-bituminous samples

The data presented in Figure 4-17 doesn't fit any of the isotherms. This is because of the equilibrium concentrations (C_e) in S(8.666 mg/L), S(13.541 mg/L), S(20.312 mg/L) and S(27.082 mg/L) are not dependent on initial concentration of NO_3-N added as presented in Figure 4-7 (or in Appendix Table 7-15). The mass sorbed per mass sorbent will then not have a logical connection with the equilibrium concentration of the nitrate-nitrogen, which makes a modulation difficult. Further research may be needed to determine these isotherms. If these 4 data have been ignored, the remaining data would have better fit to the Langmuir isotherm.

4.3.2 *Hydrodarco*

Table 4-3: Adsorption capacity of nitrate-nitrogen by Hydrodarco

Sample ID	Adsorption capacity mg/ kg (q_e)	Adsorption capacity* mg/ g (q_e)
H(0.589 mg/L)	32.547	0.033
H(1.178 mg/L)	46.200	0.046
H(4.714 mg/L)	265.514	0.266
H(14.730 mg/L)	674.753	0.675
H(18.855 mg/L)	881.124	0.881
H(29.461 mg/L)	1089.790	1.090
H(44.191 mg/L)	1260.213	1.260
H(58.922 mg/L)	5192.875	5.193

*Adsorption capacity is also illustrated in mg/g so it will be easier to compare the results with earlier research

The adsorption capacity in sample H(0.589 mg/L) - H(58.922 mg/L) shown in Table 4-3 is determined to be between 32.547 - 5192.875 mg/kg.

Freundlich

$$y = 0{,}6571x + 2{,}4121$$
$$R^2 = 0{,}7304$$
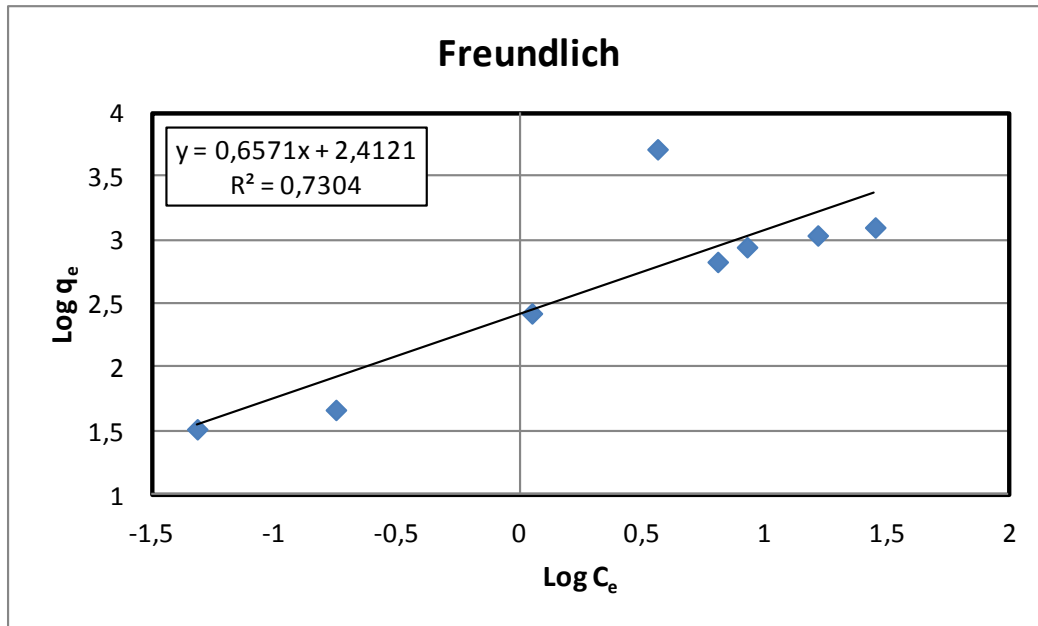
Figure 4-18: Determination of constants for Freundlich isotherm

Langmuir

$$y = 0{,}0015x + 0{,}0023$$
$$R^2 = 0{,}856$$
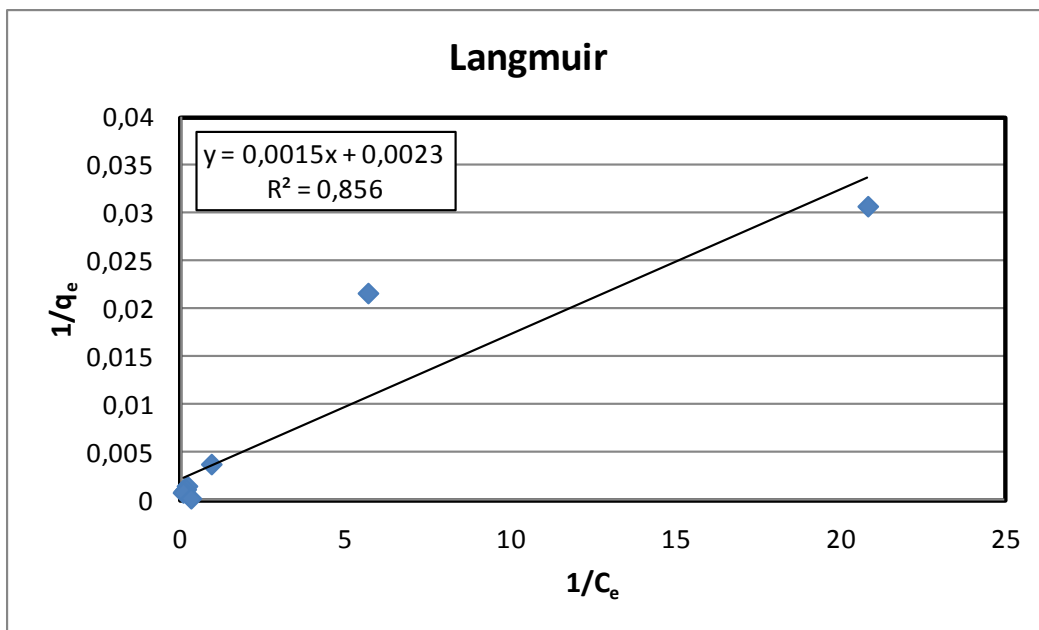
Figure 4-19: Determination of constants for Langmuir isotherm

Figure 4-18 and Figure 4-19 were used to determine the constants to make the isotherms in Figure 4-20. One particular deviation in Figure 4-18 makes the correlations coefficient to differ from 1, which is data from the H(58.922 mg/L) sample. Data from H(1.178 mg/L) in Figure 4-19 makes the correlation coefficient also to differ from 1. This due to an abnormal equilibrium concentration (C_e). In theory, the samples with the highest initial nitrate-nitrogen concentrations should have given the highest C_e. H(1.178 mg/L) and H(58.922 mg/L) differ from this theory and are thereby causing deviation in the plotted data.
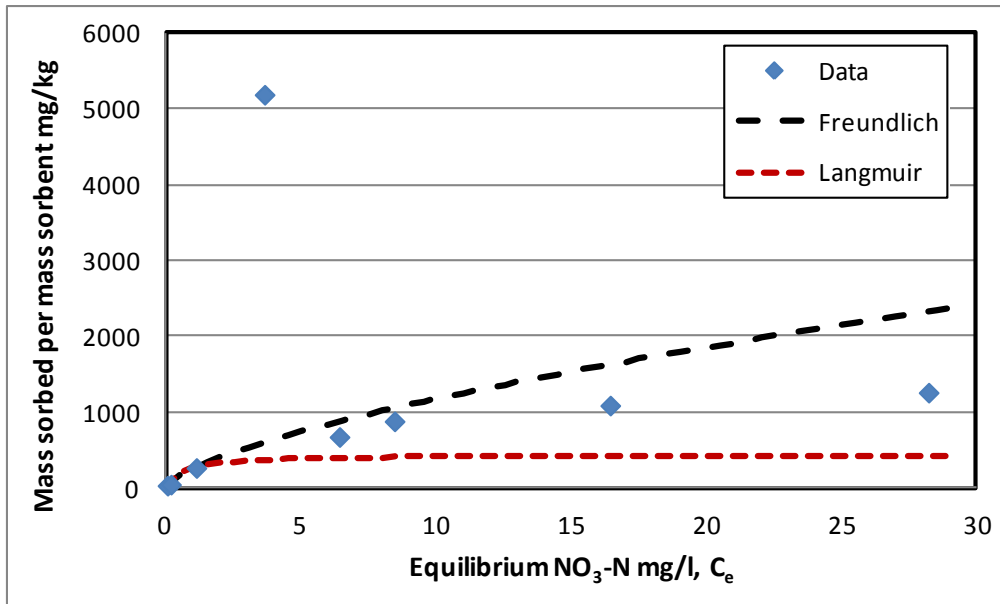
Figure 4-20: Langmuir and Freundlich isotherm plotted together with data from Hydrodarco samples

The Freundlich isotherm seems to be the closest fit to the data and best modulation option, but not optimal. This might indicate heterogeneity of the sorbents surface. There is one outliner in Figure 4-20, but this is possibly an error. This particular data origin from the 96 hour samples H(58.922mg/L) that was run with broken glass in bottom as discussed earlier. If this data is deleted, the isotherms will look like presented in Figure 4-21. The data fit better the Freundlich isotherm in this scenario.
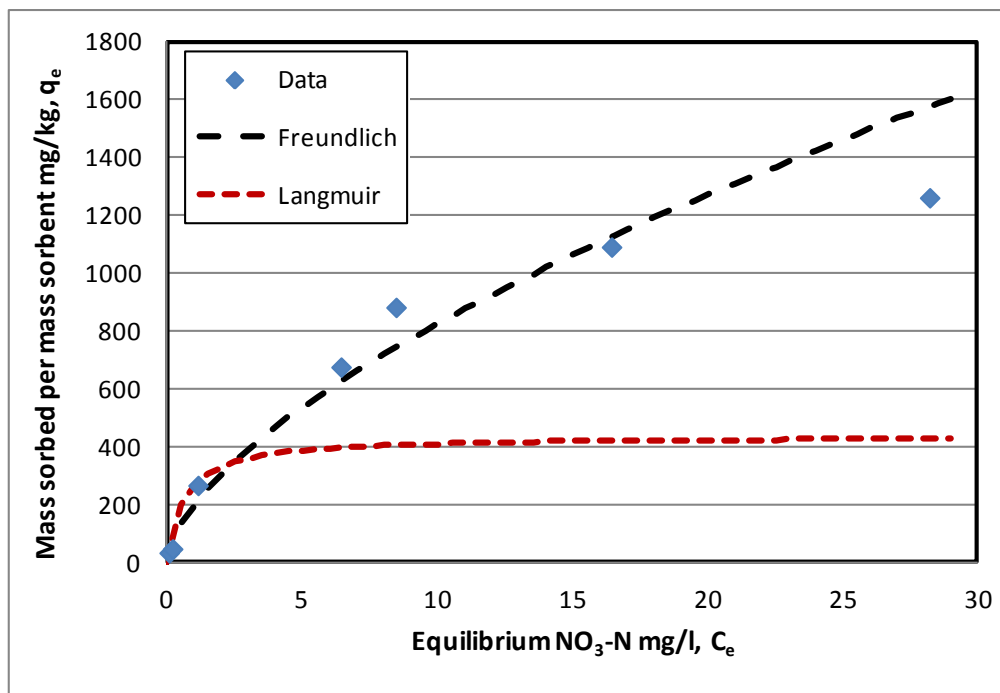
Figure 4-21: Langmuir and Freundlich isotherm plotted together with data from Hydrodarco samples, where sample H(58.922mg/L) is deleted

4.3.3 *Constants*

Constants (Table 4-4) were determined by reading the slope and the intercept of the trend line made of the data as shown in Figure 4-15, Figure 4-16, Figure 4-18 and Figure 4-19 below. Slope equals "1/n" and intercept equals "Log K_f" for Freundlich isotherms according to equation 2-9. Slope equals "1/ab" and intercept equals "1/a" for the Langmuir isotherms according to equation 2-11.

Table 4-4: Isotherm constants

Adsorbent	Temp (K)	Langmuir			Freundlich		
*		a	b	R^2	K_f	n	R^2
Sub-bituminous	298	1295.202	0.146	0.897	456.182	0.750	0.685
Hydrodarco	298	434.783	1.533	0.856	258.285	1.522	0.730

*a = mg/kg, b = L/mg, K_f = (mg/kg)/(L/mg)$^{1/n}$

K_f and n have an impact on the adsorption capacity and intensity of adsorption. An increasing K_f value is normally increasing the adsorbents capacity (Öztürk and Bektaş, 2004). According to this and Table 4-4 Sub-bituminous carbon has more capacity than the Hydrodarco carbon. The constant n indicates beneficial adsorption (Demiral and Gündüzoğlu, 2010). Calculations in a study has shown that n should be between 1 and 10 to give the favourable adsorption (Öztürk and Bektaş, 2004). Hydrodarco carbon has an n value of 1.5 (Table 4-4) which represents the favourable adsorption of nitrate-nitrogen. However, values of R^2 closer to 1 would inspire more confidence in these results.

Constant a is the monolayer capacity of the adsorbent. The other constant b says something about the energy of the adsorption (Öztürk and Bektaş, 2004).

4.4   Comparison with earlier research

A study presented in Table 4-5 below with AC from sugar beet bagasse can be compared to the results of this study. Because the materials and conditions are significantly different between these two studies, direct comparison is not possible.

Table 4-5: Constants from a study where activated carbon (AC**) is made of sugar beet bagasse (Demiral and Gündüzoğlu, 2010) compared with constants from this study (units are changed from Table 4-4*)

Adsorbent	Temp (K)	Langmuir			Freundlich		
*		a	b	R^2	K_f	n	R^2
Sub-bituminous	298	1.295	0.146	0.897	0.456	0.750	0.685
Hydrodarco	298	0.435	1.53	0.856	0.258	1.522	0.730
AC**	298	9.14	0.07	0.984	1.45	2.49	0.936

*a = mg/g, b = L/mg, K_f = (mg/g)/(L/mg)$^{1/n}$

There are few relevant studies to compare results against. Some earlier research results presented in the theory chapter can only be useful to support the claim that nitrate is removed by carbon materials and that a quick adsorption occurs, where equilibrium is reached rapidly after adsorbent is added.

4.5   Further research

The next step in this study will be to perform experiments in situations more similar to stormwater treatment, such as column studies. Thus, adsorption of nitrate will take place in columns which contain activated carbon and probably sand and silt. Synthetic stormwater with nitrate content will run through the columns, and samples will be collected from the input and output for analysis. The desired final outcome is design guidance for a full-scale sand filter. Stormwater is transported to the sand filter by drainage systems where it seeps through the pores and is filtered. Small suspended and dissolved pollutants are sorbed by the activated carbon. The filtered water is then transported to the receiving water body through perforated pipes in the bottom of the sand filter (Erickson, 2012).

5. Conclusion

When Hydrodarco 3000 and Sub-bituminous CR830A activated carbon are added to the synthetic stormwater, adsorption happens quickly. Where equilibrium is reached soon after the adsorbent is added. These observation fit with other studies made.

Percent removal of nitrate-nitrogen by sub-bituminous activated carbon was between 49 - 95% for various samples containing a initial nitrate-nitrogen concentration between 0.174 - 24.788 mg/L. Average percent removal was calculated to be 75%. Adsorption capacity was determined to be 11.662 - 2363.814 mg/kg.The Freundlich and Langmuir isotherms are not suitable to be used as models for sub-bituminous activated carbon. This is due to an nitrate-nitrogen uptake which is not dependent on initial nitrate-nitrogen added.

Samples with an initial nitrate-nitrogen concentration between 0.373 - 55.524 mg/L and hydrodarco activated carbon had a percent removal of nitrate-nitrogen between 31 - 93 %. Average percent removal was calculated to be 67%. Adsorption capacity was determined to be between 32.547 - 5192.875 mg/kg. The Freundlich isotherm was found to be the best fit for modulation.

Sulfate is released in the samples with both types of activated carbon added. According to the data measured from carbon blanks which do not contain nitrate-nitrogen, the released sulfate is dependent on activated carbon only, and not nitrate-nitrogen amount in the solution. Blanks with nitrate-nitrogen and no activated carbon had no release of sulfate. Various concentrations of chloride are present in all samples tested in this study, which is reasonable due to chloride content in the synthetic stormwater.

6. References

AFKHAMI, A., MADRAKIAN, T. & KARIMI, Z. 2007. The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions. *Journal of Hazardous Materials,* 144**,** 427-431.

AHMADZADEH TOFIGHY, M. & MOHAMMADI, T. 2012. Nitrate removal from water using functionalized carbon nanotube sheets. *Chemical Engineering Research and Design.*

AKAN, A. O. & HOUGHTALEN, R. J. 2003. *Urban hydrology, hydraulics, and stormwater quality: engineering applications and computer modeling,* Hoboken, N.J., Wiley.

BHATNAGAR, A., KUMAR, E. & SILLANPÄÄ, M. 2010. Nitrate removal from water by nano-alumina: Characterization and sorption studies. *Chemical Engineering Journal,* 163**,** 317-323.

BHATNAGAR, A. & SILLANPÄÄ, M. 2011. A review of emerging adsorbents for nitrate removal from water. *Chemical Engineering Journal,* 168**,** 493-504.

BREZONIK, P. L. & ARNOLD, W. A. 2011. *Water chemistry: an introduction to the chemistry of natural and engineered aquatic systems,* Oxford, Oxford University Press.

CARBON-RESOURCES. 2010. *Technical Specifications; Granular activated carbon CR830A* [Online]. 2535 Jason Court, Oceanside, CA 92056. Available: www.carbonresources.com.

DEMIRAL, H. & GÜNDÜZOĞLU, G. 2010. Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresource Technology,* 101**,** 1675-1680.

EATON, A. D., CLECERI, L. S. & GREENBERG, A. E. 1995. *Standard Methods for the Examination of Water and Wastewater,* Washington, DC, American Public Health Association.

ERICKSON, A. J. 2012. *RE: Personal Communication.*

HAN, Y., LAU, S.-L., KAYHANIAN, M. & STENSTROM, M. K. 2006. Characteristics of Highway Stormwater Runoff.

METCALF & EDDY, I., TCHOBANOGLOUS, G., BURTON, F. L. & STENSEL, H. D. 2003. *Wastewater engineering: treatment and reuse,* Boston, McGraw-Hill.

NORIT. 2012. *Datasheet; Hydrodarco 3000 granular activated carbon* [Online]. 3200 University Avenue
Marshall, TX 75670 Norit Americas inc. Available: www.norit-americas.com.

PITT, R., MAESTRE, A., MORQUECHO, R., BROWN, T., SCHUELER, T., CAPPIELLA, K. & STURM, P. 2005. Evaluation of NPDES Phase 1 Municipal Stormwater Monitoring Data. University of Alabama and the Center for Watershed Protection.

SHRIMALI, M. & SINGH, K. P. 2001. New methods of nitrate removal from water. *Environmental Pollution,* 112**,** 351-359.

U.S.EPA 2008. Urban Stormwater Management in the United State. 500 Fifth Street, N.W Washington, D.C.

U.S.EPA. 2012. *United States Environmetal Protection Agency* [Online]. Available: http://www.epa.gov/.

WHO 2011. Guidelines for drinking-water quality. 4th ed. 20 Avenue Appia,
1211 Geneva 27, Switzerland.

ÖZTÜRK, N. & BEKTAŞ, T. E. L. 2004. Nitrate removal from aqueous solution by adsorption onto various materials. *Journal of Hazardous Materials,* 112**,** 155-162.

7. Appendix

Table 7-1: Date and time for sampling

Experiment	Date	Time
1 (Batch1)	14.02.12	09:30:00
	15.02.12	09:30:00
	16.02.12	10:30:00
	17.02.12	09:00:00
	18.02.12	08:00:00
2 (Batch 2)	19.02.12	11:00:00
	20.02.12	11:00:00
	21.02.12	11:00:00
	22.02.12	11:00:00
	23.02.12	10:15:00
3.4 (Batch 3)	06.03.12	13:15:00
	07.03.12	13:15:00
	08.03.12	13:15:00
	09.03.12	13:15:00
	10.03.12	13:15:00
5.6.7 (Batch 4)	12.03.12	15:45:00
	13.03.12	15:15:00
	14.03.12	13:30:00
	15.03.12	15:30:00
	16.03.12	14:45:00
8.9.10 (Batch 5)	19.03.12	12:30:00
	20.03.12	14:30:00
	21.03.12	14:30:00
	22.03.12	13:30:00
	23.03.12	11:15:00

7.1 Experiment 1

Table 7-2: Chloride data, Ex.1

CHLORIDE	Area Us/cm*sec 1	Area Us/cm*sec 2	Area Us/cm*sec 3	Area Us/cm*sec Average	STDAV	Cov	Average mg/l	mg/l 1	mg/l 2	mg/l 3	STDAV	Cov
B Initial	307,783	274,142	274,066	285,330	19,445	0,068	13,9601497	15,058675	13,4127463	13,4090279	0,951	0,068
B 0	308,124	282,285	272,866	287,758	18,255	0,063	14,0789427	15,0753589	13,8111529	13,3503164	0,893	0,063
B 24	320,128	281,028	286,879	296,012	21,089	0,071	14,4827476	15,6626699	14,0359202	13,7496526	1,032	0,071
B 48	338,58	307,417	269,308	305,102	34,694	0,114	14,9274874	16,5654575	15,040768	13,1762367	1,697	0,114
B 72	357,734	260,963	288,804	302,500	49,818	0,165	14,8002138	17,5025913	14,1301033	12,7679469	2,437	0,165
B 96	420,753	302,9	282,71	335,454	74,557	0,222	16,4125302	20,5858761	14,819768	13,8319466	3,648	0,222
S Initial	339,058	394,397	415,812	383,089	39,607	0,103	18,7431169	16,5888442	19,2963752	20,3441314	1,938	0,103
S 0	304,682	308,456	301,161	304,766	3,648	0,012	14,9110808	14,9069547	15,0916024	14,7346853	0,178	0,012
S 24	284,099	328,75	346,403	319,751	32,112	0,100	15,6442084	13,8999052	16,0845122	16,9482077	1,571	0,100
S 48	347,818	364,781	399,505	370,701	26,347	0,071	18,1370346	17,8473747	19,5462906	17,0174384	1,289	0,071
S 72	335,252	343,211	390,585	356,349	29,915	0,084	17,43484447	16,4026308	16,792035	19,1098683	1,464	0,084
S 96	310,255	333,324	345,414	329,664	17,863	0,054	16,1292471	15,1796208	16,308301	16,8998196	0,874	0,054
H initial	334,681	372,162	398,415	368,419	32,031	0,087	18,0253848	16,3746939	18,2084996	19,492961	1,567	0,087
H 0	311,441	313,443	361,162	328,682	28,146	0,086	16,0811852	15,2376473	15,3355977	17,6703106	1,377	0,086
H 24	352,229	461,611	535,478	449,773	92,196	0,205	22,0057002	22,5849057	26,1989427	17,2332522	4,511	0,205
H 48	498,49	517,067	560,422	525,326	31,781	0,060	25,7022595	24,3892578	25,2981611	27,4193597	1,555	0,060
H 72	531,664	523,002	572,769	542,478	26,588	0,049	26,541443	26,0123379	25,5885386	28,0234524	1,301	0,049
H 96	512,716	502,315	487,285	500,772	12,786	0,026	24,5009075	25,0852829	24,5764007	23,8410389	0,626	0,026

Table 7-3: Nitrate-nitrogen data, Ex.1

NO₃-N	Area Us/cm*sec 1	Area Us/cm*sec 2	Area Us/cm*sec 3	Area Us/cm*sec Average	STDAV	Cov	Average mg/l	mg/l 1	mg/l 2	mg/l 3	STDAV	Cov
B Initial	4,214	3,429	4,278	3,974	0,473	0,119	0,07661964	0,08125371	0,0661746	0,08248775	0,009	0,119
B 0	4	4,459	3,106	3,855	0,688	0,178	0,07433153	0,0771274	0,08597777	0,05988942	0,013	0,178
B 24	3,785	2,36	4,097	3,414	0,926	0,271	0,06582823	0,0729818	0,04550516	0,07899774	0,018	0,271
B 48	3,125	2,564	3,856	3,182	0,648	0,204	0,06134842	0,06025578	0,04943866	0,07435081	0,012	0,204
B 72	3,225	3,681	3,74	3,549	0,282	0,079	0,06842486	0,06218396	0,07097649	0,07211412	0,005	0,079
B 96	2,46	3,115	3,307	2,961	0,444	0,150	0,05708713	0,04743335	0,06006296	0,06376508	0,009	0,150
S Initial	8,138	9,524	9,455	9,039	0,781	0,086	0,17428863	0,15691569	0,18364033	0,18230988	0,015	0,086
S 0	6,189	7,688	7,156	7,011	0,760	0,108	0,13518504	0,11933536	0,14823886	0,13798091	0,015	0,108
S 24	3,052	2,983	3,784	3,273	0,444	0,136	0,06310949	0,0588482	0,0575176	0,07296252	0,009	0,136
S 48	3,492	3,444	3,601	3,512	0,080	0,023	0,06772428	0,06733222	0,06640669	0,06943394	0,002	0,023
S 72	2,786	3,854	2,418	3,019	0,746	0,247	0,05821833	0,05371923	0,07431225	0,04662351	0,014	0,247
S 96	3,151	2,606	3,263	3,007	0,351	0,117	0,05797409	0,06075711	0,0502485	0,06291667	0,007	0,117
H initial	18,702	19,805	19,462	19,323	0,564	0,029	0,37258317	0,36060914	0,3818702	0,37526335	0,011	0,029
H 0	13,29	12,977	13,245	13,171	0,169	0,013	0,25395481	0,25625577	0,25022056	0,25538809	0,003	0,013
H 24	2,611	2,644	4,183	3,146	0,898	0,286	0,0606607	0,05034491	0,05098121	0,08065597	0,017	0,286
H 48	2,397	1,851	3,777	2,675	0,993	0,371	0,05157895	0,04621859	0,0356907	0,07282754	0,019	0,371
H 72	0,414	2,233	1,905	1,517	0,969	0,639	0,02925699	0,00798269	0,04305637	0,03673192	0,019	0,639
H 96	2,108	3,69	1,671	2,490	1,062	0,427	0,04800538	0,04064614	0,07115002	0,03221997	0,020	0,427

Table 7-4: Sulfate data, Ex.1

SULFATE	Area Us/cm*sec 1	Area Us/cm*sec 2	Area Us/cm*sec 3	Area Us/cm*sec Average	STDAV	Cov	Average mg/l	mg/l 1	mg/l 2	mg/l 3	STDAV	Cov
B Initial	1,864	1,342	1,59	1,599	0,261	0,163	0,13396646	0,15620109	0,11245808	0,1332402	0,022	0,163
B 0	1,238	1,634	1,171	1,348	0,250	0,186	0,11293294	0,103743	0,13692735	0,09812847	0,021	0,186
B 24	1,491	1,32	1,156	1,322	0,168	0,127	0,11081004	0,1249411	0,11061451	0,09687149	0,014	0,127
B 48	0,995	1,536	1,292	1,274	0,271	0,213	0,10678769	0,08337987	0,1287506	0,10826814	0,023	0,213
B 72	1,16	1,057	1,388	1,202	0,169	0,141	0,10069831	0,09720669	0,0885754	0,11631283	0,014	0,141
B 96	1,098	1,166	1,298	1,187	0,102	0,086	0,09949719	0,09201116	0,0970948	0,1087093	0,009	0,086
S Initial	1,106	1,054	1,085	1,082	0,026	0,024	0,09064244	0,09268155	0,08832401	0,09092177	0,002	0,024
S 0	38,647	40,596	35,277	38,173	2,691	0,070	3,19888212	3,40189884	2,95617266	3,23857485	0,225	0,070
S 24	77,005	109,53	77,174	87,903	18,730	0,213	7,36617189	6,45293182	9,17849	6,46709383	1,570	0,213
S 48	95,402	124,227	91,167	103,599	17,990	0,174	8,68145098	7,9945796	10,410082	7,63969139	1,508	0,174
S 72	95,178	122,002	94,072	103,751	15,816	0,152	8,69418841	7,97580865	10,2236295	7,8831271	1,325	0,152
S 96	88,419	114,13	83,266	95,272	16,534	0,174	7,98365781	7,4094121	9,5636479	6,97759654	1,386	0,174
H Initial	1,494	1,311	1,17	1,325	0,162	0,123	0,1110335	0,12519551	0,10986032	0,09804468	0,014	0,123
H 0	203,638	194,968	220,448	206,351	12,955	0,063	17,2920081	17,0646339	16,3380977	18,4732928	1,086	0,063
H 24	330,094	451,629	498,604	426,776	86,961	0,204	35,7633177	27,6615035	37,8459989	41,7824507	7,287	0,204
H 48	532,05	533,65	539,292	534,997	3,804	0,007	44,8321709	44,5851877	44,7192659	45,1920591	0,319	0,007
H 72	590,999	562,302	592,82	582,040	17,118	0,029	48,774321	49,5250471	47,120271	49,6776449	1,434	0,029
H 96	566,201	537,764	514,448	539,471	25,919	0,048	45,2070591	47,4470028	45,0640144	43,11016	2,172	0,048

Table 7-5: Adsorption capacity of nitrate at different time intervals, Ex.1

NITRATE	Volume	Mass Sorbent	Mass Sorbed	Mass Sorbed
NO$_3$-N	(Liter)	(kg)	(mg)	Mass Sorbent
				(mg/kg)
B Initial	0,50113333			
B 0	0,50113333		0,0011	
B 24	0,50113333		0,0054	
B 48	0,50113333		0,0077	
B 72	0,50113333		0,0041	
B 96	0,50113333		0,0098	
S Initial	0,50137			
S 0	0,50137	0,0050008	0,0196	3,9205
S 24	0,50137	0,0050008	0,0557	11,1467
S 48	0,50137	0,0050008	0,0534	10,6840
S 72	0,50137	0,0050008	0,0582	11,6370
S 96	0,50137	0,0050008	0,0583	11,6615
H initial	0,5014			
H 0	0,5014	0,0050002	0,0595	11,8956
H 24	0,5014	0,0050002	0,1564	31,2783
H 48	0,5014	0,0050002	0,1610	32,1890
H 72	0,5014	0,0050002	0,1721	34,4274
H 96	0,5014	0,0050002	0,1627	32,5474

7.2 Experiment 1-10

Table 7-6: Duplicates from raw data

	Sample ID	Chloride (mg/L)	Nitrate, NO$_3^-$ (mg/L)	Sulfate (mg/L)
ex.2	H2 96h 2 dup	47,70310851	0,731300701	58,31752055
ex.2	H2 96h 2 dup	47,73839031	0,722711647	58,40347133
ex.4	S1 96h 4 Dup	18,6265	1,6944	5,0250
ex.4	S1 96h 4 Dup	18,6180	1,7299	5,6394
ex.7	S3 Initial 7 Dup	36,96175403	35,89782129	0,851572333
ex.7	S2-Initial-7-Dup	n.a.	n.a.	n.a.
ex.7	H2 96h 7 Dup	42,73643364	37,56864699	55,93455947
ex.7	H2 96h 7 Dup	43,07655596	37,69965618	56,39646727
ex.8	H2 96h 8 Dup	46,05998134	72,12371789	60,05012561
ex.8	H2 Initial 8 Dup	43,13072735	122,4495351	n.a.
ex.9	H2 96h 9 Dup	46,22328195	125,266737	63,78381192

Table 7-7: Raw data Experiment 2

CHLORIDE						
	mg/L	mg/L	mg/L	Average		
ex.2	1	2	3	mg/l	STDEV	Cov
S Initial	31,6287	24,4994	29,2701	28,4661	3,632	0,128
S 96	40,2785	42,2085	44,2102	42,2324	1,966	0,047
H initial	21,6678	27,1733	17,7101	22,1837	4,753	0,214
H 96	48,7193	49,9897	43,4117	47,3736	3,489	0,074

NITRATE						
(NO$_3$-N)	mg/L	mg/L	mg/L	Average		
ex.2	1	2	3	mg/l	STDEV	Cov
S Initial	0,4527	0,2947	0,3886	0,3786	0,079	0,210
S 96	0,2427	0,1661	0,1673	0,1920	0,044	0,229
H initial	0,5878	0,6147	0,7124	0,6383	0,066	0,103
H 96	0,1977	0,1803	0,1527	0,1769	0,023	0,128

SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.2	1	2	3	mg/l	STDEV	Cov
S Initial	-	-	-	-	-	-
S 96	9,5866	14,9865	9,8920	11,4884	3,033	0,264
H initial	-	-	-	-	-	-
H 96	62,3221	57,7418	52,6200	57,5613	4,854	0,084

CHLORIDE						
	mg/L	mg/L	mg/L	Average		
ex.2	1	2	3	mg/l	STDEV	Cov
SB initial	26,1085	33,4943	25,0129	28,2052	4,613	0,164
SB 96	30,4772	29,6701	32,5035	30,8836	1,460	0,047
HB initial	30,3681	31,9887	30,3553	30,9040	0,939	0,030
HB 96	30,7547	36,7998	36,0829	34,5458	3,303	0,096

NITRATE						
(NO$_3$-N)	mg/L	mg/L	mg/L	Average		
ex.2	1	2	3	mg/l	STDEV	Cov
SB initial	-	0,100802	-	0,1008	-	-
SB 96	0,00462594	-	-	0,0046	-	-
HB initial	-	-	-	-	-	-
HB 96	0,0033616	-	-	0,0034	-	-

SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.2	1	2	3	mg/l	STDEV	Cov
SB initial	-	-	0,2737	0,2737	-	-
SB 96	7,3674	7,1396	7,9755	7,4941	0,432	0,058
HB initial	-	-	-	-	-	-
HB 96	35,5874	44,0916	43,5210	41,0666	4,754	0,116

Table 7-8: Raw data in Experiment 4

CHLORIDE						
	mg/L	mg/L	mg/L	Average		
ex.4	1	2	3	mg/l	STDEV	Cov
S Initial	33,2178	36,8082	34,3916	34,8059	1,831	0,053
S 96	18,4996	35,5985	30,7080	28,2687	8,807	0,312
H initial	32,9398	30,3434	34,9239	32,7357	2,297	0,070
H 96	36,3905	35,9450	49,1780	40,5045	7,515	0,186
NITRATE						
(NO$_3$-N)	mg/L	mg/L	mg/L	Average		
ex.4	1	2	3	mg/l	STDEV	Cov
S Initial	1,8687	1,9973	1,8177	1,8946	0,093	0,049
S 96	0,3854	0,7865	0,6515	0,6078	0,204	0,336
H initial	3,7248	3,4718	4,1114	3,7693	0,322	0,085
H 96	0,9031	0,9544	1,4957	1,1178	0,328	0,294
SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.4	1	2	3	mg/l	STDEV	Cov
S Initial	0,1207	0,1280	0,0727	0,1071	0,030	0,280
S 96	5,1020	8,5109	6,8503	6,8211	1,705	0,250
H initial	0,0996	0,1763	0,0975	0,1245	0,045	0,361
H 96	48,3451	44,3381	61,3159	51,3330	8,875	0,173

Table 7-9: Raw data in Experiment 6

CHLORIDE						
	mg/L	mg/L	mg/L	Average		
ex.6	1	2	3	mg/l	STDEV	Cov
S Initial	36,3758	35,5803	35,3935	35,7832	0,522	0,015
S 96	34,6457	34,3448	33,7786	34,2563	0,440	0,013
H initial	37,5204	35,3413	34,9411	35,9343	1,388	0,039
H 96	45,5598	44,0274	-	44,7936	1,084	0,024
NITRATE						
(NO$_3$-N)	mg/L	mg/L	mg/L	Average		
ex.6	1	2	3	mg/l	STDEV	Cov
S Initial	5,6284	5,5669	5,5954	5,5969	0,031	0,005
S 96	2,5925	2,7031	2,6720	2,6559	0,057	0,021
H initial	13,1677	13,3202	12,9744	13,1541	0,173	0,013
H 96	6,4633	6,3699	-	6,4166	0,066	0,010
SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.6	1	2	3	mg/l	STDEV	Cov
S Initial	0,1836	0,1990	0,1713	0,1846	0,014	0,075
S 96	10,0848	9,7780	9,8933	9,9187	0,155	0,016
H initial	0,1808	0,1218	0,1746	0,1591	0,032	0,204
H 96	55,5978	57,3144	-	56,4561	1,214	0,022

Table 7-10: Raw data in Experiment 7

CHLORIDE						
	mg/L	mg/L	mg/L	Average		
ex.7	1	2	3	mg/l	STDEV	Cov
S Initial	-	38,5840	36,5034	37,5437	1,471	0,039
S 96	18,2509	11,0135	-	14,6322	5,118	0,350
H initial	41,2631	41,8780	38,5971	40,5794	1,744	0,043
H 96	-	42,5817	-	42,5817	-	-
NITRATE						
(NO$_3$-N)	mg/L	mg/L	mg/L	Average		
ex.7	1	2	3	mg/l	STDEV	Cov
S Initial	-	7,8517	7,9614	7,9065	0,078	0,010
S 96	1,9958	1,1589	-	1,5773	0,592	0,375
H initial	16,7157	16,7344	18,3235	17,2579	0,923	0,053
H 96	-	8,4548	-	8,4548	-	-
SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.7	1	2	3	mg/l	STDEV	Cov
S Initial	-	0,2212	1,0563	0,6387	0,591	0,924
S 96	5,1655	3,2369	-	4,2012	1,364	0,325
H initial	0,3544	0,1674	0,1793	0,2337	0,105	0,448
H 96	-	55,8159	-	55,8159	-	-

Table 7-11: Raw data in Experiment 8

CHLORIDE						
	mg/L	mg/L	mg/L	Average		
ex.8	1	2	3	mg/l	STDEV	Cov
S Initial	35,9088	35,0928	36,5249	35,8422	0,718	0,020
S 96	-	5,8479	7,0617	6,4548	0,858	0,133
H initial	42,5934	37,3329	45,1185	41,6816	3,972	0,095
H 96	46,9202	45,4232	-	46,1717	1,059	0,023
NITRATE						
(NO_3-N)	mg/L	mg/L	mg/L	Average		
ex.8	1	2	3	mg/l	STDEV	Cov
S Initial	12,7414	12,4657	12,5969	12,6013	0,138	0,011
S 96	-	1,2320	1,2997	1,2658	0,048	0,038
H initial	27,5346	27,3147	27,1189	27,3227	0,208	0,008
H 96	16,8511	16,0289	-	16,4400	0,581	0,035
SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.8	1	2	3	mg/l	STDEV	Cov
S Initial	0,2157	0,2200	0,1993	0,2117	0,011	0,052
S 96	-	2,6263	1,9745	2,3004	0,461	0,200
H initial	0,6384	0,4743	0,6980	0,6036	0,116	0,192
H 96	61,7245	59,2193	-	60,4719	1,771	0,029

Table 7-12: Raw data in Experiment 9

CHLORIDE	mg/L	mg/L	mg/L	Average		
ex.9	1	2	3	mg/l	STDEV	Cov
S Initial	36,8335	37,6031	40,7331	38,3899	2,065	0,054
S 96	2,8958	-	-	2,8958	-	-
H initial	37,1298	37,0607	-	37,0952	0,049	0,001
H 96	-	46,0074	-	46,0074	-	-
NITRATE						
(NO$_3$-N)	mg/L	mg/L	mg/L	Average		
ex.9	1	2	3	mg/l	STDEV	Cov
S Initial	18,6305	18,5302	18,4662	18,5423	0,083	0,004
S 96	0,9173	-	-	0,9173	-	-
H initial	40,8044	40,8187	-	40,8115	0,010	0,000
H 96	-	28,2263	-	28,2263	-	-
SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.9	1	2	3	mg/l	STDEV	Cov
S Initial	0,4337	0,3787	0,4762	0,4295	0,049	0,114
S 96	0,7745	-	-	0,7745	-	-
H initial	0,3856	0,7016	-	0,5436	0,223	0,411
H 96	-	63,6353	-	63,6353	-	-

Table 7-13: Raw data in Experiment 10

CHLORIDE	mg/L	mg/L	mg/L	Average		
ex.10	1	2	3	mg/l	STDEV	Cov
S Initial	41,9492	42,0516	37,2968	40,4325	2,716	0,067
S 96	3,8022	2,6772	-	3,2397	0,796	0,246
H initial	-	-	44,7126	44,7126	-	-
H 96	4,4533	6,7485	-	5,6009	1,623	0,290

NITRATE						
(NO_3-N)	mg/L	mg/L	mg/L	Average		
ex.10	1	2	3	mg/l	STDEV	Cov
S Initial	24,7864	24,6534	24,9232	24,7877	0,135	0,005
S 96	1,4969	0,8720	-	1,1845	0,442	0,373
H initial	-	-	55,5240	55,5240	-	-
H 96	4,0601	3,2266	-	3,6433	0,589	0,162

SULFATE						
	mg/L	mg/L	mg/L	Average		
ex.10	1	2	3	mg/l	STDEV	Cov
S Initial	0,3256	0,4017	0,5217	0,4163	0,099	0,237
S 96	1,4148	1,2726	-	1,3437	0,101	0,075
H initial	-	-	0,5183	0,5183	-	-
H 96	6,5177	6,1273	-	6,3225	0,276	0,044

Table 7-14: Values of standards from 2 different IC machines

	Ex. 1			Ex. 2-10		
Standard made	IC values from Saint Paul			IC values from Duluth		
Cl^-, NO_3-N and SO_4^{2-}	Chloride	NO3-N	Sulfate	Chloride	NO3-N	Sulfate
(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
0,05	1,00	0,11	0,26	0,07	0,04	0,10
0,1	0,48	0,14	0,31	0,16	0,08	0,19
0,2	0,98	0,24	0,44	0,18	0,16	0,26
1,0	1,15	0,99	1,04	0,85	0,78	1,04
2,5	2,61	2,49	2,48	2,07	2,04	2,56
5,0	5,10	5,01	5,02	4,48	4,48	5,25
5,0	5,12	5,04	5,00	4,48	4,48	5,25

Table 7-15: Sub-bituminous samples; initial and 96 hour data

Sample ID		CHLORIDE Average mg/l	CHLORIDE STDEV	CHLORIDE Cov	NITRATE(NO₃-N) Average mg/l	NITRATE(NO₃-N) STDEV	NITRATE(NO₃-N) Cov	SULFATE Average mg/l	SULFATE STDEV	SULFATE Cov
S(0.271 mg/L)	S initial 1	18,7431169	1,937812283	0,103387942	0,17428863	0,015060112	0,086409029	0,090642442	0,00219216	0,02418468
S(0.542 mg/L)	S Initial 2	28,4660506	3,63202156	0,127591341	0,37863925	0,079472103	0,209888705	-	-	-
S(2.167 mg/L)	S initial 4	34,8058702	1,830704499	0,052597579	1,89458326	0,092548703	0,048849109	0,107128369	0,02999572	0,27999792
S(6.771 mg/L)	S initial 6	35,7831898	0,521611037	0,014576985	5,59691095	0,030749978	0,005494098	0,184621649	0,01389977	0,07528788
S(8.666 mg/L)	S initial 7	37,5436895	1,471240034	0,039187412	7,90651366	0,07582188	0,00981244	0,6387386	0,59050691	0,92448916
S(13.541 mg/L)	S initial 8	35,8421606	0,718378347	0,02004283	12,6013051	0,137923147	0,010945148	0,211685256	0,01094631	0,05171031
S(20.312 mg/L)	S initial 9	38,389888	2,065418461	0,053801107	18,5423191	0,08280902	0,004465947	0,429523017	0,04885037	0,11373167
S(27.082 mg/L)	S initial 10	40,4325315	2,716109328	0,067176336	24,7876744	0,134871944	0,005441089	0,416324914	0,09886443	0,23746941
S (0 mg/L)Blank	SB initial	28,2052456	4,613064561	0,163553427	0,100802	-	-	0,273652898	-	-

Sample ID		CHLORIDE Average mg/l	CHLORIDE STDEV	CHLORIDE Cov	NITRATE(NO₃-N) Average mg/l	NITRATE(NO₃-N) STDEV	NITRATE(NO₃-N) Cov	SULFATE Average mg/l	SULFATE STDEV	SULFATE Cov
S(0.271 mg/L)	S 96 1	16,1292471	0,87396579	0,05418515	0,05797409	0,00677713	0,116899343	7,983657811	1,38551211	0,17354352
S(0.542 mg/L)	S 96 2	42,2324211	1,965964145	0,046551064	0,1919964	0,043872944	0,2285092	11,4883742	3,03334576	0,26403612
S(2.167 mg/L)	S 96 4	28,2686874	8,806577302	0,31153171	0,6077813	0,204101471	0,335814	6,82106034	1,70466146	0,24991151
S(6.771 mg/L)	S 96 6	34,2563398	0,440238396	0,012851297	2,65586557	0,057045058	0,021478895	9,918694674	0,15497875	0,01562491
S(8.666 mg/L)	S 96 7	14,6322316	5,11760879	0,349749028	1,57733378	0,591731969	0,375146957	4,201225023	1,36372354	0,3246014
S(13.541 mg/L)	S 96 8	6,45478108	0,858324694	0,132975028	1,26584856	0,047810919	0,037769857	2,300425767	0,46087368	0,20034278
S(20.312 mg/L)	S 96 9	2,89583462	-	-	0,917252	-	-	0,77455239	-	-
S(27.082 mg/L)	S 96 10	3,239725	0,79550057	0,245545709	1,18445991	0,441834037	0,37302574	1,343713914	0,10057888	0,07485141
S(0 mg/L)Blank	SB 96	30,8835706	1,459763309	0,047266663	0,00462594	-	-	7,49414159	0,43212419	0,0576616

Table 7-16: Initial and 96 hour data from Hydrodarco samples

Sample ID		CHLORIDE Average mg/l	STDEV	Cov	NITRATE(NO$_3$-N) Average mg/l	STDEV	Cov	SULFATE Average mg/l	STDEV	Cov
H(0.589 mg/L)	Hinitial 1	18,0253848	1,56717603	0,08694281	0,37258317	0,010884309	0,02921309	0,1110335	0,01361338	0,12260609
H(1.178 mg/L)	Hinitial 2	22,183737	4,752654841	0,214240497	0,63829167	0,065583372	0,102748281	-	-	-
H(4.714 mg/L)	Hinitial 4	32,7357307	2,297068928	0,070170083	3,76932056	0,322106238	0,085454721	0,124487303	0,0448835	0,36054683
H(14.730 mg/L)	Hinitial 6	35,9342721	1,388126009	0,038629585	13,15409994	0,173311306	0,01317546	0,159074602	0,03238379	0,20357614
H(18.855 mg/L)	Hinitial 7	40,5793856	1,744045393	0,042978605	17,25786607	0,922938479	0,05347931	0,233687318	0,10468706	0,44797921
H(29.461mg/L)	Hinitial 8	41,6816132	3,972100921	0,095296238	27,3227048	0,207963538	0,007611382	0,603583922	0,11583268	0,19190816
H(44.191 mg/L)	Hinitial 9	37,095237	0,04890891	0,001318469	40,8115481	0,010115929	0,000247869	0,543584588	0,2234062	0,410987
H(58.922 mg/L)	Hinitial 10	30,904003	0,939371759	0,030396443	55,5240306	-	-	0,518344508	-	-
H (0 mg/L)Blank	HB initial	44,7125757	-	-	-	-	-	-	-	-

Sample ID		CHLORIDE Average mg/l	STDEV	Cov	NITRATE(NO$_3$-N) Average mg/l	STDEV	Cov	SULFATE Average mg/l	STDEV	Cov
H(0.589 mg/L)	H 96 1	24,5009075	0,625547946	0,025531624	0,04800538	0,020481847	0,42657355	45,20705907	2,17195712	0,04804465
H(1.178 mg/L)	H 96 2	47,3735901	3,489393953	0,073655946	0,17691172	0,022681149	0,128206028	57,5612956	4,8535806	0,08432021
H(4.714 mg/L)	H 96 4	40,5045023	7,5147607	0,185529022	1,11776486	0,328343763	0,293750299	51,33303397	8,87456167	0,17288208
H(14.730 mg/L)	H 96 6	44,793601	1,083635561	0,024191749	6,41657988	0,066048304	0,010293381	56,45612908	1,21382698	0,02150036
H(18.855 mg/L)	H 96 7	42,5817244	-	-	8,45475785	-	-	55,8158856	-	-
H(29.461mg/L)	H 96 8	46,1716836	1,058511767	0,022925561	16,4400389	0,581377573	0,035363516	60,47189661	1,77140217	0,02929298
H(44.191 mg/L)	H 96 9	46,0073955	-	-	28,2262763	-	-	63,63530576	-	-
H(58.922 mg/L)	H 96 10	5,60090136	1,622949198	0,289765717	3,64334595	0,589346984	0,16175982	6,322500967	0,27609708	0,04366897
H(0 mg/L)Blank	HB 96	34,5458035	3,302684153	0,095603049	0,0033616	-	-	41,06663318	4,75374693	0,11575692

Table 7-17: Adsorption capacity of nitrate in sub-bituminous samples

Sample ID		NITRATE(NO$_3$-N)			
		Volume (Liter)	Mass Sorbent (kg)	Mass Sorbed (mg)	Mass Sorbed / Mass Sorbent (mg/kg)
S 1	S(0.271 mg/L)	0,5014	0,0050008	0,0583	11,6615
S 2	S(0.542 mg/L)	0,5007	0,0050002	0,0935	18,6898
S 4	S(2.167 mg/L)	0,5007	0,0050005	0,6442	128,8337
S 6	S(6.771 mg/L)	0,5007	0,0050012	1,4726	294,4456
S 7	S(8.666 mg/L)	0,5007	0,0050004	3,1690	633,7534
S 8	S(13.541 mg/L)	0,5006	0,0050005	5,6749	1134,8756
S 9	S(20.312 mg/L)	0,5008	0,0050008	8,8258	1764,8681
S 10	S(27.082 mg/L)	0,5008	0,0050008	11,8209	2363,8142
S1-S10	Average				793,8677367

Table 7-18: Adsorption capacity of nitrate in Hydrodarco samples

Sample ID		NITRATE(NO$_3$-N)			
		Volume (Liter)	Mass Sorbent (kg)	Mass Sorbed (mg)	Mass Sorbed / Mass Sorbent (mg/kg)
H 1	H(0.589 mg/L)	0,5014	0,0050002	0,1627	32,5474
H 2	H(1.178 mg/L)	0,5007	0,0050002	0,2310	46,2004
H 4	H(4.714 mg/L)	0,5007	0,0050002	1,3276	265,5144
H 6	H(14.730 mg/L)	0,5008	0,0050006	3,3741	674,7535
H 7	H(18.855 mg/L)	0,5005	0,0050005	4,4061	881,1245
H 8	H(29.461mg/L)	0,5008	0,0050008	5,4499	1089,7899
H 9	H(44.191 mg/L)	0,5008	0,0050008	6,3021	1260,2133
H 10	H(58.922 mg/L)	0,5006	0,0050009	25,9689	5192,8752
H1-H10	Average				1180,3773