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Electrochemical Regeneration of Natural Organic Matter (NOM) Loaded Granular Activated Carbon

Masters Thesis

by

Jeff McEwen

Submitted to the School of Graduate Studies and Research

Under supervision of Dr. R.M. Narbaitz

In partial fulfillment of the requirements for the degree of M.A.Sc. in Civil Engineering (Environmental)

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ABSTRACT

Granular activated carbon (GAC) is used in municipal drinking water treatment plants for the removal of organic compounds (natural and synthetic), taste and odour compounds, as well as for the removal of disinfection by-products (DBPs). Once the adsorptive capacity of the GAC is exhausted, the GAC is sent to a landfill or thermally regenerated for reuse. Many alternative technologies for GAC regeneration, such as bioregeneration, chemical regeneration, chemical desorption regeneration, and steam regeneration, have been tested in attempts to overcome the shortcomings of thermal regeneration. Research by Narbaitz and Cen (1994) and Karimi-Jashni (2001) into electrochemical regeneration of phenol and nitrophenol loaded GAC showed regeneration efficiencies in excess of 100%. This development showed promise for drinking water treatment applications. In this study, the suitability of electrochemical regeneration for municipal drinking water systems was investigated. To achieve this objective GAC samples were obtained from two municipal drinking water facilities equipped with on-site thermal reactivation: Buffalo Pound Water Plant, Regina, Sask. and Richard Miller Water Treatment Plant, Cincinnati, Ohio. Three different sample types were obtained; virgin, field spent and field-thermally reactivated GAC. Along with the carbon samples, pre-GAC water was obtained from both treatment plants. The waters had natural organic material (NOM) concentrations of 3.5 and 1.5 mg/L TOC for Buffalo Pound and Richard Miller treatment plants, respectively. The field spent samples were electrochemically regenerated at 10, 50, 100 and 200mA in a divided cell

electrochemical reactor for 5 h. The virgin, the thermal and the electrochemical regenerated samples were analysed for aqueous NOM adsorption, iodine number, surface chemistry, pore size distribution and surface area to evaluate the regeneration efficiency and to characterize the regeneration. The electrochemical reactor was able to regenerate 8-15% of the adsorption capacity of the field spent GAC compared to approximately 100% regeneration efficiency for the thermally regenerated samples. Laboratory batch-loaded, electrochemically regenerated GAC had much higher regeneration efficiencies (83±5%) than the field-loaded GAC, thus the type of NOM loading used is critical in obtaining a representative evaluation of the regeneration process. The iodine number analysis did not give an accurate estimate of the regeneration efficiency of the electrochemical regenerated samples. The surface functional groups of the virgin, thermal and electrochemically regenerated (5 hrs at 100 mA) GAC samples were tested using a method adapted from Boehm (1967). There was a slight decreased in the overall surface acidity from the virgin to the electrochemically regenerated. The field-thermally regenerated GAC showed decreased microporosity and increased meso and macroporosity. The electrochemically regenerated and the field-loaded (non-regenerated) GAC had similar pore size distributions with only a slight increase with increasing current. Both GAC sources were impacted similarly for all parameters tested.

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AC	activated carbon
ASTM	American Standards Testing Methods
AWWA	American Water Works Association
b	Langmuir constant
BC	Base consumed
BET	Brunaur-Emmett-Teller
Co	initial liquid-phase concentration
Ce	equilibrium liquid-phase concentration
CHA	commercial humic acid
DBPs	disinfection by-products
Do	GAC dose
FA	fulvic acid
GAC	granular activated carbon
HA	humic acid
K	Freundlich constant
1/n	Freundlich constant
LaHA	Laurentian humic acid
M	mass
MB	methylene blue
NOM	natural organic matter
PAC	powdered activated carbon
ppb	parts per billion
ppm	parts per million
q	solid-phase concentration
q_e	solid-phase equilibrium concentration
RE	regeneration efficiency
SFA	soil fulvic acid
SOCs	synthetic organic compounds
SPR	Sn-Pd-Ru oxide coated titanium electrode
TDS	total dissolved solids
THMs	trihalomethanes
TOC	total organic carbon

1 Introduction

1.1 Introduction

The use of granular activated carbon (GAC) for the treatment of drinking water has increased, due to more strict water quality legislation. In water treatment GAC is used for the removal of taste and odour compounds, toxic organic compounds, natural organic matter (NOM), as well as for the removal of disinfection by-products (DBPs). Activated carbon's main mechanism for contaminant removal is through adsorption. This involves a process where the contaminant leaves the liquid phase and is concentrated on the surface of the activated carbon. Activated carbon's effectiveness is derived from its large internal surface area (500-1500 m^2/g). However, it is finite and will eventually become exhausted. Once the adsorption capacity of the GAC is saturated, it must be replaced with new or regenerated GAC to continue removing contaminants.

The key features of GAC column adsorbers are that they can remove up to 100% of target toxic contaminants and their ability to remove a wide range of contaminants. This last advantage can become a disadvantage when various contaminants compete for adsorption sites. The presence of NOM in the source water has been proven to dramatically reduced GAC adsorption capacity for toxic contaminants (Murin and Snoeyink, 1979), requiring more frequent replacement or regeneration, and thus increasing the operating cost of running a water treatment plant.

1.2 Statement of Problem

In North America, the use of GAC post-filtration adsorbers for drinking water treatment applications has primarily been limited to large treatment facilities due to the high cost of operating and maintenance costs. The principal exception is in cases of groundwater treatment for toxic contaminant removal. In Europe, which has higher population density and more contaminated rivers, GAC coupled with ozonation has been used more extensively over a wider range of plant sizes. In North America, there have been many activated carbon (AC) applications for taste and odor removal in a wide range of plant sizes, however they utilized powdered activated carbon (PAC) or GAC as a replacement for anthracite in dual media granular filters. The latter tends to be quite effective and the GAC only needs to be regenerated every three to five years. Thus, their GAC usage rate is low.

Figure 1-1 shows the cost of replacement GAC as a function of the GAC usage. This figure shows that the unit cost of GAC treatment can be reduced with increasing GAC utilization rates. Currently, GAC regeneration at full-scale water treatment plants is accomplished via thermal regeneration, in part because it provides a product with comparable contaminant removal to that of virgin GAC. There are, however, a number of disadvantages with thermal regeneration, such as: the high energy required for heating the GAC; on-site regeneration is cost effective only for large operations (680 kg/d); and off-site regeneration requires transportation, which involves (3%) mass loss (Clark and Lykins, 1989). Thermal regeneration creates

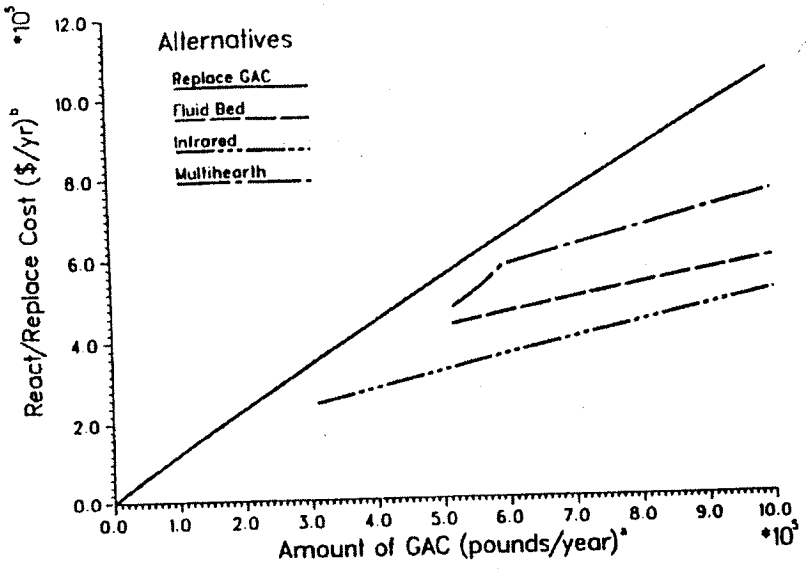

Figure 1-1 Cost of Replacement and Regenerated GAC (Source: Clark and Lykins, 1989)

wider pores plus causes significant mass and volume losses (5 to 15%) (Clark and Lykins, 1989). To overcome these deficiencies chemical and electrochemical regeneration have been developed to regenerate GAC, but are currently limited to a few industrial and research applications.

Electrochemical regeneration while still in the development phase has shown to be an effective method for regeneration of phenol-loaded GAC (Karimi-Jashni, 2001). Electrochemical regeneration has a number of advantages over thermal regeneration. Studies into electrochemical regeneration of GAC loaded with industrial contaminants, such as phenol and nitro-phenol (Narbaitz and Cen, 1994; Karimi-Jashni, 2001) have demonstrated high regeneration efficiencies with no measurable GAC mass loss. Further advantages of electrochemical regeneration include: the possibility of in-situ designs, the destruction of desorbed contaminants, and the

flexibility in the design making it suitability for all size operations. Thus, electrochemical regeneration has the potential to be superior to thermal regeneration.

Previous research (Narbaitz and Cen, 1994; Karimi-Jashni, 2001) into electrochemical regeneration has primarily evaluated GAC loaded with high concentrations of phenolics, such as those encountered in an industrial wastewater treatment application. However, the largest application of GAC adsorption is in the drinking water treatment sector. Figure 1-2 shows the amount of AC used in various American industrial sectors as of 1987. The bars on the left are for GAC, the bars in the middle are PAC and the bars on the right are the sum of the two AC types. This figure demonstrates that the greatest use of AC is in the water treatment sector. To date only a few tests have been conducted to evaluate the electrochemical regeneration efficiency of NOM-loaded GAC (Karimi-Jashni, 2001). As they only involved iodine number comparisons, they have limited value. Thus, there is a great need for an in-depth evaluation of this novel technology for the largest application of activated carbon, water treatment.

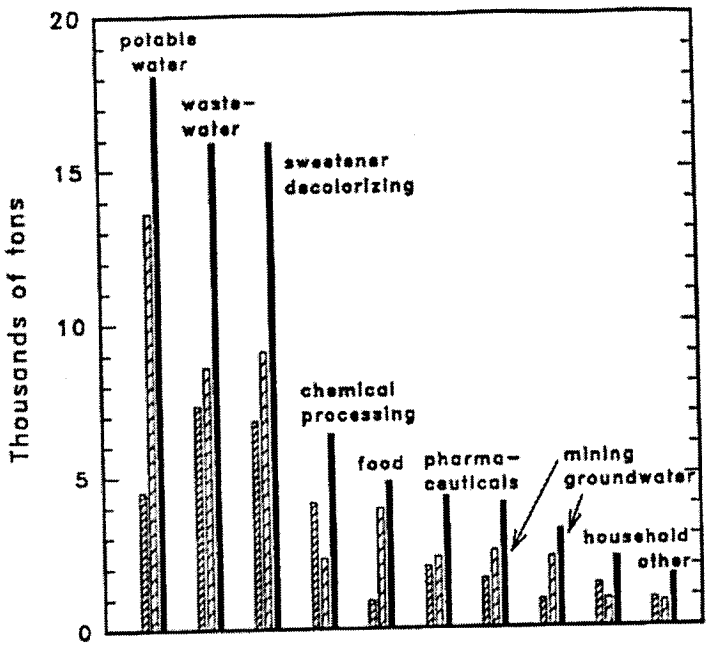

Figure 1-2 Activated Carbon Uses (Source: Kirk-Othmer, 1992)

1.3 Objectives

The objective of the research is to more thoroughly investigate the applicability of GAC electrochemical regeneration to the drinking water treatment industry and provide a direct comparison between electrochemical and thermal regeneration. The objective will be accomplished through experiments measuring the effectiveness of electrochemical and thermal regeneration of NOM-loaded GAC samples in terms of regeneration efficiency, iodine number, surface chemistry, porosity, and surface area analysis.

2 Literature Review

2.1 Introduction

Natural organic material (NOM) is present in all surface water. GAC regeneration methods used in drinking water treatment for surface waters must be capable of removing adsorbed NOM contaminants. This chapter reviews the technical literature on adsorption, activated carbon (AC), factors affecting activated carbon adsorption, activated carbon regeneration methods and methods of evaluating regeneration efficiency.

2.2 Adsorption

Adsorption is the process by which contaminants in a liquid or gas phase are concentrated on an interface, such as the surface of activated carbon. The reverse process is called desorption. The adsorbent (e.g. AC) is the material whose surface removes the adsorbate (e.g. NOM, phenol, nitro-phenol) from solution. The adsorption process can occur via physical or chemical mechanisms (Sontheimer et al., 1988). Physical adsorption involves physical interactive forces, such as hydrogen bonding, dipole-dipole, and van der Waals forces that allow the contaminant to adsorb to the surface of the AC. These are relatively weak forces that are non-specific and operate over relatively long distances. Because of the weakness of the forces, physical adsorption is reversible (Sontheimer et al., 1988). Chemical adsorption (or chemisorption) involves the use of high-energy forces that form chemical bonds between the contaminant and the surface of the AC. Based on the

strength of the bonds this type of adsorption is considered irreversible (Sontheimer et al., 1988).

Contaminant removal via adsorption is controlled by two phenomena. First, by the adsorption equilibrium capacity or the maximum amount of mass a given material can hold per unit mass. Secondly, by the "kinetics" or rate of adsorption, that is controlled by the diffusion or migration of the contaminant into the internal pores of the adsorbent.

2.2.1 Adsorption Equilibrium Capacity

Although large, the surface area of AC is finite and this limits its capacity for adsorption. The maximum or equilibrium adsorption capacity is determined through a procedure called the adsorption isotherm. Isotherm refers to the constant temperature of the test conditions. The adsorption isotherm is generally conducted via a set of batch equilibrium tests called the "bottle-point" method. This method involves the addition of a carefully weighed mass of activated carbon to a known volume of solution with a known adsorbate concentration. The activated carbon and the adsorbate are kept in constant contact until equilibrium is reached. The experiment involves numerous bottles with different activated carbon dosages. After equilibration the solutions are separated from the AC and the adsorbate concentrations within the liquid samples are measured. The solid-phase equilibrium concentration is calculated with the following mass balance equation:

$$q_e = \frac{V}{M}(C_0 - C_e) \tag{2.1}$$

Where q_e = the solid-phase equilibrium adsorbate concentration (mg/g)

V = the volume of the adsorbate (L),

M = the mass of activated carbon (mg),

C_o = the initial liquid-phase adsorbate concentration (mg/L)

C_e = the liquid-phase equilibrium adsorbate concentration (mg/L).

When the calculated value for the q_e for different masses of activated carbon is plotted vs. C_e an isotherm graph is developed. Each bottle yields a point on the graph, hence the name bottle-point method.

The isotherm can be modeled using a number of different methods, including the Langmuir or Freundlich isotherm equations, which are the most popular (Sontheimer et al., 1988).

The Langmuir isotherm is based on a number of assumptions including monolayer adsorption, uniform energies of adsorption, homeogeneous adsorbent, and the molecules are adsorbed on definite adsorption sites (Faust and Aly, 1987; Sontheimer et al., 1988). Based on these assumptions one can generate the following equation (Faust and Aly, 1987; Sontheimer et al., 1988):

$$q_e = \frac{q_m b C_e}{(1 + bC_e)} \tag{2.2}$$

Where q_e is the solid phase equilibrium concentration

q_m is the maximum amount that can be adsorbed in the monolayer. The units are mass of adsorbate per unit weight of adsorbent.

b is a constant that represents the energy of the adsorption, the units are related to the units used in q and Ce.

C_e is the liquid adsorbate equilibrium concentration.

The Langmuir method is often not used in water treatment because q_m and b are not constant over the experimental range. This is because several of the model assumptions are violated, that the adsorbent has a homogenous surface, and the adjacent adsorbate molecules on the surface of the activated carbon do not interact with each other. For more in depth information refer to Faust and Aly (1987), Sontheimer et al. (1988) and Snoeyink (1990)

The Freundlich model is an empirically based model (Faust and Aly, 1987).

$$q_e = KC_e^{1/n} \tag{2.3}$$

Where q_e is the solid adsorbate concentration (mg/g)

C_e is the liquid equilibrium adsorbate concentration (mg/L)

K and 1/n are Freundlich constants.

The Freundlich constants are derived from a linear regression of the plot of log C_e vs. log q_e. The value of q at C_e=1 is K and the slope of the line of log C_e vs. log q is the value of 1/n. Halsey and Taylor (1947) developed theoretical interperatation of the Freundlich model, i.e. it involves adsorption with an exponential distribution of adsorption energies as opposed to the constant adsorption energise of the Langmuir model. The K constant was related to the capacity of the adsorbent for the adsorbate,

a higher value would represent a greater capacity. The 1/n constant was said to represent the strength of the adsorption, a lower value would represent a stronger adsorptive force. The Freundlich or Langmuir adsorption equations provide an estimate of the solid adsorbate adsorption capacity for a particular liquid adsorbate concentration within the experimental range.

Sontheimer et al. (1988) discussed a number of alternative methods (e.g. Toth; Myers; Radke and Prausntz) that have been used to describe data in the literature. These contain three or more adjustable parameters and they are necessary for applications where the two-parameter Freundlich and Langmuir do not provide satisfactory simulations.

2.2.2 Adsorption Kinetics

Adsorption onto activated carbon does not happen instantaneously, it requires some time. Sontheimer et al. (1988) indicated:

> "The rate of adsorption is limited by external mass transfer, and internal mass transfer rates that depend on the properties of the adsorbate and adsorbent".

Figure 2-1 illustrates the path the adsorbate must take to adsorb onto the surface of the activated carbon. The mass transfer steps can be broken down into the bulk solution transport, film diffusion, pore transport, and finally adsorption. The slowest rate in this chain of events is the rate determining step. The adsorbate must diffuse

from the bulk solution to the liquid phase then diffuse along the surface or through the pores to adsorb into the internal surface of the activated carbon.

The equilibrium time (t) required to reach equilibrium can be determined with a kinetic study. These studies can be conducted via a number of different experimental setups, including batch tests. The batch kinetic studies generally involve the addition of activated carbon into many bottles with the same activated carbon dosage and contacting for different time periods. The adsorbate concentrations for the bottles are analysed over a range of contact periods that extended beyond the time at which the adsorbate concentration remains constant. In some cases the time required to reach equilibrium can be extremely long. However, Randtke and Snoeyink (1983) demonstrated that the equilibrium time for peat fulvic acid adsorption can be reduced from 5299 to 2 days by decreasing the particle size from 0.230 to 0.0044 cm. In some cases it is not possible to reduce the particle diameter (i.e. if you need to reuse the GAC again). In this case the equilibrium time (t) can be defined as the time to approach equilibrium (t_f) and can be defined as A) the time required for q to reach some fraction of q_e or B) the time required for C to reach some fraction of C_e (i.e. q $= 0.99q_e$ or $C=1.01C_e$) (Randke and Snoeyink, 1983).

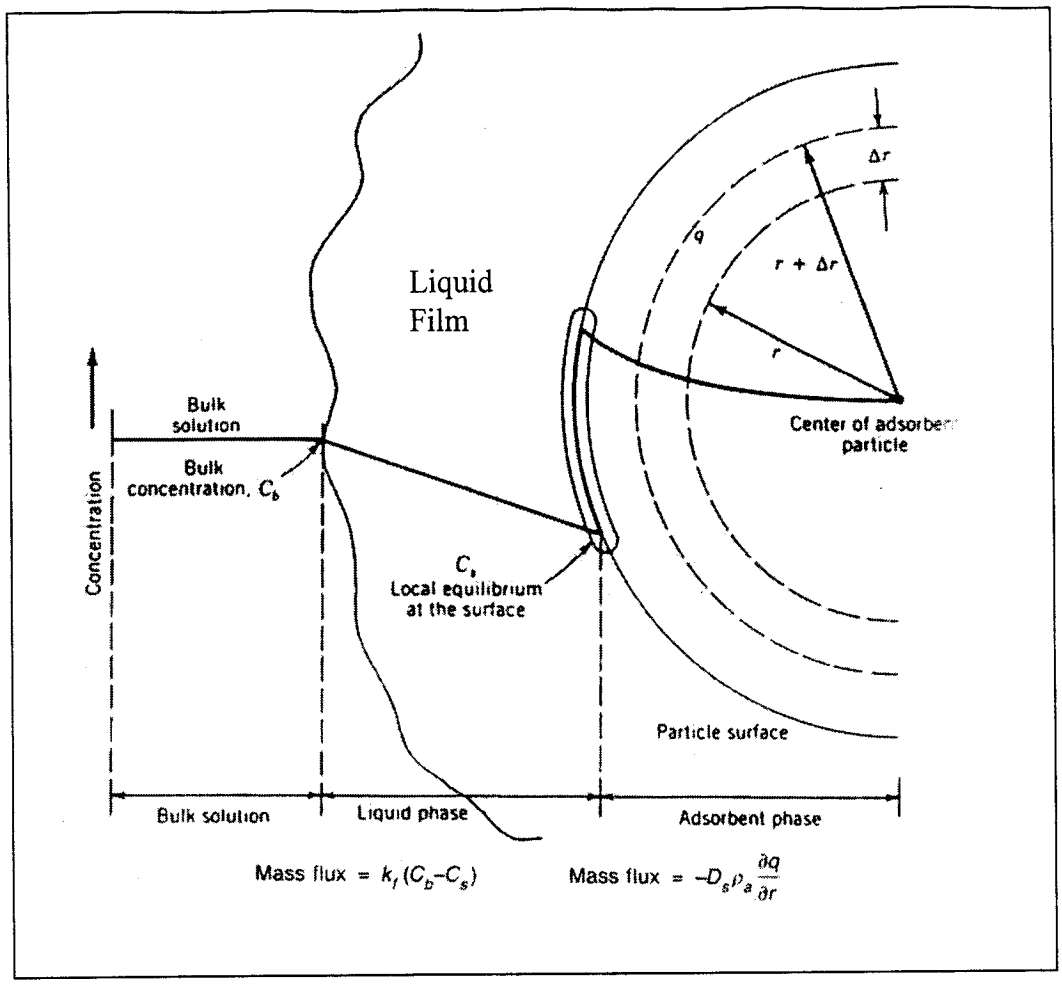

Figure 2-1 GAC Adsorption Kinetic Pathway (Source: Clark and Lykins, 1989)

2.3 Activated Carbon

Activated carbon is manufactured from many organic raw materials, such as coconut shells, wood, coal, and peat. The manufacturing of activated carbon consists of three-stage process: drying (170 °C), carbonization (400-600 °C) and activation (700-1100 °C) (Simske, 1970). Carbonization involves heating the source material in the absence of oxygen or any other oxidizing agents. The heating causes non-carbon elements, such as hydrogen and oxygen, to be removed from the material as gases. Left behind are elementary graphic crystallites with tar deposited in the interspaces (Smiske, 1970). The activation step involves further heating and involves chemical

(phosphoric acid, zinc acid, etc.), physical (gas or steam) activation or a combination of both (Smiske, 1970). The activation step removes the tarry deposits and the microporous structure is developed. The finished product can be classified according to appearance, pore size distribution or according to the field of application. In general activated carbons are classified according to their particle size: granular activated carbon (GAC), which has 90% of the particles larger than 0.180 mm (80 US Mesh) with the average size of approximately 1.12 mm, and powdered activated carbon (PAC), which has particles smaller than 0.140 mm (100 US Mesh), and more than half smaller than 0.045 mm. Activated carbon is also available as irregular shaped particles, cylindrical pellets, spherical pellets, activated carbon fibres, and activated coke. Activated carbon is used in water and wastewater treatment, personal air respirators, vehicle air emission control devices, gas stack air scrubbers, and in industrial applications, such as coffee decaffeinating (Ullmann's Encyclopaedia of Industrial Chemistry, 2003). Activated carbon's ability to adsorb a wide range of organic and inorganic compounds is the main reason its diverse applications. For a more in-depth review of activated carbon properties and applications see Ullmann's Encyclopaedia of Industrial Chemistry (2003), Smiske (1970), Faust and Ali (1987), Sontheimer et al. (1988), and Clark and Lykins (1989).

2.4 Factors Affecting Activated Carbon Adsorption

There are a number of factors that affect the adsorption, and conversely desorption, of a contaminant on activated carbon. They are governed by the properties of the activated carbon, by properties of the adsorbate and the environmental conditions.

This section will discuss the effect of GAC surface area, GAC pore size distribution, GAC surface chemistry, solution temperature, solution salt concentration, presence of dissolved molecular oxygen, and solution pH on AC adsorption capacity.

2.5 GAC Characteristics that Affect Adsorption

2.5.1 Surface Area

The surface area of GAC can vary from activated carbon to activated carbon and from batch to batch of the same type of activated carbon. The incredibly large internal surface area of activated carbon is responsible for activated carbons ability to remove 100% of contaminants. The surface area alone is not a good indicator of the adsorption capacity of a specific contaminant. The surface area of activated carbon is generally evaluated via mercury porosimetry or via Nitrogen/Argon adsorption (i.e., BET (Brunaur-Emmett-Teller) surface area calculations) (Knappe et al., 1992; Drombrowski et al., 2000; Moore et al., 2001). This surface area is measured from the adsorption of N_2 (a very small molecule) onto the surface of activated carbon. Larger contaminants such as humic acid may not be able to access the small pores, thus reducing the actual adsorption capacity.

Puri (1983) investigated the effect of de-ashing and carbon "burn off" on the surface area of activated carbon. The results demonstrated that the phenol adsorption capacity increased with increasing surface area.

Summers and Roberts (1988b) show decreased adsorption of larger size fractions of commercial humic acid (CHA) on F-300 GAC. They attributed the decreased adsorption to a size exclusion effect.

The size of the contaminant and the pore sizes distribution of the GAC may not allow the contaminant to access all of the BET surface area. Thus, the amount of surface area is important but so is the distribution of the surface area throughout the GAC. These studies show that surface area is one factor that needs to be considered when evaluating the effectiveness of a particular regeneration method.

2.5.2 Pore Size Distribution

AC is composed of a large internal surface area that is divided into different regions based on the size of the pores. There are three main regions based on their diameters: micropores (less than 2 nm), mesopores (2-50 nm) and macropores (greater than 50 nm). The pore size distribution of the GAC allows the removal of many different sizes of contaminants. For some ACs the micropores can account for 95% of the total surface area (Černỳ, 1970). The majority of adsorption occurs in the micropores, provided that the contaminant can access these pores. Mesopores are involved in capillary condensation and they are paths for the contaminants to access the micropores. The macropores are mainly pathways for the contaminant to reach the mesopores (as seen in Fig 2-2)

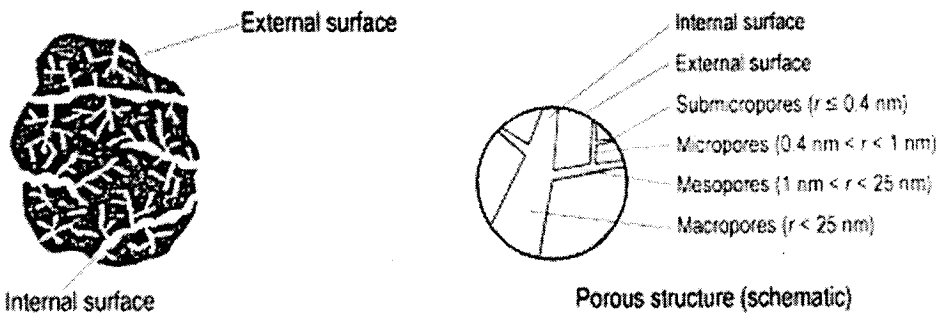

Figure 2-2 Activated Carbon Pore Structure (Source: Ullmann's Encyclopedia of Industrial Chemistry)

Hashimoto et al. (1979) studied the effect of percent burn-off on the adsorption capacity and the surface characteristics of activated carbon. They found that the adsorption capacity increased at a rate greater than pore surface area. This was attributed to a significant change in the pore distribution during activation. They suggested that large molecular weight contaminants were blocked from entering the smallest pores within virgin GAC but that their adsorption increased after the pore enlargement associated with thermal regeneration.

Hsieh and Teng (2000) demonstrated that the phenol adsorption on activated carbon occurred mainly in the microporous region. Lee et al. (1981) performed a study of the relationship between pore size distribution and the adsorption capacity of GAC for humic compounds. They found that the pore size was an important parameter in the adsorption capacity for humic compounds. The pore volume associated with the pore sizes less than 70 Å correlated with NOM with molecular weight less than 1000; the quantity of pores with diameters smaller than 400 Å correlated well with

NOM with molecular weight of more than 50 000. Moore et al. (2001) showed that the thermally regenerated GAC was mostly mesoporous while the virgin GAC was mostly microporous. They found that NOM filled the pore volumes of the virgin GAC differently than the thermally regenerated GAC. The NOM adsorption for the regenerated GAC occurred in the mesopores while in the virgin the NOM adsorption occurred in the micropores. Waer et al. (1992) found that the best thermal regeneration conditions were those that redevelop the pore volume distribution as close as possible to that of virgin GAC.

The pore size can limit the amount of contaminant that can reach the adsorption sites. Therefore, it is important not only to look at the impact on surface area but also on the impact on porosity when evaluating regeneration methods.

2.5.3 Surface Chemistry

The internal pores of AC are composed of irregular surfaces containing molecules of oxygen, nitrogen, sulphur and hydrogen that are bonded chemically to the surface (Černỳ, 1970). These molecules form surface functional groups (SFGs) such as carbonyl, carboxyl, phenol, lactone, quintone and ether. Due to the SFGs, the surface of GAC can be polar, non-polar, acidic or basic. These functional groups can interact with the adsorbing solution to form chemical bonds or physical attractive forces such as van der Waals, to remove the contaminant from solution.

Coughlin and Ezra (1968) noted a decrease in adsorption of phenol and nitrobenzene when there is an increase in the surface acid groups. Metha and Flora (1997) studied

the effect of electrochemical treatment of GAC on the adsorption of phenol and on the changes in the surface chemistry of the treated carbons. They documented a relationship between an increase in the concentration of surface acid groups and decreased adsorption of phenol due to anodic treatment. Tessmer et al. (1997) investigated the impact of oxygen containing SFGs on AC for the adsorption of phenol following thermal treatment. The AC was outgassed at varying temperatures under argon to remove the SFGs. They demonstrated that the change in adsorptive capacity was a result of the change in the SFGs and not to the change in surface textural characteristics of the AC. Work by Salame and Bandosz (2001) also confirmed the findings of a decrease in adsorption capacity with increase in SFGs.

Metha and Flora (1997) speculated that the use of electrochemical regeneration may increase the surface acid groups of the AC; it is therefore wise to investigate the effect of electrochemical regeneration on the surface chemistry. The researchers above did not correlate the effects of individual surface chemical groups with the GAC adsorption capacity rather; they compared the change in overall surface acidity on the GAC adsorption capacity.

2.5.4 Particle Size

Some researchers (Randtke and Snoeyink, 1983; Narbaitz, 1985) observed that the particle size affected the adsorption capacity of AC. Narbaitz (1985) observed higher adsorption capacities with 40X50 Mesh GAC as opposed to ground GAC (larger than mesh 40). He reasoned that the GAC may not have been activated to the core of

the particle, when ground the unactivated core was exposed it resulted in lower adsorption capacity. However, the majority of researchers found that particle size had no impact on adsorption capacity (Crittenden et al., 1987; Najm et al., 1990; Warta et al., 1995).

The relationship between particle size and the rate of adsorption was explained by the following relationship (Faust and Aly, 1987, Sontheimer et al., 1988)

$$r_{ads} \alpha \frac{1}{d_p^2} \tag{2.4}$$

Where r_{ads} = the rate of adsorption

dp = the particle diameter

Thus, equilibrium time can be reduced by utilising smaller GAC particle sizes.

Randtke and Snoeyink (1983) demonstrated that the adsorption equilibrium time for humic acid can be reduced from 5299 to 2 days by reducing the GAC particle size from 0.2380 to 0.044 cm. Figure 2-3 further illustrates the effect of decreasing GAC particle size has on the equilibrium time for humic acid.

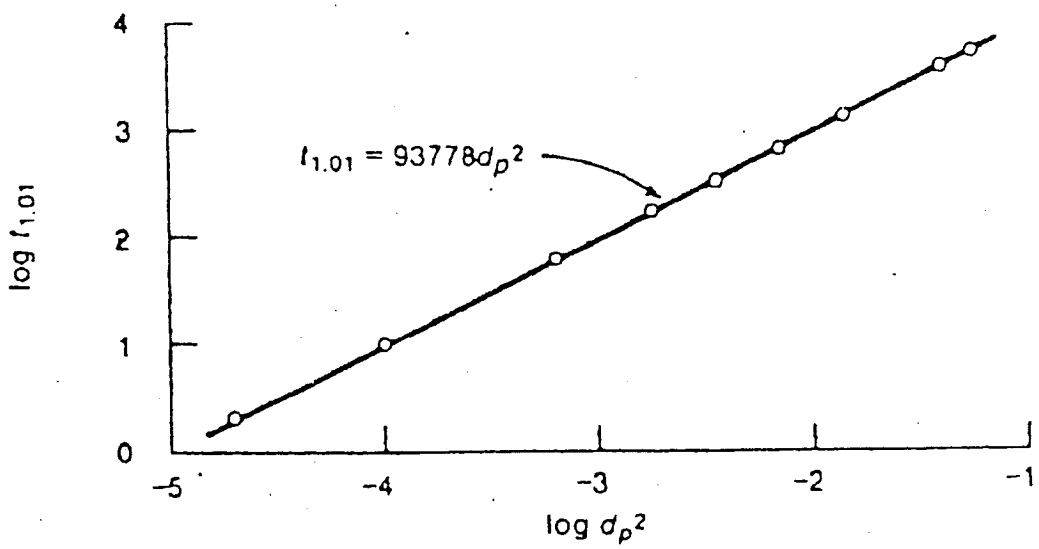

Figure 2-3 Equilibrium Time ($t_{1.01}$) versus the square of the particle diameter (d_p^2) for simulated adsorption of humic acid (Source: Randtke and Snoeyink, 1983)

2.5.5 Dose

Through simulations, Randtke and Snoeyink (1983) demonstrated that the equilibrium time for peat fulvic acid can be reduced from 155 days to approximately 7.6 days by increasing the GAC dose from 0.01 to 2.5 g/L for GAC with an average particle diameter of 0.0595 cm (30 mesh).

Summers and Roberts (1988a) investigated the effect of GAC dose on the adsorption capacity of GAC for commercial humic acid (CHA) and soil fulvic acid (SFA). Figures 2-4 and 2-5 are constant-dose and constant initial concentration for CHA and SFA adsorption. They were able to correlate the constant dose experiments but not the constant initial concentration data. This showed greater adsorption capacity with lower GAC doses, respectively. However, when they displayed their data on an available surface area basis (Fig 2-6 and 2-7) they develop an isotherm with good fit,

(i.e. there was no difference in the isotherm for different doses). The modified Freundlich equation used to calculate the solid phase equilibrium loading q_e is:

$$q_e = K\left(\frac{C_e}{D_o}\right)^{\frac{1}{n}} \tag{2.5}$$

Where C_e is the equilibrium concentration (mg/L)

D_0 is the GAC dose (mg/L)

K and 1/n are the Freundlich coefficient (unitless)

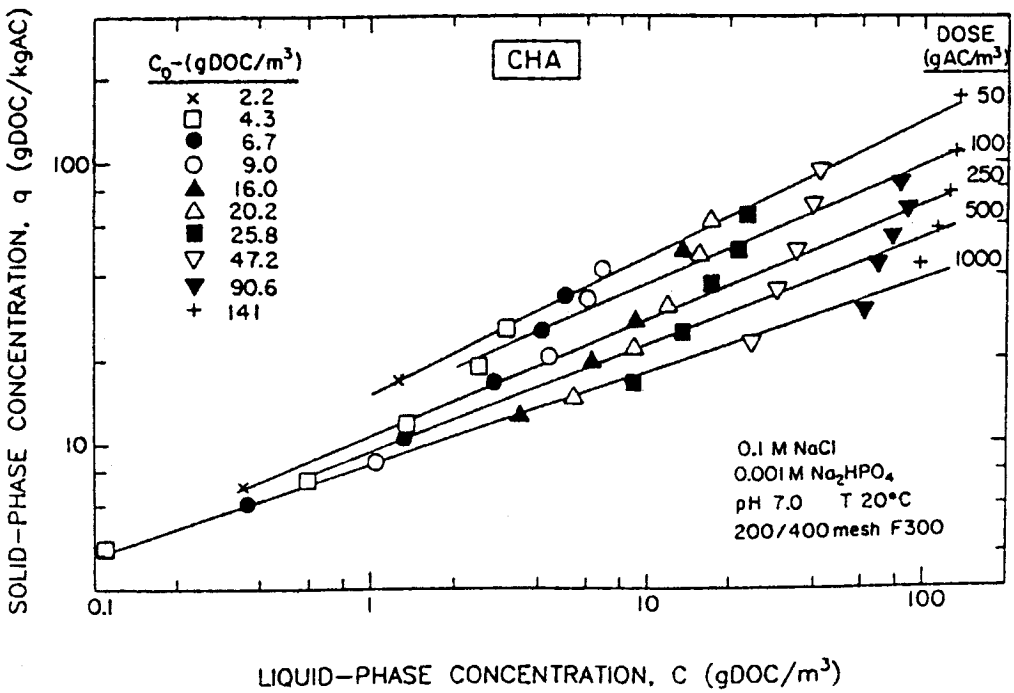

Figure 2-4 Effect of Dose for CHA Adsorption on Activated Carbon (Source Summers and Roberts, 1988a)

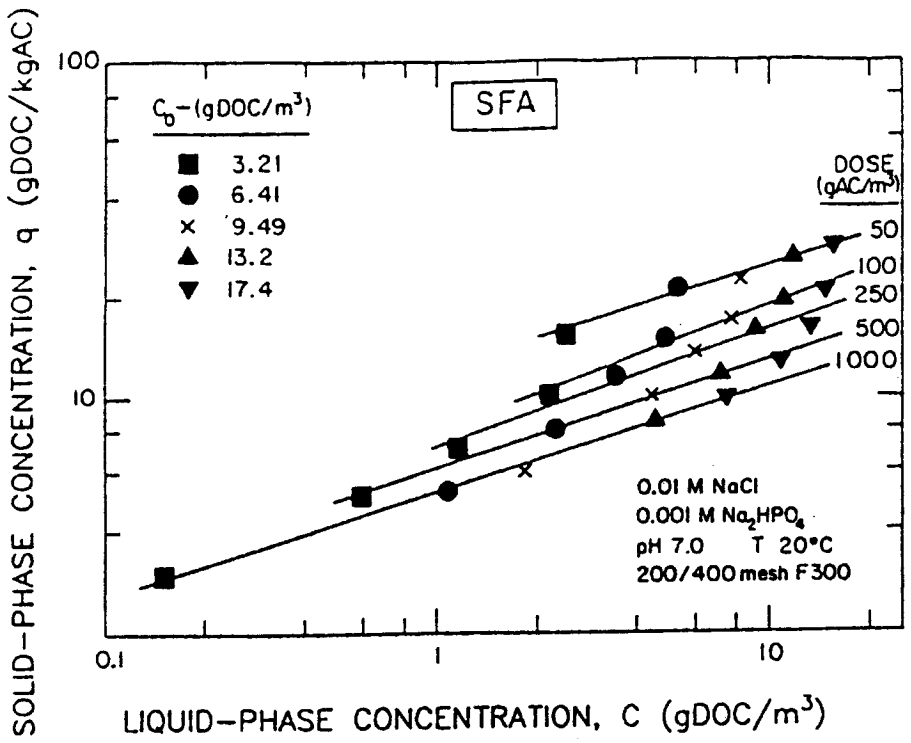

Figure 2-5 Effect of GAC Dose for SFA Adsorption on Activated Carbon (Source: Summers and Roberts, 1988a)

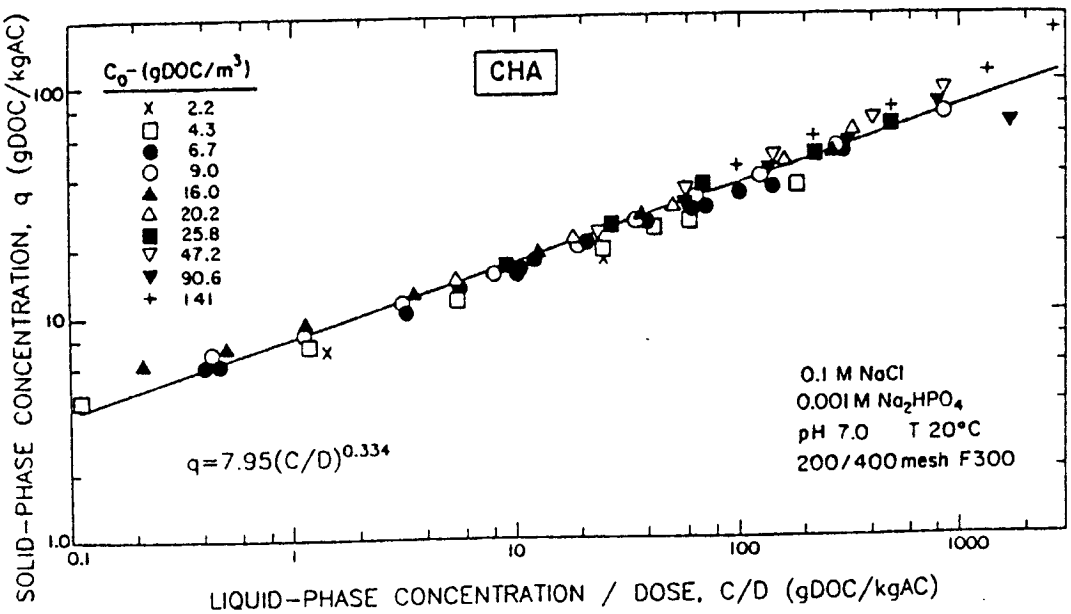

Figure 2-6 GAC Dose Normalized CHA Adsorption Isotherm (Source: Summers and Roberts, 1988a)

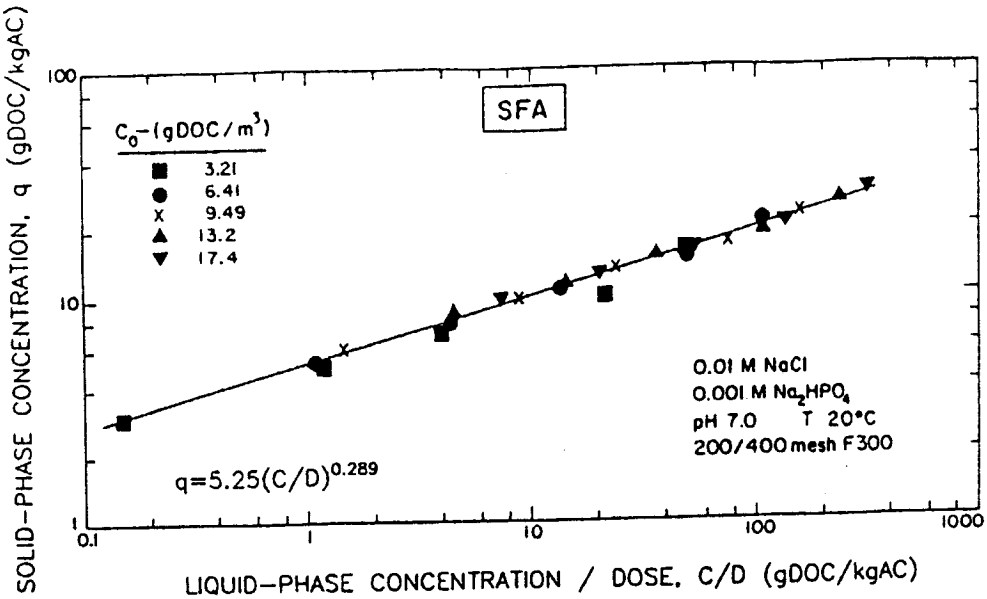

Figure 2-7 GAC Dose Normalized SFA Adsorption Isotherm (Source: Summers and Roberts, 1988a)

Kilduff et al. (1996a) studied how the GAC dose affects the molecular size distribution of the NOM remaining in solution. They observed an increase in the average molecular weight of the Laurentian Humic Acid (LaHA) remaining in solution after equilibrium with increasing doses of F-400 AC. They also used the modified Freundlich equation (equation 2.5) to normalize for the AC dose.

Therefore using a large GAC dose will decrease the equilibrium time and the effects of using large doses can be normalized to limit the effect on the equilibrium capacity.

2.6 Adsorbate Characteristics that Affect Adsorption

2.6.1 Adsorbate Molecular Size

Traub's Rule states that the adsorption of organic substances from aqueous solutions increases strongly and regularly as the homologous series ascends (i.e. adsorption increases with increasing molecular weight) (Faust and Aly, 1998). However, if the molecular size is larger than the available pore volume decreased adsorption is observed (Warta et al., 1995).

McCreary and Snoeyink (1980) observed the opposite of Traub's Rule for the adsorption of soil fulvic acid. They observed a decrease in adsorption with increasing molecular weights (see Fig 2-8). They explained that either large molecules may not have able to enter the small pores or that the migration of these

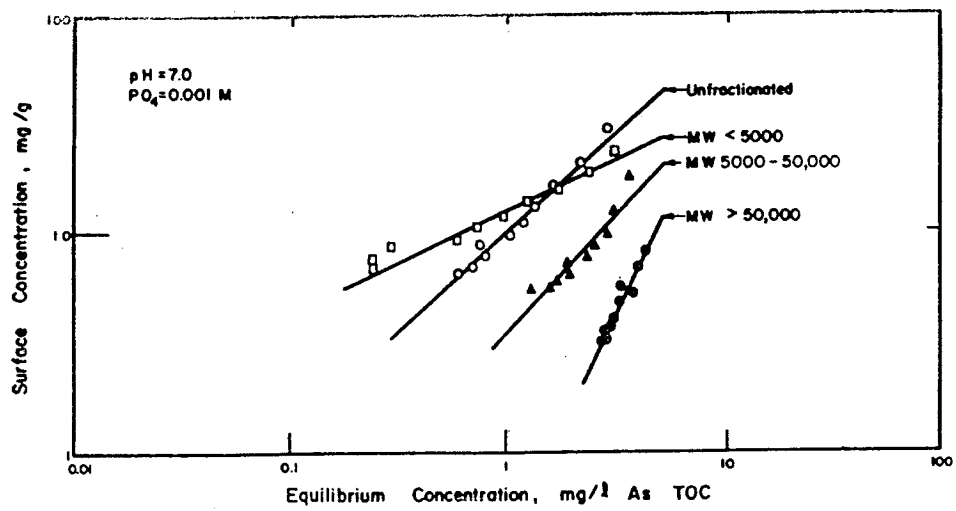

Figure 2-8 Adsorption of Molecular Weight Fractions of soil fulvic acid (Source: McCreary and Snoeyink, 1980)

particles was incomplete after the allotted 7 day contact period. Traub's Rule was developed for homogenous chemicals with distinct chemical structures. NOM, such as SFA and HA are heterogeneous and the chemical structures of the various molecular weight fractions are not necessarily uniform.

Lee et al. (1981) investigated the adsorption of humic substances on AC. They observed that that the adsorption capacity increased with decreasing molecular weight (see Fig 2-9). They explained that the adsorption was pore size dependent.

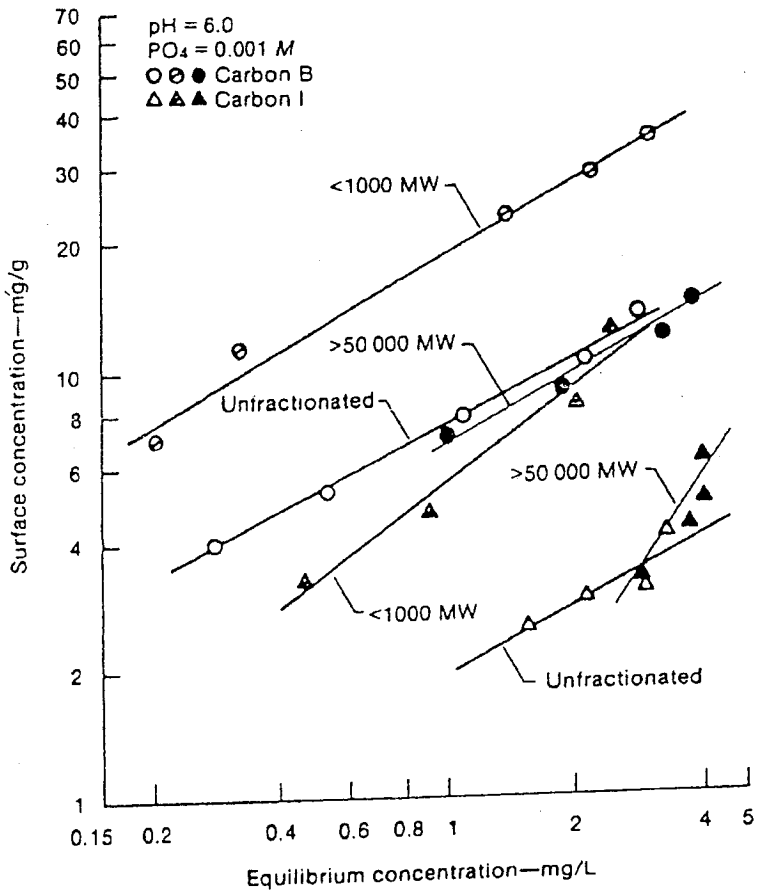

Figure 2-9 Adsorption Isotherms for Different Molecular Weight Fractions and Unfractioned Peat Fulvic Acid (Source: Lee et al., 1981)

Summers and Roberts (1988b) also showed that the adsorption capacity of F-300 and F400 GAC for commercial humic acid (CHA) decreases with increasing molecular weight, when displayed on a GAC mass basis (Fig 2-10). However, when they displayed their data on a surface area basis there was little difference in the adsorption capacities for the various molecular weights (seen in Fig 2-11).

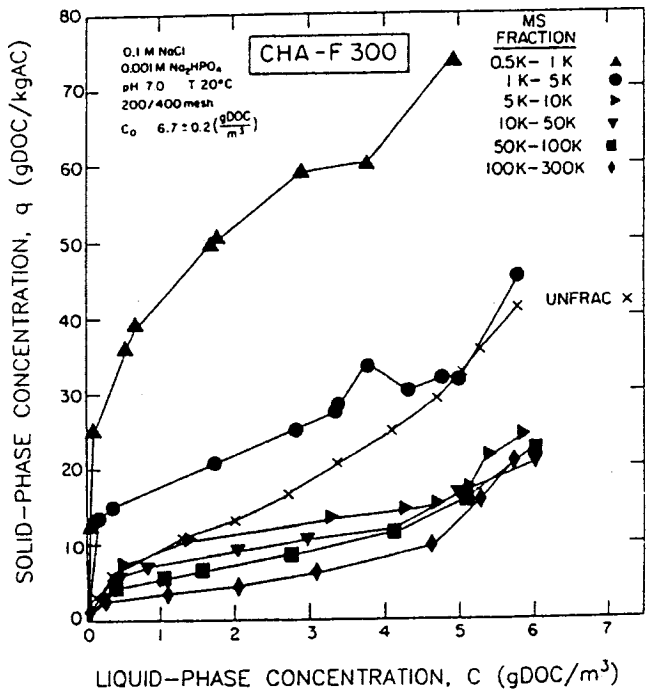

Figure 2-10 Effect of Molecular Size Fraction on the Adsorption Capacity of F-300 for CHA (Source: Summers and Roberts 1988b)

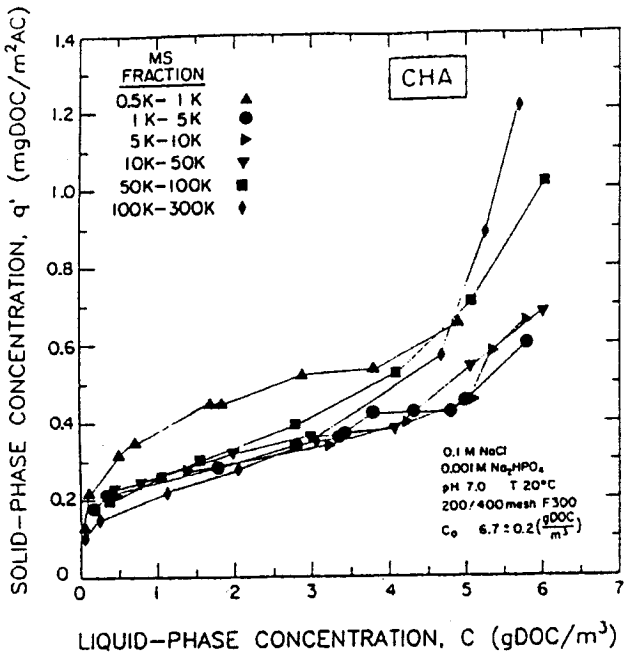

Figure 2-11 Adsorption Isotherms for F-300 for CHA, Available Surface Area Basis (Source: Summers and Roberts, 1988b)

The adsorption of natural and synthetic organic molecules was observed to decrease with increasing molecular size. Kilduff et al. (1996a) saw preferential adsorption of organic polyelectrolyte solutions due to molecular size, with the small molecular weight compounds adsorbing preferentially. Kilduff et al. (1996b) suggest that increasing the salt concentration of the adsorbing solution results in a decrease in the adsorbate molecular size. This allows the adsorbate to reach adsorption sites which were previously inaccessible. This was also observed in Newcombe (1999), the increased adsorption was attributed to a decrease in molecular size. The molecular size is said to decrease because of the decrease in its electro-repulsive effect.

In summary, increasing adsorbate molecular weight has the following impact on adsorption. For individual compounds with a homologous series, adsorption increases with increasing molecular weight (Traube's Rule), presumably due to decreased solubility. For NOM, which is composed of a heterogeneous mixture of large molecular weight organic compounds, the adsorption capacity decreases with increasing molecular weight, presumably because the large molecular weight compounds are too large to access the surface within the small pores.

2.6.2 Adsorbate Solubility

The solute solubility is one of the primary indicators of the solutes absorbability. The Polanyi generalized isotherm predicts the adsorption of individual solutes based on their solubility (Sontheimer et al., 1988). The Polanyi potential theory defines the adsorption potential (ε) as the amount of free energy essential to remove the solute from the solvent.

$$\varepsilon = RT \ln\left(\frac{c_s}{c}\right) \tag{2.6}$$

Where c_s = the solute solubility limit

From this equation it can be seen that an increase in the solubility of a substance results in an increase in the adsorption potential (i.e. the amount of energy required for adsorption). Thus, the adsorption capacity would decreases with increasing solubility.

Traube's Rule is also explained by solubility. As the molecular sizes of organic molecules are increased by additions of hydrophobic groups ($-CH_2-$) their solubility

decreases (Snoeyink, 1990). Decreases in solubility result in increases in adsorption capacity. However, if the AC is highly micro-porous the less soluble NOM may not be able to access the pores.

Leng and Pinto (1996) used surfactants and altered the pH to increase the solubility of phenolics adsorbed to AC. Through altering the solubility they were able to achieve regeneration efficiencies of 99%.

Solubility is also influenced by the polarity of the adsorbate; greater polarity increases the solubility of the adsorbate (Faust and Aly, 1998). The solubility of an adsorbate can be adjusted by altering the pH of the adsorbing solution. As discussed later in Section 2.7.4. Greater adsorption observed by Newcomb (1999) at lower pH 3 was attributed to the lower solubility of NOM.

Solubility is a major factor in adsorption; adsorption capacity can be increased by decreasing the adsorbate solubility.

2.7 Environmental Factors Affecting Adsorption

2.7.1 Temperature

As mentioned in Section 2.2, adsorption can be physical or chemical in nature. Physical adsorption is an exothermic reaction, thus an increase in temperature results in a decrease in adsorption capacity (Faust and Aly, 1998). Salame and Bandosz

(2001) experienced greater phenol adsorption onto Westvaco WVA 1100 GAC at 303°K as apposed to 333°K.

However, several researchers have observed an increase in AC adsorption capacity with increased adsorbate solution temperature (Faust and Aly, 1987; Summers and Roberts, 1988a and 1988b; Lin and Teng, 2002). For aqueous adsorption, an increase in the adsorbate temperature can also lead to an increase in the diffusion rates, thus leading to an increase in the rate of adsorption (Faust and Aly, 1987).

Summers and Roberts (1988a and 1988b) noted an increase in adsorption capacity of commercial humic acid (CHA) with an increase in adsorbate temperature from 1±0.5°C to 41±0.5°C (see Fig 2-12). The increase in adsorption capacity was attributed to an increase in entropy. At the higher temperatures more solvent molecules (H_20) were released from the surface of the GAC providing space for greater adsorption capacity. Also, chemical adsorption sometimes requires a certain amount of energy to be supplied "activated adsorption" (Cerny, 1970). This may explain why increased adsorption was observed.

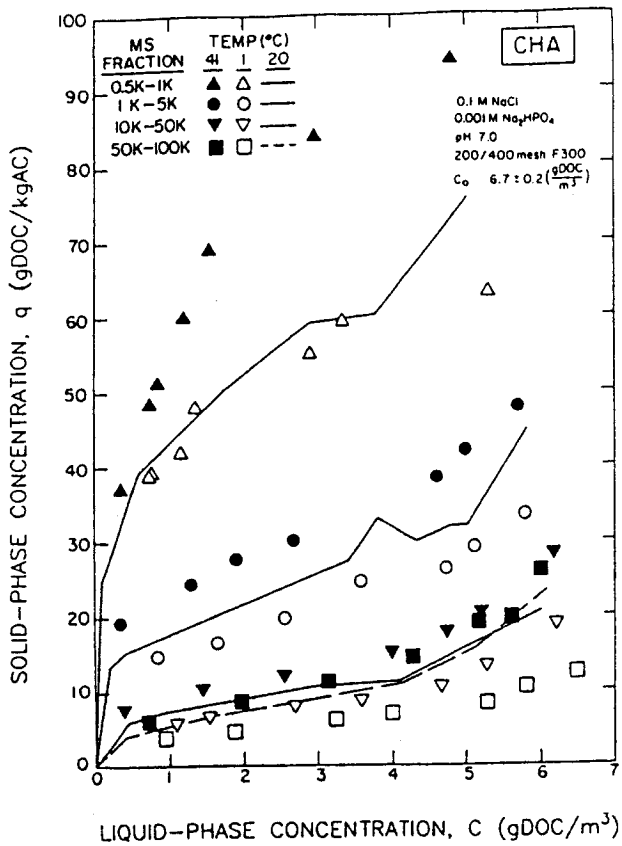

Figure 2-12 Temperature Effect on Adsorption Isotherms of CHA fractions on F-300 AC (Source: Summers and Roberts, 1988b)

Therefore, maintaining the same temperature conditions for each adsorption test is essential to be able to compare results from each test.

2.7.2 Salt Concentration

Summers and Roberts (1988b) observed an increase in the adsorption capacity of positively charged and negatively charged adsorbents for CHA. In Fig 2-13 F-300 and WV-B ACs are positively and negatively charged, respectively. This seems to be a violation of electrostatic theory; ion shielding should decrease the adsorption of adsorbates onto oppositely charged AC surfaces and increase the adsorption of

adsorbates onto similarly charged AC surfaces. After they normalized the data with regards to the available surface area they observed a slight decrease in adsorption of the positively charged adsorbent.

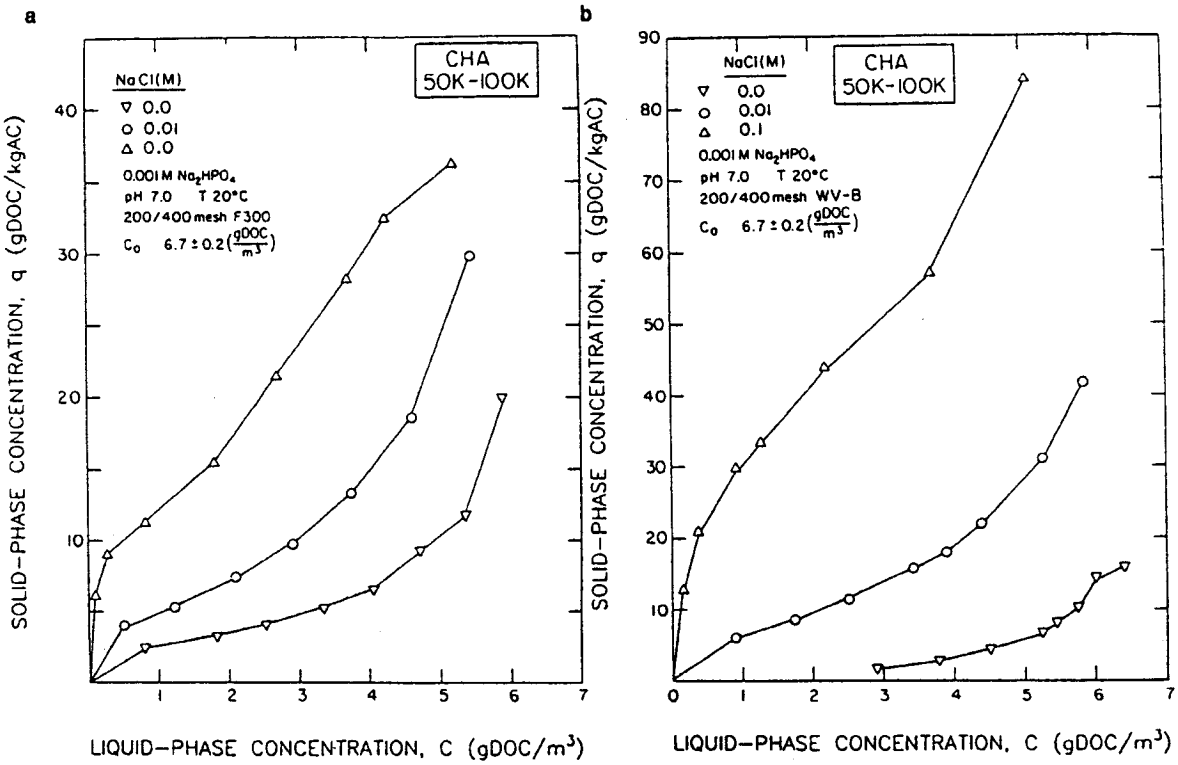

Figure 2-13 Effect of Ionic Strength on the Adsorption Isotherm for a) F-300 and b) WV-B AC (Source: Summers and Roberts, 1988b)

Kilduff et al. (1996b) demonstrated increased polyelectrolyte adsorption with an increase in ionic strength and calcium content of the adsorbate (see Fig 2-14). An increase in the ion strength from 0.01 to 0.1 N the Freundlich K coefficient for Laurentian humic acid (LaHA) increased from 6.50 to 17.96 (no units), Kilduff et al. (1996b).

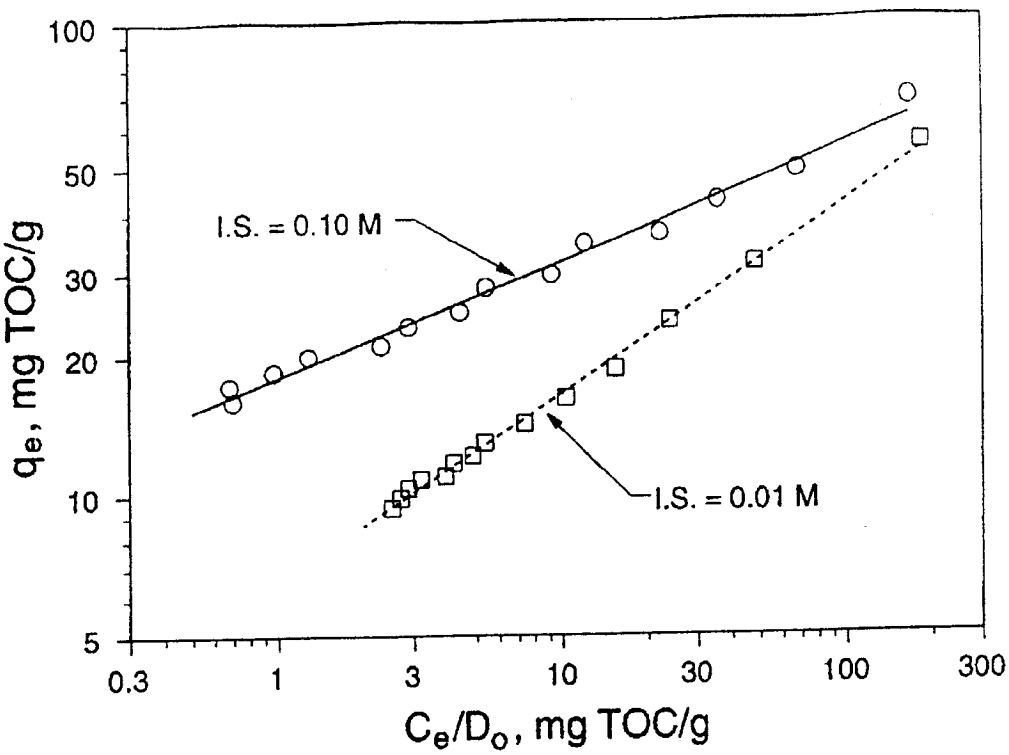

Figure 2-14 Effect of Ion Strengh on the Adsorption Isotherm of LaHA on F-400 (Source: Kilduff et al., 1996b)

Newcombe (1999) demonstrated that increasing the ion concentration increased the NOM adsorption capacity at high surface concentrations but decreased the adsorption at low adsorbate surface concentrations. At high surface concentrations the NOM – NOM electrostatic repulsion forces were reduced due to the high ion concentration, resulting in an increase in adsorption. However, at low surface concentrations the electrostatic attractive forces between the NOM and the GAC were reduced due to the increased ion concentration, which resulted in lower adsorption. Therefore, the impact of salt concentration on the adsorption capacity cannot be ignored.

At high ion strength the counter ions compress the adsorbates double layer, effectively lowering the molecular size, resulting in more surface area for adsorption (Summers and Roberts, 1988b). Thus, higher ion concentrations increased the adsorption capacity.

2.7.3 Molecular Oxygen

Vidic et al. (1990) investigated the impact of molecular oxygen on the adsorption capacity of GAC. They found that the capacity of GAC for o-cresol increased up to 3-fold in the presence of oxygen; similar results were seen for phenol (see Fig 2-15). They speculated that there are chemical reactions with the molecular oxygen that are catalyzed by the AC, which increased the adsorption capacity.

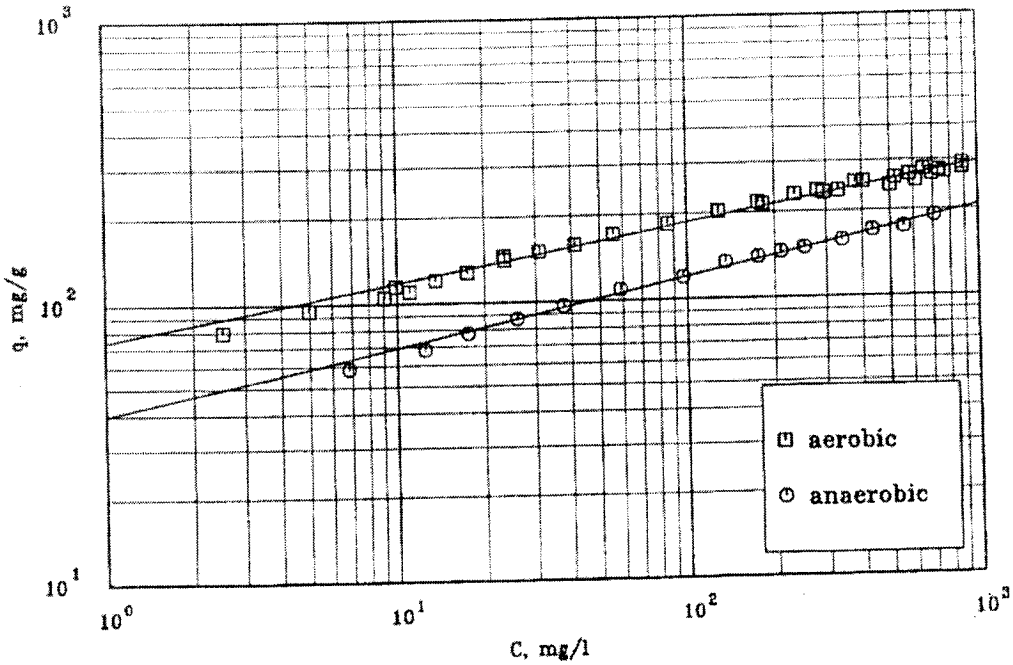

Figure 2-15 Adsorption Isotherms for phenol on F-400 AC (Source: Vidic et al., 1990)

Metha and Flora (1997) studied the adsorption capacities of phenol by electrochemically treated GAC under oxic (presence of dissolved oxygen) and anoxic (absence of dissolved oxygen) conditions. They had experienced higher adsorption capacities in the oxic adsorption isotherms.

Tessmer et al. (1997) studied the impact of oxygen containing surface functional groups on the adsorption of phenols on AC. In all their tests they observed increased adsorption of phenols in the presence of oxygen. This was attributed to the "oligomerization of these compounds through oxidative coupling reactions".

Vidic and Suidan (1991) studied the effect of dissolved oxygen on the adsorption of 5 synthetic organic compounds (o-cresol, phenol, o-chloro-pheonl, 3-ethylphenol. trichloroethylene) and NOM. They found that the presence of dissolved oxygen greatly increased the adsorption of four of the five synthetic compounds while one (trichloroethelyene) was not significantly affected due to the presence of dissolved oxygen. The increase in adsorption was attributed to polymerization of the contaminant in the presence of molecular oxygen. Thus, there was increased removal of the contaminant from solution.

Warta et al. (1995) conducted oxic and anoxic isotherms for NOM from Ohio River water and observed that the oxic isotherms had greater adsorption capacity than the anoxic (see Fig 2-16). The increase in adsorption capacity was attributed to polymerization of the contaminant on the GAC surface.

Karanfil et al. (1996b) also saw increases in adsorption capacity with an increase in molecular oxygen. In their work, six of the nine natural and synthetic macromolecular dissolved organic materials (DOMs) studied experienced an increase in the adsorption. The sensitivity to dissolved oxygen was observed to increase with; decreasing molecular size, polydispersity, aromaticity and with increasing acidity.

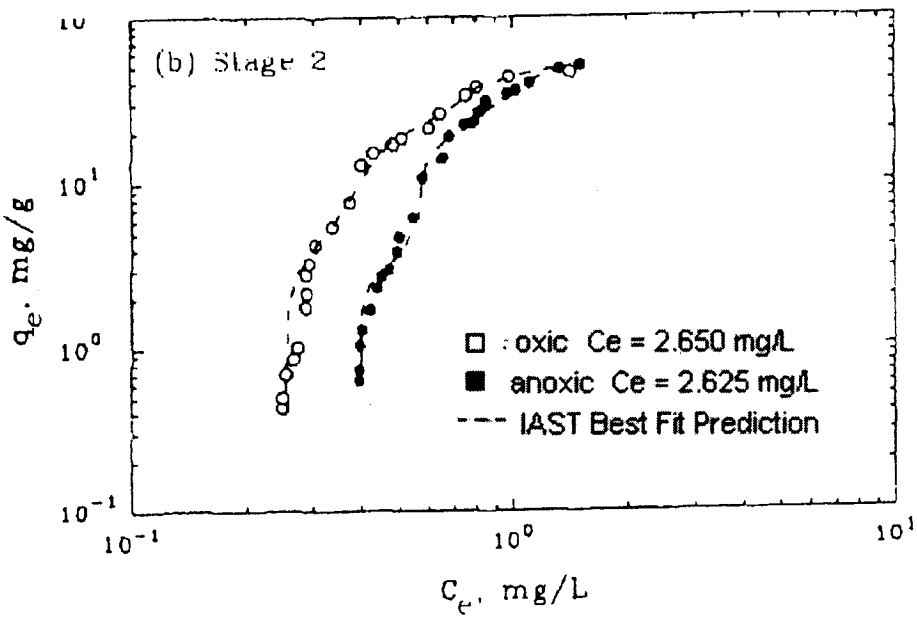

Figure 2-16 Adsorption Isotherms for Ohio river water as a source of NOM (Source: Warta et al., 1995)

Thus, the presence of dissolved oxygen can greatly enhance the GAC adsorption capacity for certain adsorbates, including NOM. Fortunately most surface waters used for drinking water treatment are highly oxygenated.

2.7.4 Effect of pH

The effect of pH is very important for the adsorption of contaminants that are capable of ionization (Faust and Aly, 1998; Cooney, 1999). Ionized forms of the contaminant are more soluble, therefore less adsorbable. Acidic species are ionized at high pH where as basic species are ionized at low pH (Cooney, 1999).

Murin and Snoeyink (1979) demonstrated that the adsorption capacity could be altered by altering the pH of the adsorption solution. They observed greater adsorption capacities in pH ranges that caused dichlorophenol and trichlorophenol to be in their unionized state as apposed to their anionic state.

McCreary and Snoeyink (1980) demonstrated that the fulvic acid adsorption capacity of F-400 increases with decreasing pH. They attributed the increase in adsorption to changes in the solubility of fulvic acid at higher pH. Figures 2-17 and 2-18 illustrate that acids adsorb higher at low pH and bases adsorb higher at high pH.

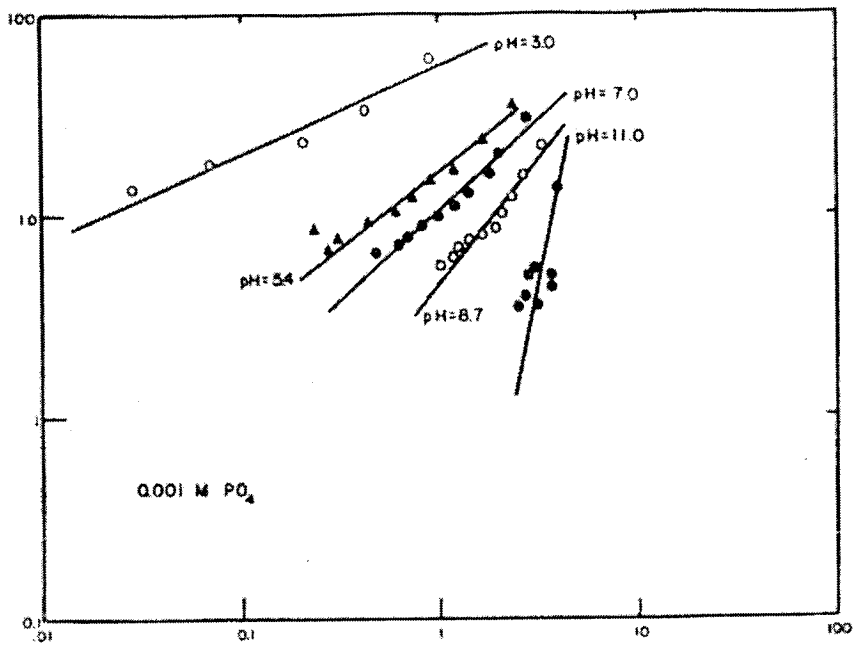

Figure 2-17 Effect of pH on the Adsorption of SFA on Activated Carbon (Source: McCreary and Snoeyink, 1980)

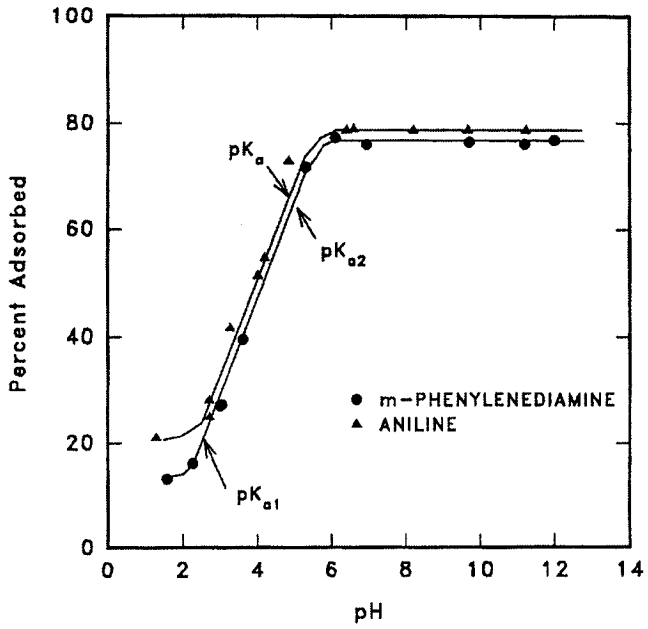

Figure 2-18 Variation of Adsorption with pH for Aromatic Bases (Source: Cooney and Wijaya, 1986)

Newcombe (1999) experienced a dramatic increase in adsorption by decreasing the pH of a NOM solution from 7 to 3. He attributed the increase in adsorption to a number of factors:

- the NOM becomes less negatively charged, resulting in a decrease in the lateral repulsion between adjacent adsorbed NOM molecules.
- there is an increase in positive charge on the AC surface; this decreases the surface-NOM repulsive interactions.
- the solubility of the NOM is decreased due to protonation (addition of H^+ ion) of the carboxyl groups; this increases the driving force for adsorption onto a hydrophobic AC surface.
- the size of the NOM molecule decreases, thus there is an increase in the pore volume available for adsorption.

At the lower pH < 3.5 the NOM macromolecules behave more like ridged spherical colloids where as at higher pH >3.5, the NOM macromolecules behave like flexible linear molecules (Summers and Roberts, 1987b). Thus, care must be taken to maintain a constant pH for adsorption experiments.

2.8 NOM Characterisation and NOM Adsorption

The removal of NOM became necessary due to recent concerns about health risks associated with disinfection by-products, especially trihalomethanes (THMs). The following discussion is a general overview of humic substances or NOM, its adsorptive capacity and its rate of adsorption. For a more in depth knowledge the

author invites the readers to review Aiken et al. (1985), Malcolm (1985, and Snoeyink (1990).

Aiken et al. (1985) defines humic substances as: "naturally occurring, biogenic, heterogeneous organic substance that can generally be characterised as ellow to black in colour, with a high molecular weight and refractory". These substances are present in all untreated water sources and are a result of biological degradation of organic matter on/in soil and water. These substances are divided into different fractions based on solubility. Fulvic acid (FA) is soluble in water at all pH conditions. Humic acid (HA) is not soluble in water below pH 2. Humin is not soluble in water at any pH, consequently it is not considered in water treatment applications.

Malcolm (1985) explained that stream humics are very different than those found in groundwater, soil, estuaries, or marine environments. The ratios of concentrations of FA to HA are 3:1 in soil and 9:1 in stream environments. Thus, commercial soil humics should be avoided when investigating surface water treatment application.

2.8.1 NOM Adsorption

Newcombe (1999) described the mechanisms of NOM adsorption as electrostatic or non-electrostatic. The electrostatic reactions occur between the negatively charged group on the NOM molecule and the positively charged group on the surface of the

GAC. He considered the non-electrostatic forces involved in adsorption to be van der Waals (London dispersion and dipole-dipole) and hydrogen bonding forces.

As discussed in Section 2.6.2 solubility plays an important role in GAC adsorption. Since humic substances are soluble above pH 2 they have relatively low adsorption capacities. Lee et al. (1981), Randtke and Snoeyink (1983), Karanfil et al. (1999) illustrate the relatively low adsorption capacities of humic substances.

NOM is composed of relatively large compounds (500-100,000 MW). These large compounds require greater time to enter the pores of the AC. Forsyth et al. (1982), Randtke and Snoeyink (1983), Koffskey and Lykins (1990), Moore et al. (2001) and Moore et al. (2003) are among the many researchers that illustrated the time required to reach equilibrium or to exhaust a GAC column. Randtke and Snoeyink (1983) demonstrated that for humic acid and mesh 16 GAC the equilibrium time was 44 months, while for peat fulvic acid and mesh 8 GAC the equilibrium time was 61 months. Moore et al. (2000) demonstrated in their full-scale GAC column adsorber experiments that the GAC continued to remove 20% of the influent TOC concentration after 7 months.

Many researchers (Murin and Snoeyink, 1979; Narbaitz and Benedek, 1984; Carter et al., 1992; Othman et al., 2000; Ebie et al., 2001; Graham et al., 2001) have investigated the impact of low concentrations of NOM on the AC adsorption capacity of other compounds. The majority have observed a decrease in adsorption

capacity of the target compound in the presence of NOM. This is illustrated by Fig 2-19, where the adsorption capacity is reduced in the NOM pre-loaded samples. The reduction in adsorption was attributed to competitive adsorption and pore blockages by the larger NOM molecules.

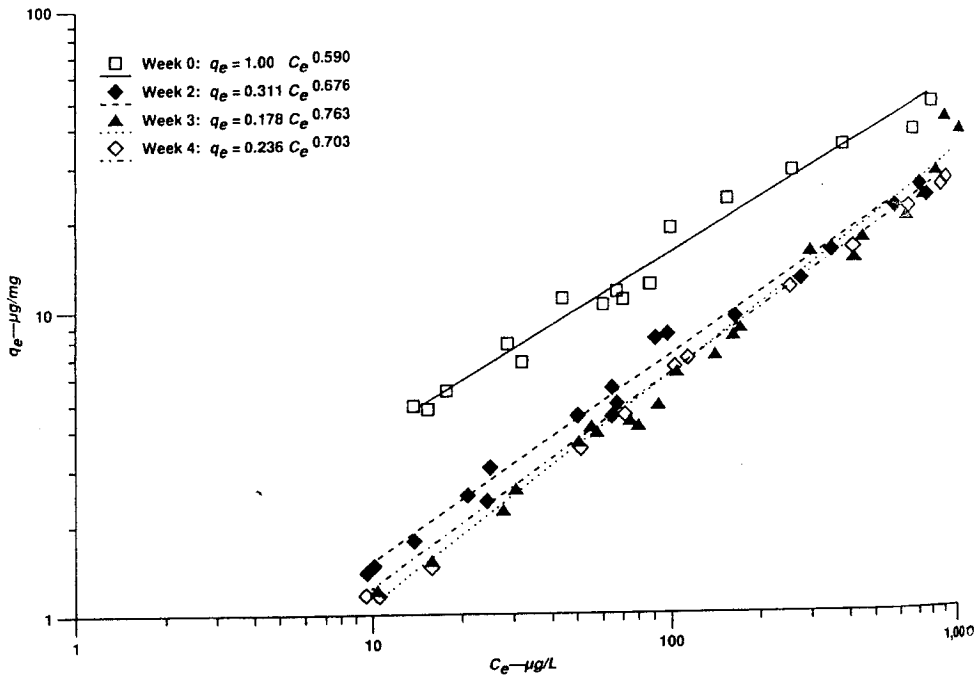

Figure 2-19 Comparison of the level of NOM Pre-loading on the TCE Adsorption Capacity (Source: Carter et al., 1992)

> In the application of activated carbon for surface water purification, the need to remove adsorbed humic substances will probably control the regeneration step even though the primary purpose in applying the activated carbon is to remove trace organic compounds (Snoeyink, 1990).

The key aspects of NOM adsorption are: smaller adsorption capacities than most synthetic organic compounds (SOCs); strong competition with SOCs; slow

adsorption rates, which result in very gradual column breakthrough that starts early in the column run; and irreversible or partially irreversible adsorption.

2.9 Regeneration Methods

To maintain sufficient organic removal in a GAC column system, exhausted GAC is replaced with virgin GAC or regenerated GAC. The next sections review the following GAC regeneration methods: thermal, chemical and electrochemical regeneration.

2.9.1 Thermal Regeneration

Thermal regeneration (the current industry standard) is a process that is derived from the original activation process. This process involves the use of heat to remove contaminants from the GAC. More specifically, thermal regeneration involves a four-step process of (1) drying of the GAC, (2) vaporization of the volatile adsorbates and decomposition of the unstable adsorbates to form volatile fragments, (3) the pyrolysis of the non-volatile adsorbates and adsorbed fragments, (4) followed by the oxidation/activation of the carbon char (Waer et al., 1992). After the oxidation process, regenerated adsorption capacities of 60-95% of the virgin AC have been achieved (San Miguel et al., 2001). The reported regeneration efficiency is highly dependent on the type of GAC and type of contaminant (San Miguel et al., 2001). San Miguel et al. (2001) showed greater regeneration efficiency (RE) for methylene blue (MB) than for phenol (71-99% and 55-85%, respectively). In this study regeneration efficiencies were determined via batch loading. MB has a larger

molecular size than phenol and the wider micropores favour removal of the larger molecule. Other researchers have shown thermal REs in excess of 95% (Moore et al., 2001). Differences in reported REs may have been due to the operational parameters (such as temperature, time and extent of oxidation) or the method of determining the regeneration efficiency. These methods include iodine number and target compound adsorption (column or batch-loaded). Thermal regeneration studies have characterized the regeneration with iodine number, apparent density, porosity, surface chemistry, and NOM column and batch adsorption capacity tests. (Chihara et al., 1982; Waer et al., 1992; Waer and Snoeyink, 1994; Moore et al., 2001; San Miguel et al., 2001; Lambert et al., 2002; Moore et al., 2003)

With thermal regeneration there is some loss of adsorption capacity. This was explained to be due to a loss in volume or mass (5-15%) caused by carbon burn-off (Knappe et al., 1992; and Moore et al., 2001). Therefore, to maintain the same empty bed contact time in the contactor, new AC must be added. It has not been shown that multiple thermal regeneration cycles adversely affect the NOM adsorption capacity to the point that the GAC would be unsuitable for adsorption. However, due to widening of the micropores, the regenerated GAC will adsorb differently than the virgin GAC (Moore et al., 2001). Larger compounds may adsorb more readily while smaller compounds will adsorb to a lesser degree.

On-site thermal regeneration facilities require a large amount of GAC (680 kg/d GAC) use to be affordable (Clark and Lykins, 1989). Therefore small drinking water

treatment plants need to replace spent GAC with virgin GAC or ship the spent GAC off site for regeneration. The mass losses due to shipping would increase the amount of virgin GAC required as make up carbon, consequently increasing the operational costs. While thermal regeneration is an effective method of treatment, it is associated with GAC mass and volume losses in the order of 5 to 15%, which provide an incentive for research into alternative forms of regeneration.

2.9.2 Chemical Regeneration

Chemical regeneration involves the use of solvents to remove contaminants from the surface of GAC. The solvents can be steam, organic solvents (such as, methanol), inorganic acids and bases (such as, 0.1 M NaOH) or supercritical CO_2. The process involves using a solvent to desorb the contaminant from the surface of the GAC due to an increase in solubility (Leng and Pinto, 1996) or through competitive adsorption (Martin and Ng, 1987) resulting in increases in the concentration of the contaminant within the regeneration solution. This concentrated contaminant solution could then be recycled or be treated for disposal.

Martin and Ng (1987) studied the use of organic reagents for the regeneration of GAC loaded with nitrobenzene, Rhodamine B, and humic acid in bench-scale column experiments. They were able to attain REs of 91% for nitrobenzene. The high regeneration was attributed to the lower molecular weight compounds of the regeneration solution displacing the higher molecular weight contaminants. Very low REs (<40%) were attained with organic solvents (acetone, ethanol, chloroform

and dichloromethane) for NOM loaded GAC, while very high REs (>150%) were attained with organic acids (formic acid and acetic acid). The drawback of this chemical regeneration method was that the chemical reagent had to be removed from the GAC before reloading. Martin and Ng (1987) found they required a boiling water rinse cycle for the leaching to be effective. Thus, the by-product of each regeneration cycle was an additional waste stream requiring treatment. This process would be unsuitable for drinking water applications due to the risk of the regenerating solution leaching into the treated water.

Leng and Pinto (1996) investigated the mechanisms of chemical regeneration of AC loaded with physically adsorbed organics (phenol, aniline, benzoic acid, and nitrobenzene). They attempted to increase the solubility of the adsorbate through the use of different pH regenerants (NaOH, HCl , acetic acid and formic acid), addition of micellar solutions, and reactive regenerants (NaOH, HCl and formic acid) that produce soluble products. They noted that in some cases the pH altering regenerants reacted with the adsorbate which may increase the regeneration of the GAC (see Table 2-1). In those cases the regenerant was considered to be a reactive regenerant and not a pH altering regenerant. The REs of the pH altering regenerants, the micellar solutions and the reactive regenerants were 10-75%, 1-66%, and 70-99%, respectively. They compared these results with the REs of water (0.15-6.2%) to demonstrate that generating soluble forms of the adsorbate enhanced the RE. The equilibrium concentrations were determined with UV absorption. Since all the regenerants had high UV adsorption the equilibrium concentration was determined

with methanol extraction of the contaminant from the regenerated AC. The REs were determined through a three step process: 1) adsorption of organic compounds onto AC; 2) regeneration with selected regenerant; 3) organic extraction from AC with methanol. The RE was comparison of the concentration of methanol extracted without regeneration to the concentration attained after regeneration. They attributed the regeneration to the solubility of the adsorbate in the regenerant solution, the relative adsorption capacity and the charge characteristics of the adsorbent surface.

Table 2-1 Summary of Regenerant and Adsorbate Reactions (source: Leng and Pinto, 1996)

NaOH	$C_6H_5OH + NaOH \Rightarrow C_6H_5O^-Na^+ + H_2O$
	$C_6H_5COOH + NaOH \Rightarrow C_6H_5COO^-Na^+ + H_2O$
	$C_6H_5NH_2 + NaOH \Rightarrow no\_reaction$
	$C_6H_5NO_2 + NaOH \Rightarrow no\_reaction$
HCl	$C_6H_5OH + HCl \Rightarrow no\_reaction$
	$C_6H_5COOH + HCl \Rightarrow no\_reaction$
	$C_6H_5NH_2 + HCl \Rightarrow C_6H_5NH_3^+$
	$C_6H_5NO_2 + HCl \Rightarrow no\_reaction$
HCOOH	$C_6H_5OH + HCOOH \Rightarrow C_6H_5OH_2^+$
	$C_6H_5COOH + HCOOH \Rightarrow no\_reaction$
	$C_6H_5NH_2 + HCOOH \Rightarrow C_6H_5NH_3^+$
	$C_6H_5NO_2 + HCOOH \Rightarrow no\_reaction$

Salvador and Sanchez-Jimerez (1999) demonstrated the effective use of high pressure and temperature water for the regeneration of phenol and azo dye loaded GAC. The contaminants were soluble in high-pressure high-temperature water and they were concentrated in the wash. This method was non-destructive and was useful for contaminant recovery processes. The criteria for determining the RE is not presented. Based on their breakthrough curves they claimed very high REs for the regenerated GAC, although no specific values were presented. They also concluded that high temperature and pressure water regeneration does not significantly alter the textural characteristics based on their analysis of the virgin and regenerated GAC's BET surface areas and apparent densities.

Mourand et al. (1995) investigated the use of H_2O_2/O_3 regeneration for GAC column-loaded with TCE (trichloroethylene). The effectiveness of the regeneration method was evaluated based on the contaminant destruction efficiency:

$$Destruction\_Efficiency = \frac{Cl_M}{Cl_{Stoc}} \times 100 \qquad (2.7)$$

Where Cl_M is the mass of chloride measured in the experiment

Cl_{Stoc} is the mass of chloride calculated from the Stoichiometry

F-400 GAC was loaded with TCE to a solid phase concentration of 72.5 mg/g of GAC. After TCE-loading, the GAC was regenerated with hydrogen peroxide and ozone for 6 days. The concentration of effluent from the regeneration step was monitored over time. They observed REs of approximately 48%. The GAC was not reloaded to determine the regenerated adsorption capacity. Their data suggested that

the regeneration was not limited by the reaction kinetics, rather they were limited by the slow rate of desorption. They found that the low REs obtained did not justify the reagent cost.

Supercritical CO_2 regeneration is another form of chemical regeneration that utilizes enhanced solubility for the removal of contaminants from the surface of AC (Tan and Liou, 1988; Madras et al., 1993; and Chihara et al., 1997). Supercritical CO_2 GAC regeneration has lower mass losses than thermal regeneration and does not have the drawback of an additional waste stream attributed to other chemical regeneration methods. Tan and Liou (1988) indicate a RE of 87% for GAC loaded with ethyl acetate at optimal parameters. Madras et al. (1993) determined the efficiency of the regeneration from the adsorption/desorption isotherms, however the values for RE are not reported. The literature on supercritical CO_2 regeneration focuses on volatile organic contaminants such as, phenol, benzene, naphthalene, ethyl acetate, and toluene that are not strongly adsorbed by activated carbon (Tan and Liou, 1988; Tan and Liou, 1990; Madras et al., 1993; and Chihara et al., 1997).

The chemical regeneration methods discussed in this section focused mainly on the regeneration of GAC for industrial or synthetic contaminants. They may not be suitable for strongly adsorbed NOM. The relatively low REs and the risk of solvent leaching into the treated drinking water make chemical GAC regeneration unsuitable for water treatment applications.

2.9.3 Electrochemical Regeneration

2.9.3.1 Electrochemical Treatment of Aqueous Wastes

Research into the electrochemical treatment of aqueous waste, where an electric current is used to oxidize a contaminant in an electrolyte solution (Gattrell and Kirk, 1990; Gattrell and Kirk, 1993), was utilized as an inspiration by Narbaitz and Cen (1994); and Karimi-Jashni (2001) in their research into electrochemical regeneration of GAC. Electrochemical regeneration applies the use of the electric current to contaminant loaded (spent) GAC in an electrolyte solution to remove adsorbed contaminants.

Gattell and Kirk (1993); Chiang et al. (1995); and Panizza et al. (2000) demonstrated that platinum electrodes are an effective electrode material for the electrochemical destruction of organic wastes. Carbon electrodes have also been studied for organic electrochemical destruction. Carbon electrodes provide a high surface area to increase contact with the contaminant solution. Gattrell and Kirk (1990) and Canizares et al. (1999) demonstrated that, with increasing electrolyte temperature, carbon electrodes could effectively oxidize organic contaminants (see Fig 2-20).

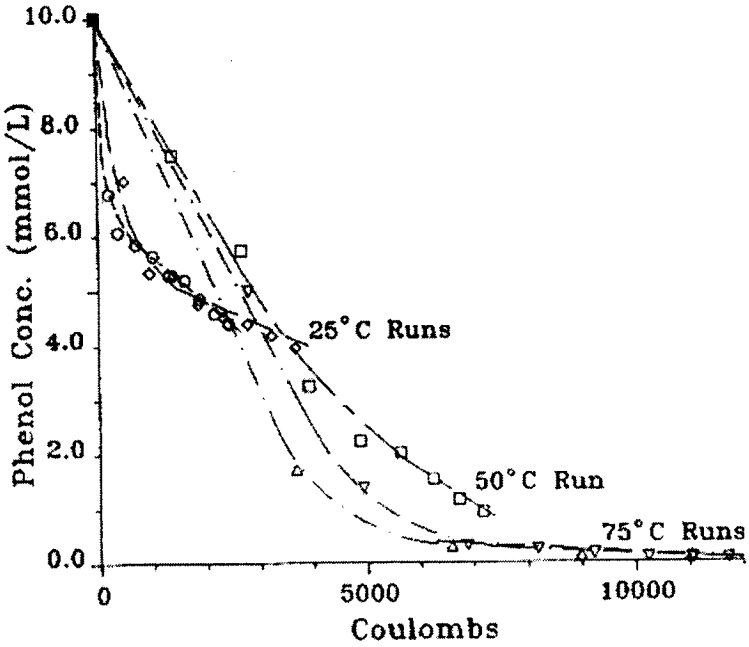

Figure 2-20 Effect of Temperature on Phenol Concentration versus Charge Employed For Carbon Electrodes (Source: Gattrell and Kirk, 1990)

Organic destruction was thought to occur at the electrode due to adsorbed hydroxide radicals $OH^{\bullet}$. The adsorbed $OH^{\bullet}$ provides an oxidation pathway at the electrode (Canizares et al., 1999).

$$M(OH^{\bullet}) + R \rightarrow mCO_2 + nH_2O + M \qquad (2.8)$$

Where R is the contaminant

M is the Metal

m is the moles of CO_2

and n is the moles of H_2O

To improve the organic destruction metal oxide electrodes (PbO_2, SnO_2, PtO_2, and tertiary oxide Sn, Pd, Ru (SPR) coated titanium) were used to promote the formation

of adsorbed hydroxide radicals ($OH^{\bullet}$) on the electrode surface. Inista et al. (2001) demonstrated the effectiveness of bismuth doped PbO_2 and pure PbO_2 anodes and attributed the organic destruction to the adsorbed $OH^{\bullet}$. Chiang et al. (2000) demonstrate the comparable contaminant destruction of humic acid with the SPR electrode (see Fig 2-21).

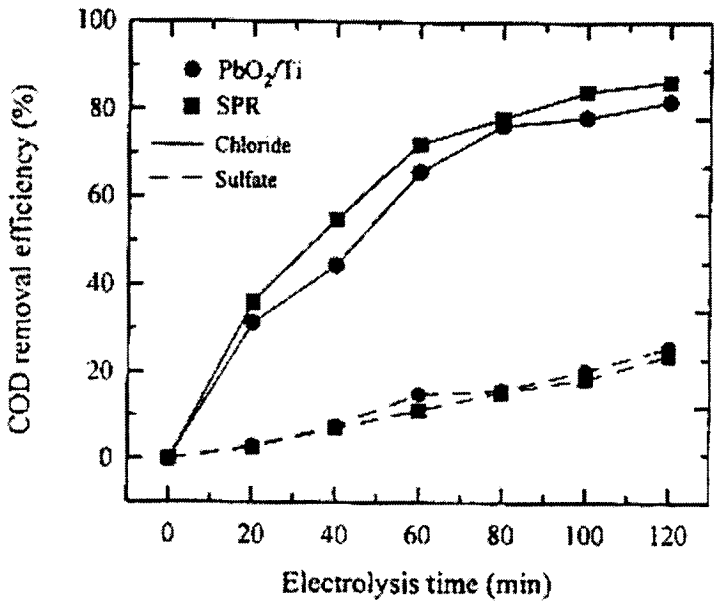

Figure 2-21 Electrochemical Oxidation of Humic Acid with PbO2/Ti and SPR Electrodes at 7.5 amp/dm^2 (Source: Chiang et al., 2000)

Chiang et al. (1995), Chiang et al. (2000), Panizza et al. (2000), and Inista et al. (2001) investigated the effect of the electrolyte on the electrochemical oxidation of organic contaminants. Chiang et al. (1995) and Inista et al. (2001) demonstrated enhanced oxidation of organic contaminants due to the presence of Cl^- ions (see Fig 2-22) particularly at low values of Q.

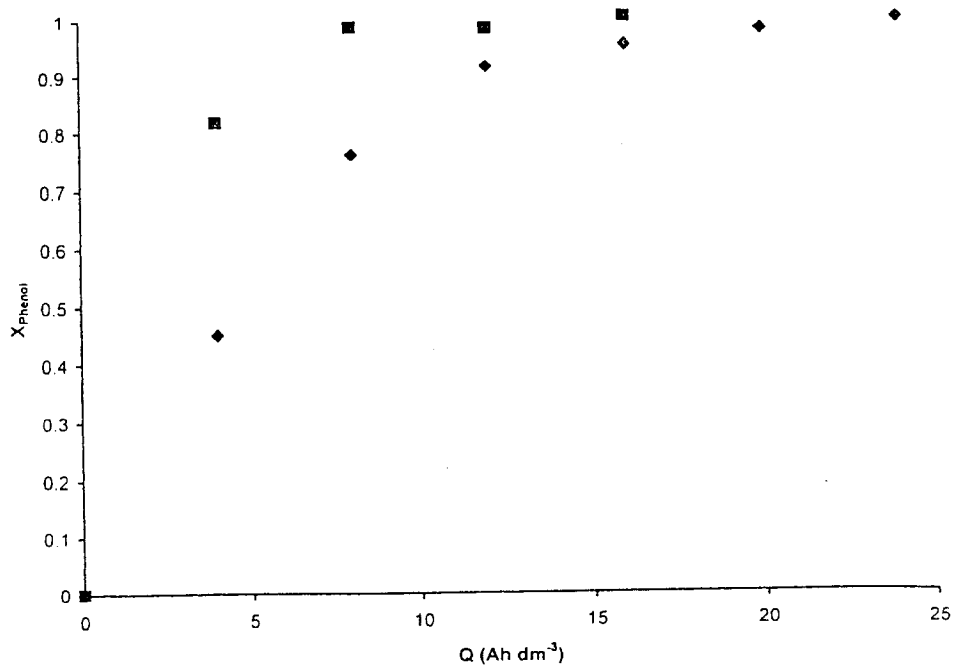

Figure 2-22 Fractional Conversion of Phenol (X_{phenol}) verses Charge Passed (Q) as a function of Chloride Concentration. Ti/$Pb0_2$ electrode ( ) absence of NaCl: (■) NaCl =0.5 M, pH 12.0 (Source Inista et al., 2001)

Chiang et al. (2000) and Panizza et al. (2000) demonstrate that indirect oxidation by chlorine/hypochlorite is more effective than by direct anodic oxidation. In the case of indirect oxidation free radicals are produced at the anode. These radicals oxidize the desorbed contaminants to CO_2 and water. Hydroxide radicals can be produced at the anode through the following reactions (Drogui et al., 2001; Pelegrino et al., 2002)

$$2H_2O \rightarrow 2OH^{\bullet} + 2H^{+} + 2e^{-} \tag{2.9}$$

$$OH^{-} \rightarrow OH^{\bullet} + e^{-} \tag{2.10}$$

When the electrolyte contains Cl^- ions (e.g. NaCl), Cl_2 gas is evolved at the anode which produces hypochlorite by the following processes.

$$2Cl^{-} - 2e^{-} \rightarrow Cl_2(g) \tag{2.11}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^{+} + Cl^{-} \tag{2.12}$$

$$HOCl \rightarrow H^{+} + OCl^{-} \quad (2.13)$$

The hypochlorite oxidizes the contaminant by the following pathway.

$$OCl^{-} + R \rightarrow CO_2 + Cl^{-} \quad (2.14)$$

Chlorine oxidation has also been proven to produce DBPs such as THMs (Glaze, 1990), which may limit the use of chlorine containing electrolytes. The effectiveness of electrochemical destruction of organic pollutants was demonstrated by Gattrell and Kirk (1990), Gattrell and Kirk (1993), Chiang et al. (1995), Panizza et al. (2000), Iniesta et al. (2001), and Canizares et al. (1999). These studies investigated the effect of electrode materials and electrolyte on the electrochemical destruction of various organic pollutants. The references discussed in this section all have involved the use of anodic destruction of organics. Karmini-Jashni (2001) demonstrated that some destruction of phenol could also be achieved with cathodic treatment, although the destruction requires more time or higher currents than anodic treatment.

2.9.3.2 Electrochemical Regeneration

Willis (1971), Owen and Barry (1972), Sveshnikova et al. (1987), Khabalov et al. (1989), Lavareva et al. (1991), Narbaitz and Cen (1994), Cooper et al. (1999), Karimi-Jashni (2001), Zhang (2002), and Zhang et al. (2002) among others who researched electrochemical regeneration of AC. By passing a current through an electrolyte solution with GAC placed on the electrode they were able to regenerate the GAC.

Willis (1971) studied the electrochemical regeneration of carbon slabs (Graphite 39, 18, and 260, Union Carbide and Catalogue No. 52306) loaded with dieldrin. He used anodic treatment (i.e. AC in contact with the anode) in the presence of 20% hydrochloric acid and the current densities ranged from 0 to 125 mA/cm^2. The current was held constant for five minutes, after which the samples were subjected to cathodic treatment (AC in contact with the cathode) at a current density of 38 mA/cm^2 for one minute to desorb the adsorbed chlorine. He reported that the adsorption capacity for treated AC that was 10% greater than the adsorption capacity for virgin GAC.

Slavinskii et al. (1984) investigated the effect of electrochemical regeneration of the adsorption capacities of AG-3 GAC loaded with p-nitrotoluene. The bench scale electrochemical reactor consisted of a steel shell cathode and a graphite rod anode what was inserted in the center. A perforated polycaprolactum liner was used to prevent direct contact between the steel anode and the GAC. The electrolyte was a sodium chloride solution. They were able to achieve adsorption capacities equal to 97.4% of the virgin GAC at optimum operating conditions ($30A/m^2$, 0.2 M NaCl, and 30 min). Sveshinikova et al. (1987) utilized phenol-loaded AC to investigate the effect of current and time on the RE. They were able to recover 70% of the adsorption capacities for BAU GAC. This remained constant after multiple regeneration cycles. Lauareva et al. (1991) evaluated the effect of repeated regeneration cycles on the adsorption capacities of microporous carbon loaded with

dyes. They concluded that the REs varied depending on the cell voltage and the nature of the adsorbate. They attained adsorption capacities of 75% of the virgin AC.

Narbaitz and Cen (1994) used a simple batch reactor with platinum plate electrodes. They investigated the effect of current, time and electrolyte type on the regeneration efficiency of phenol loaded GAC. They observed that the RE increased with time and current (see Fig 2-23) and that the REs were higher with NaCl electrolyte as apposed to the other electrolytes tested ($NaHCO_3$, $NaSO_4$, and CH_3COONa). They compared the REs of operating the reactor with the GAC on the cathode vs. on the anode. They observed that cathodic regeneration had higher REs than anodic regeneration. Using cathodic regeneration they were able to achieve REs of 93 to 95%. In these experiments there was no apparent loss of activated carbon mass with each regeneration cycle. Zhang (2002) and Zhang et al. (2002) confirmed the findings of Narbaitz and Cen (1994) through similar experiments.

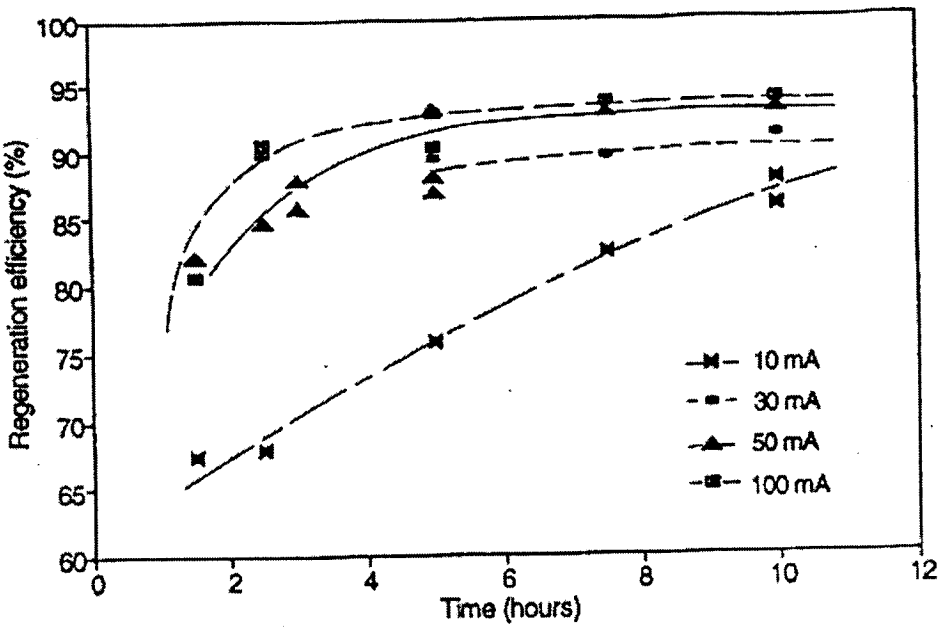

Figure 2-23 Effect of Current on Regeneration of Phenol-Loaded F-400 GAC (Source: Narbaitz and Cen, 1994)

Clifford et al. (1999) developed a patent for the regeneration of AC and other polymeric adsorbents. They developed an electrochemical reactor that treated industrial waste, such as phenol.

Karimi-Jashni (2001) compared cathodic (GAC placed on the cathode) vs. anodic (GAC placed on the anode) regeneration, using three reactor set-ups (batch, column, and divided cell), and for three ACs with phenol and 2-nitrophenol. He also conducted a limited number of tests with NOM-loaded GAC.

His comparison of anodic regeneration vs. cathodic regeneration also demonstrated that cathodic regeneration was more effective than anodic regeneration. He proved

that the greater regeneration in the cathode compartment was attributed to the higher pH in the cathode compartment compared to the anodic compartment. The high pH is produced at the cathode due to the electrochemical splitting of water (H_20) into H_2 and OH^- by the following process.

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \qquad (2.15)$$

The build up of OH^- ions close to the electrode increases the local pH. This local increase in pH, which caused a shift in the solubility of the adsorbed organics resulting in contaminant desorption from the GAC. Along with this pH enhances desorption, desorption was also attributed to an increased in the surface charge of the GAC. The surface charge was increased due to direct contact with the electrode.

The reactor setups investigated by Karimi-Jashni (2001) included the simple batch reactor used in Narbatiz and Cen (1994) (described above) plus two others. The second reactor was a column reactor consisting of a stainless steel cylindrical shell acting as the cathode with a stainless steel rod anode which was inserted into the center of the column. The third system was a divided cell reactor which consisted of two compartments with platinum wire mesh electrodes separated by an ion exchange membrane. Karimi-Jashni (2001) demonstrated that the divided cell reactor with cathodic regeneration had superior GAC regeneration efficiencies. The cation exchange membrane prevented the hydroxyl ions produced at the cathode from entering the anodic compartment, resulting in an increase in the pH in the cathodic compartment. This increase in pH aided in the contaminant desorption from the AC, providing greater REs than the undivided reactor. With the use of a divided cell

reactor a separate step was required for contaminant destruction. After removing the ion exchange membrane the contaminant in the electrolyte was oxidized at the anode (direct oxidation) and/or in the bulk (indirect oxidation) solution with further electrochemical treatment.

Karimi-Jashni (2001) investigated the RE of phenol and nitro-phenol loaded on three different GAC types. He found that the RE was dependent of the contaminant and the GAC type.

Karimi-Jashni (2001) performed limited experiments with NOM-loaded GAC at the Britannia Water Treatment Pilot Plant, located in Ottawa, ON. His experiments used iodine number analysis to determine the regeneration efficiency. He showed that the iodine number regeneration efficiency ranged from 70 to 75% as the current was increased from 10 to 200 mA. This implied that electrochemical regeneration was able to desorb NOM from the spent GAC.

The added benefit of contaminant destruction makes electrochemical regeneration an attractive option. Karimi-Jashni (2001) researched the effect of reactor configuration, adsorbate, adsorbent, and operating conditions on the RE of GAC. A number of conclusions of the study were:

- RE was contaminant dependent due to the reversible/irreversible nature of the adsorption.
- RE increased with increasing current or time.

- High pH is critical to the regeneration of phenolics-loaded GAC, pH induced desorption accounts for 60% of the RE.
- GACs with lower electrical resistance showed greater RE.
- Total electrochemical destruction of contaminants to CO_2 and H_2O was possible
- Electrochemical regeneration was shown to be feasible with RE up to 108% for nitro-phenol loaded GAC.

Given that drinking water treatment is such an important application for GAC, and that electrochemical reactivation is in it infancy, this is an avenue that is ripe for research. Further areas of research include direct comparison between thermal and electrochemical regeneration, investigation of the effect of current on NOM adsorption capacity, surface chemistry, porosity, and surface area.

2.10 Regeneration Efficiency

AC regeneration studies can be directly compared only if they have similar methods for determining or characterizing the RE. The main methods for determining the RE are iodine number, apparent density, column aqueous adsorption tests and batch aqueous adsorption tests.

2.10.1 Iodine Number and Apparent Density

Iodine number and apparent density are two measures of RE used by the water treatment industry for monitoring thermal regeneration. Iodine number is a quick test

(contact time 30 s) that can act as an indicator of the surface area of the GAC. An iodine solution is added to three flasks containing three different masses of powdered GAC. The equilibrium concentration of the iodine solution is determined by titration and an isotherm is developed. The iodine number is the mass of iodine adsorbed by the GAC at the filtrate residual of 0.02N (for more information, see ASTM 4607, 1995). A large iodine number indicates large surface area (i.e. large adsorption capacity). Comparing the regenerated AC iodine number with the virgin AC iodine number provides the RE. The iodine number for virgin GAC is generally greater than 900 mg/g.

The apparent density can also be a very quick test. The apparent density is obtained by weighing the mass of GAC that will fill a 100 mL container. The apparent density is also an estimate of the bed density of the GAC. The bed density is required for purchase estimates of GAC required to fill an adsorption contactor. Waer et al. (1992) found that the apparent density was a good operational check for the RE of thermally reactivated GAC.

2.10.2 Column Loading- Breakthrough Curves

Small scale column loading is used to predict the adsorption loadings experienced in full-scale operations. In column loading AC is loaded by passing the adsorbate solution through a column of GAC. The outlet concentration is monitored as the adsorbate passes through the column. The solid phase contaminant concentration adsorption capacity is derived from a plot of the inlet and outlet concentrations with

time; it is the shaded area in Fig 2-24 divided by the mass of GAC in the column calculated by equation 2.17.

$$q_e = \frac{\int_0^{\infty} Q(C_o - C)dt}{M} \tag{2.16}$$

Where Q = Flow rate of influent (L/min)

M = Mass of GAC (g)

C_0 = Inlet concentration (mg/L)

C = Effluent concentration (mg/L)

Many researchers have used column loading to illustrate the effect of the regeneration method on adsorption (Cooney et al., 1983; Moore et al., 2001; Parette et al., 2001; Matatov-Meytal and Sheintuch, 2000; and Berčič et al., 1996).

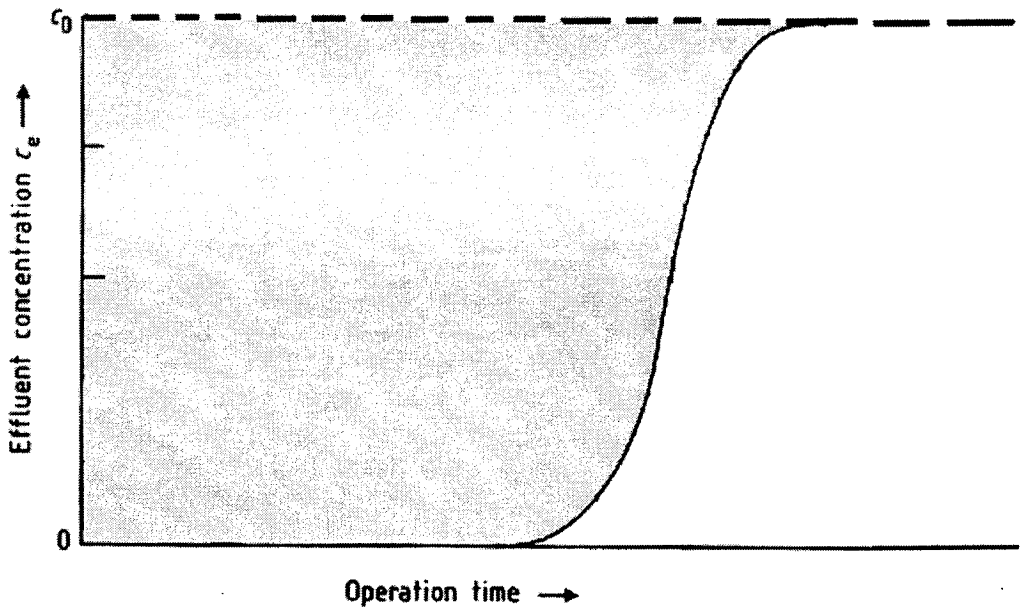

Figure 2-24 Breakthrough Curve for Target contaminant

In full-scale adsorption operations the column of GAC is exposed to a constant

supply of adsorbate solution. However, NOM is a heterogeneous mixture of organics. There is a fraction that adsorbs strongly, another that adsorbs less strongly and another that may not adsorb at all (non-adsorbable) (Newcombe et al., 1997; McCreary and Snoeyink, 1980; Lee et al., 1981; Summers and Roberts, 1988; Kilduff et al., 1996a; and Kilduff et al., 1996b). The strongly adsorbed fraction is adsorbed by the top layers of the bed, while the other fractions are adsorbed further down in the bed or emitted as an immediate breakthrough concentration. As time progresses the stronger adsorbing fraction displaces the weaker adsorbing fractions. This is seen in a typical NOM breakthrough curve (Fig 2-25); NOM (measured as TOC) breaks through almost immediately and the NOM column bed outlet concentration increases. Eventually the outlet concentration will equal the inlet concentration and then the carbon bed will be exhausted.

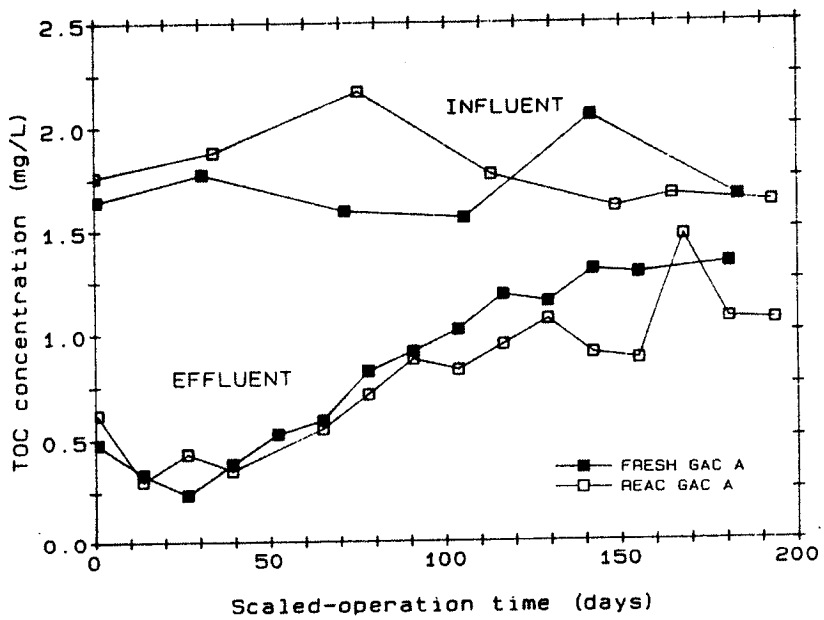

Figure 2-25 NOM Breakthrough Curve (Source: Summers et al., 1992)

The RE is calculated as:

$$RE = \frac{q_r}{q_v} \times 100\% \qquad (2.17)$$

Where q_r is the solid phase adsorbate concentration calculated from the area above the breakthrough curve and below the influent concentration curve for the regenerated GAC (mg/g) (see shaded area in Fig 2-24)

q_v is the solid phase adsorbate concentration calculated from area above breakthrough curve and below the influent concentration curve for the virgin GAC (mg/g) (see shaded area in Fig 2-24)

The benefit of using column loading to evaluate the RE is clear; the AC is saturated to the same extent and fashion as the full-scale operation. In addition bottle point isotherm and kinetic experiments are not necessary to estimate the full-scale performance (Summers et al., 1995). The drawbacks of the column loading approach include the large number of samples that must be analysed during the breakthrough, the long time required for the entire breakthrough curve to occur, the large amount of GAC required to properly scale up the column and the large amount of adsorbate solution required.

2.10.3 Batch-Loading: Bottle-Point Method

This approach uses the bottle-point loading method (discussed in section 2.2) to load the GAC prior and after regeneration to evaluate the RE.

Narbaitz and Cen (1994), and Karmini-Jashni (2001) were among the many researchers to use batch bottle loading to evaluate the RE of their regeneration

methods. Narbaitz and Cen (1997) re-examined the RE calculations of Narbaitz and Cen (1994) because of the surprisingly high values of the control experiments. They compared four different mathematical methods to determine the correct method of calculating the RE using batch-loading of the virgin GAC and batch-loading of the regenerated GAC. They were:

Method 1

$$RE1 = \frac{q_{ee}}{q_{e1}} = \frac{K_{REG} C_{e1}^{1/n_{REG}}}{K C_{e1}^{1/n}} \tag{2.18}$$

where q_{ee} = the adsorption capacity of the regenerated GAC at equilibrium at the liquid phase concentration achieved during initial loading (mg/g)

q_{e1} = the adsorption capacity of the virgin GAC at equilibrium at the liquid phase concentration achieved during the initial loading (mg/g)

K_{REG} = Freundlich isotherm constant for the regenerated GAC (L/g)

$1/n_{REG}$ = Freundlich isotherm constant for the regenerated GAC

K = Freundlich isotherm constant for the virgin GAC (L/g)

1/n = Freundlich isotherm constant for the virgin GAC

C_{e1} = equilibrium concentration achieved during the initial loading (mg/L)

Method 2

$$RE2 = \frac{q_{e2}}{q_{e1}} \frac{[C_{O2} - C_{e2}]V / M}{q_{e1}} \tag{2.19}$$

where V = the volume of adsorbate solution during the reloading step (L)

M = the mass of GAC during the reloading step (g)

C_{O2} = the initial contaminant concentration in the reloading step (mg/L)

C_{e2} = the equilibrium contaminant concentration after the reloading step (mg/L)

q_{e1} = the virgin adsorption capacity at C_{e1} (mg/g)

q_{e2} = the adsorption capacity of the regenerated GAC at the equilibrium liquid-phase concentration achieved during the reloading step (mg/g)

Method 3

$$RE3 = \frac{q_{e2}}{q_{e11}} = \frac{[C_{o2} - C_{e2}]V / M}{KC_{e2}^{1/n}} \tag{2.20}$$

Where V, M, C_{o2} , C_{e2}, K and 1/n are described above

q_{e11} = the adsorption capacity of the virgin GAC at the equilibrium liquid-phase concentration achieved during the reloading step (mg/g)

Method 4

$$RE4 = \frac{q_{e1} + \Delta q_2 - KC_{e2}^{1/n}}{q_{e1}} \tag{2.21}$$

where q_{e1} C_{e2}, K and 1/n are defined above

$$\Delta q_2 = \frac{V}{M}(C_{o2} - C_{e2})$$

where V, M, C_{o2} and C_{e2} are as previously defined.

Method 1 is the most accurate measure of the RE but requires that an adsorption isotherm be produced for each regeneration condition (i.e. RE = q_{ee}/q_{e1}). Method 2 compares the adsorption capacity at two different liquid equilibrium concentrations (i.e. C_{e2} and C_{e1}, RE=q_{eR3}/q_{e1}). Method 4 was derived for cases where no regeneration occurs because alternative methods yield unrealistically high REs. Method 3 is analogous to method 1 because the virgin and regenerated adsorption capacities are calculated with the same liquid equilibrium concentration (see Fig. 2-26) So it represents a comparison on an equal basis and it has the added advantage of requiring less experimental effort, i.e. a single reloading test is required instead of a full set of isotherms for each test condition. Narbaitz and Cen (1997) showed that Method 3 yielded similar values to Method 1.

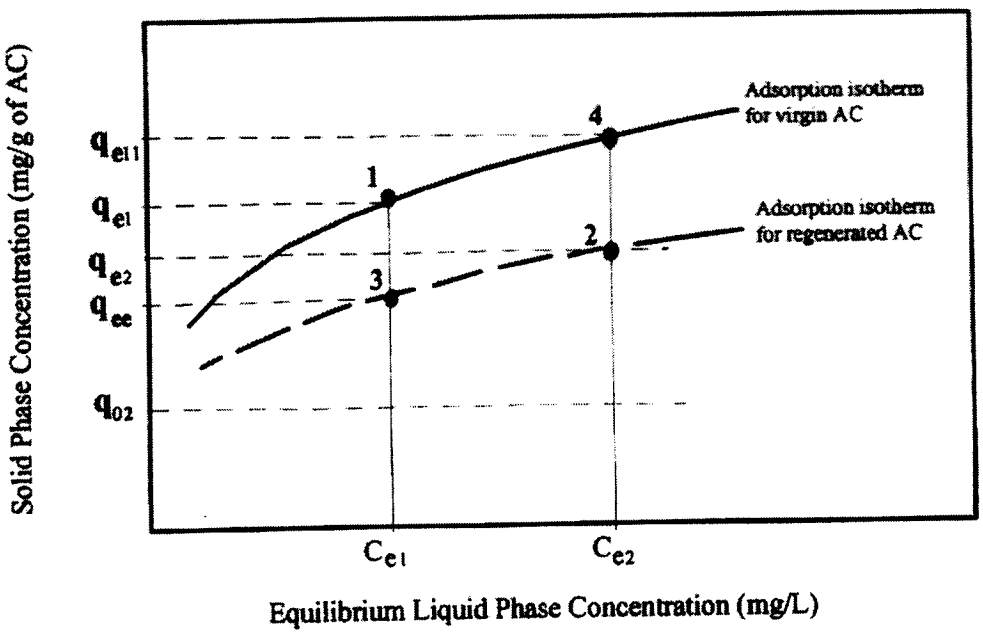

Figure 2-26 Adsorption Isotherms for Virgin and Regnerated GAC (Source: Narbaitz and Cen, 1994)

The benefits of using bottle batch loading are that the method does not require large masses of GAC or large volumes of adsorbate solution to evaluate the RE. The drawback is that the tests do not give direct estimates of GAC column performance.

2.11 Summary

Thermal GAC regeneration provides high REs with a number of drawbacks, which include 10-15% mass/volume loss, increase in pore sizes, transfer of contaminant to the gas phase, and high energy. Chemical GAC regeneration avoids GAC mass losses and provides significant, but lower REs for industrial applications and it is not suitable for the drinking water industry. Electrochemical regeneration has demonstrated significant REs for phenol and nitrophenol loaded GAC with no apparent mass losses. There has been limited work performed on electrochemical GAC regeneration with water treatment applications. There are a number of areas that require further study, they include:

- Confirmation of the REs observed by Karmini-Jashni (2001) for NOM-loaded GAC
- Direct comparison with thermal regeneration (Iodine number, NOM adsorption)
- Effect of electrochemical regeneration on surface chemistry
- Effect of electrochemical regeneration on surface area and pore size distribution

The above questions are the main focus for the following research chapters.

3 Materials and Methods

3.1 Introduction

This chapter discusses the different materials used in this study, the preliminary experiments (adsorption isotherms, adsorption kinetics, desorption kinetics), the electrochemical regeneration method, the evaluation of the regeneration efficiency (NOM reloading, iodine number, surface chemistry, surface area and pore size distribution) and the experimental plan.

3.1.1 Adsorbents

This work is focused on the effect of electrochemical regeneration of NOM loaded GAC. Virgin, thermal regenerated, and field spent GAC was obtained from the Buffalo Pound Water Treatment Plant, Regina, Sask. *(denoted as virgin, thermal, and field spent Regina GAC)* and The Richard Miller Water Treatment Plant, Cincinnati OH *(denoted as virgin, thermal, and field spent Cincinnati GAC)*. Regina utilizes Calgon F-400 GAC and/or Norit 830 GAC while the Richard Miller Water Treatment Plant uses Jacobi Brand GAC in their adsorption columns. The AC filter beds are located down stream of the mixed media filtration units for both water treatment plants. See Table 3-1 for the characteristics of the AC used in this work.

Table 3-1 GAC Characteristics

Reported Parameter	Jacobi Aquasorb 400	Calgon F-400	Norit GAC 830
Iodine No. (mg/g)	1045	1050	920
Moisture Content (%)	0.9	0.9	2
Ash content (%)	7.1	-	-
Volatile Content (%)	2.4	-	-
Water Soluble Matter (%)	0.1	-	-
Apparent Density (g/L)	481	-	510
Abrasion No. (%)	86	78	75

3.1.2 Adsorbates

In this work the REs of electrochemical and thermal methods were investigated and compared using field spent GAC from the above water treatment plants (i.e. NOM-loaded). The adsorbate was water obtained after mixed media filtration (pre-GAC) obtained from the Buffalo Pound Water Treatment Plant, Regina (denoted as Regina water) and from the Richard Miller Water Treatment Plant, Cincinnati (denoted as Cincinnati water). These pre-GAC waters had TOC concentrations of 3.5 and 1.5 mg/L, respectively. These waters had undergone coagulation, flocculation, sedimentation and filtration, which remove 20-50% of the TOC (depending on the alkalinity) (Faust and Aly, 1998). These processes generally remove primarily the higher molecular weight and less soluble fractions of NOM. The waters were shipped from the source in polyethylene barrels and were refrigerated at 2°C until used. The pre-GAC waters were used to conduct the adsorption isotherms, the adsorption kinetic tests, and the reloading experiments to quantify the REs of thermal and electrochemical regeneration techniques.

Phenol (reagent grade, Aldrich Chemical Company, Milwaukee WI) loading and reloading experiments involved the use of 300 mg/L phenol solutions prepared from distilled deionised water. Phenol regeneration was used to confirm results obtained by Karimi-Jashni (2001).

All NOM and phenol reloading solutions were buffered with 0.05 M potassium phosphate (Reagent grade, BDH Chemicals, Toronto) to a pH of 5.3.

3.1.3 Electrolyte

Unless otherwise stated the electrolyte used in this study was 0.1 M NaCl (reagent grade, BDH Inc, Toronto) solution prepared with distilled water. This electrolyte was chosen to allow for greater comparison with the studies conducted by Karimi-Jashni (2001) and Narbaitz and Cen (1994). Narbaitz and Cen (1994) showed that 0.1M NaCl had better performance than other salts tested for electrochemical regeneration of phenol loaded GAC.

3.2 Analytical Technique

NOM concentrations were quantified as total organic carbon (TOC) via Method 5310 for TOC from Standard Methods (1995). This is accomplished with a UV-persulfate based TOC analyser (DC-180, Dohrmann Division Rosemount Analytical Inc., Santa Clara, CA). The analyser uses UV promoted persulfate oxidation to convert the aqueous organics to CO_2 within the analyser. The CO_2 is analysed with a non-dispersive infrared (NDIR) detector. The amount of CO_2 detected is converted

to a TOC concentration in mg/L. The analyser has a nominal detection range from 0.010 mg/L to 30,000 mg/L (Dohrman, 1993), however only levels of 0.1 mg/L and higher could be measured consistently. The precision of this analysis within this study was ± 5% based on repeat analysis. A 10 ml pickup loop with the auto-sampler option was used to analyse each sample. All samples were analysed in triplicate with the average value reported. The instrument was calibrated using potassium hydrogen phthalate (primary standard, BDH Inc., Toronto) prepared with distilled deionised water to ensure that the analyser was operating satisfactorily. The carrier solution was made with distilled deionized water and potassium persulphate (analytical reagent, BDH, Toronto). Distilled deionised water and standard samples were analysed with each batch of tests to confirm proper functioning of the TOC analyser.

The phenol samples were analysed for TOC via Standard Methods 5310 for TOC (Standard Methods, 1995) using a high temperature TOC analyser (DC-190, Dohrmann Division Rosemount Analytical Inc., Santa Clara, CA). The analyser utilizes high temperature catalytic-combustion and a NDIR CO_2 detector to calculate the TOC concentration. The reactor furnace was maintained at 680°C and the high purity O_2 carrier gas was maintained at 200 cc/min. The nominal detection limit for this method was 0.1 mg/L.

3.2.1 pH

All water samples were analysed for pH with a pH meter (Accumet pH Meter 910, Fisher Scientific, Nepean, ON). The pH meter was standardized with 4, 7 and 10 pH buffers (analytical, VWR, Montreal, PQ) before analysis.

3.2.2 Alkalinity

All alkalinity analyses were performed according to Method 2320 B Titration Method (Standard Methods, 1995). Water samples were titrated to the end point using a methyl orange indicator. The alkalinity was calculated according to equation 3.1.

$$Alkalinity = \frac{(TA)(N)(50000)}{V_S} \tag{3.1}$$

Where TA is the volume of titrant to reach the endpoint (ml)

N is the normality of the titrant N

V_S is the volume of the sample (ml)

3.2.3 Total Hardness

Total hardness analyses were performed according 2340 C EDTA Method (Standard Methods, 1995). Water samples were titrated with EDTA using erichrome black T indicator to the end point. The hardness was calculated according to the following equation.

$$Hardness = \frac{(T)(E)(1000)}{V_S} \tag{3.2}$$

Where T is the volume of titrant (mL)

E is the EDTA equivalency

V_s is the volume of the sample (mL)

3.2.4 Total Dissolved Solids (TDS)

Total dissolved solids analysis was conducted according to a modified version of Method 2540 C for TDS. The difference being that the drying oven was set to 105°C and that the dish was placed in the oven for 24 hrs. The TDS was calculated as follows:

$$TDS = (Wtdry - Wtdish)/V \tag{3.3}$$

Where Wtdry is the weight of the dish after the sample has been dried (g)

Wtdish is the weight of the dish alone (g)

V is the volume of water added to the dish (ml)

3.2.5 Turbidity

Turbidity analyses were performed with a turbidimeter (2100AN, HACH, Loveland, CO). The turbidimeter was standardized with turbidity standards provided by HACH. The water sample was placed in the turbidity meter and the turbidity value was recorded.

3.3 Apparatus

This section discusses the apparatus used in this study: the glassware, divided cell glass reactor and the power source.

3.3.1 Glassware

Glass bottles (500 mL) were used for loading the GAC with the NOM water. 50 mL glass vials were used to hold the filtrate sample while it is analysed for TOC. All glassware used in this study was washed in chromic acid and rinsed three times with distilled water before being placed in an oven at 105°C to dry. The glassware was then cooled to room temperature before use.

3.3.2 Divided Cell Glass Reactor

This study used the same divided cell reactor used in Karimi-Jashni (2001). The reactor consists of two glass cylindrical sections clamped together. They each have an internal diameter of 7.6 cm and a height of 15 cm (see Fig 3.1). The diagram shown is not drawn to scale and the distance between the electrodes was 12 cm. The reactor also has access ports for measuring pH, for electrolyte addition and extraction. The electrodes were made from platinum wire mesh, supported by two Teflon® rings around the edge. The field loaded GAC was placed on top of the cathode within the cathode compartment. A cation exchange membrane (Raipore PTFE RF4010, Electrosynthesis, Lancaster, NY.) was used to divide the reactor into cathode and anode compartments. The ion exchange membrane prevents the movement of hydroxide ions from traveling from the cathode compartment to the anode compartment. This creates a high pH environment within the cathode compartment suitable for contaminant desorption.

3.3.3 Power Supply

The power supply used in the setup mentioned above was the same used by Karimi-Jashni (2001). He discussed the three ways to provide a constant supply of power to the electrochemical cell: constant electrode potential, constant current and constant cell voltage. Karimi-Jashni (2001) determined that the use of constant current was the most economical and practical. Therefore, the electrical power was supplied with a potentiostatic controller (model 410, Electrosynthesis, Buffalo, NY), and an accessory power supply (Model 420A, Electrosynthesis, Buffalo, NY) to operate as a constant current system.

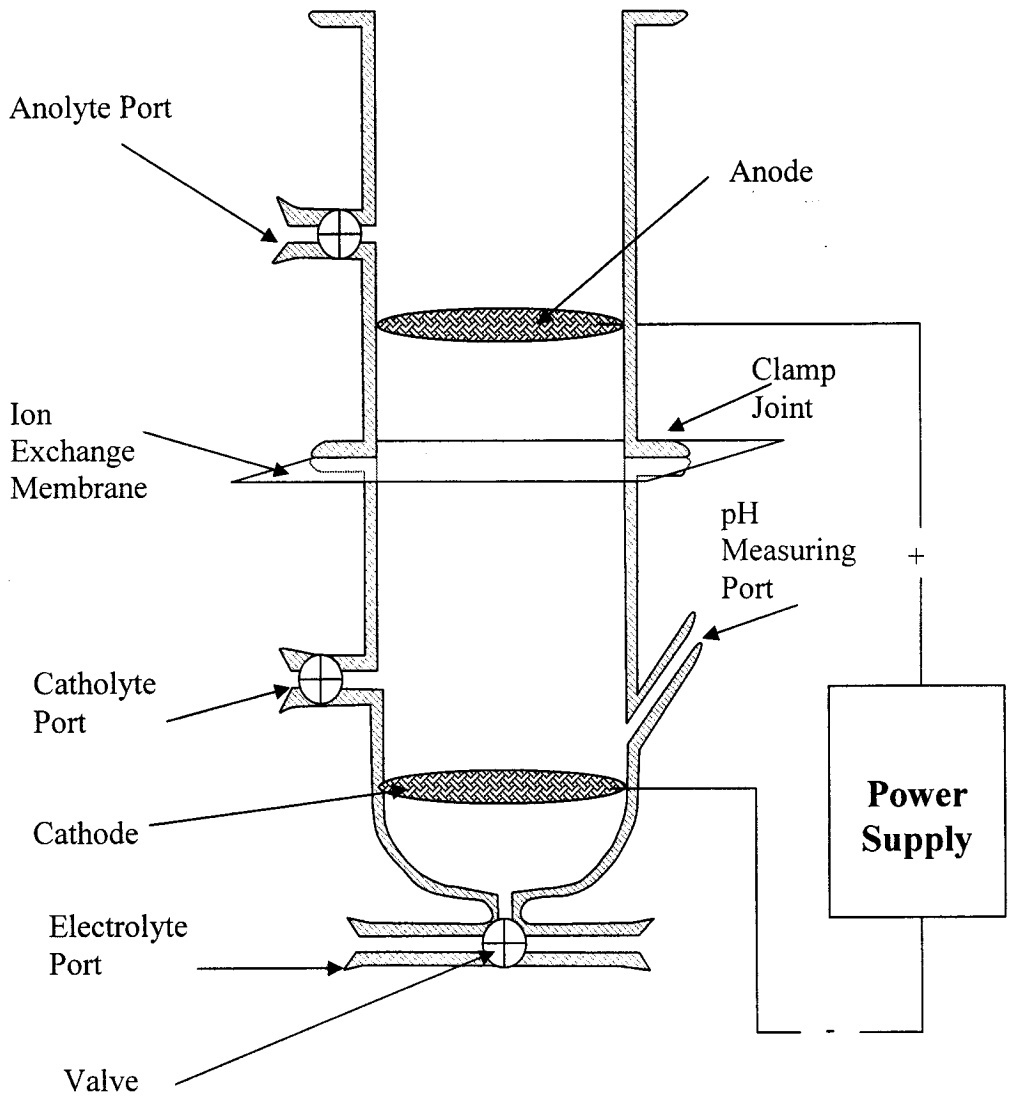

Figure 3-1 Electrochemical Reactor Set-up

3.4 Preliminary Experiments

This section discusses the preliminary experiments conducted in this study. The adsorption isotherms and adsorption rate studies were conducted with virgin GAC from Regina and Cincinnati with their respective pre-GAC water.

3.4.1 Adsorption Isotherm

In order to calculate the regeneration efficiency for the NOM loading, an adsorption isotherm was developed (see literature review Section 2.3). The adsorption isotherm was conducted via the batch bottle point method. Virgin GAC masses ranging from 0.2 to 5 mg were weighed using an analytical balance (R200D, Sartorius, Germany). This was performed as quickly as possible to avoid weight gain due to moisture adsorption from the air. Virgin GAC sample preparation consisted of washing with distilled water to remove the fines followed by oven drying at 105°C to remove excesses moisture. The virgin GAC was cooled in a desiccator then stored in an airtight container until used. The AC was combined with the adsorbate solution in 500 mL amber glass bottles and sealed with Teflon lined caps. The bottles were then placed in the end-over-end tumbler for four weeks to allow for the samples to reach equilibrium (see Fig 3.2 for the flow chart of the loading procedure). The GAC was then separated from the solution via vacuum filtration with 47 mm diameter 0.22-micron Nuclepore® polyester filters. The filtrate was analysed for TOC using the UV-persulfate based TOC analyser. In the case of the phenol isotherm the TOC was analysed with the high temperature TOC analyser. Blanks (consisting of only

distilled water and distilled deionized water with a GAC dose of 2 g/L), controls (NOM water without GAC addition) and duplicates were also tested to ensure that there were no losses, leaching from the glassware or the AC.

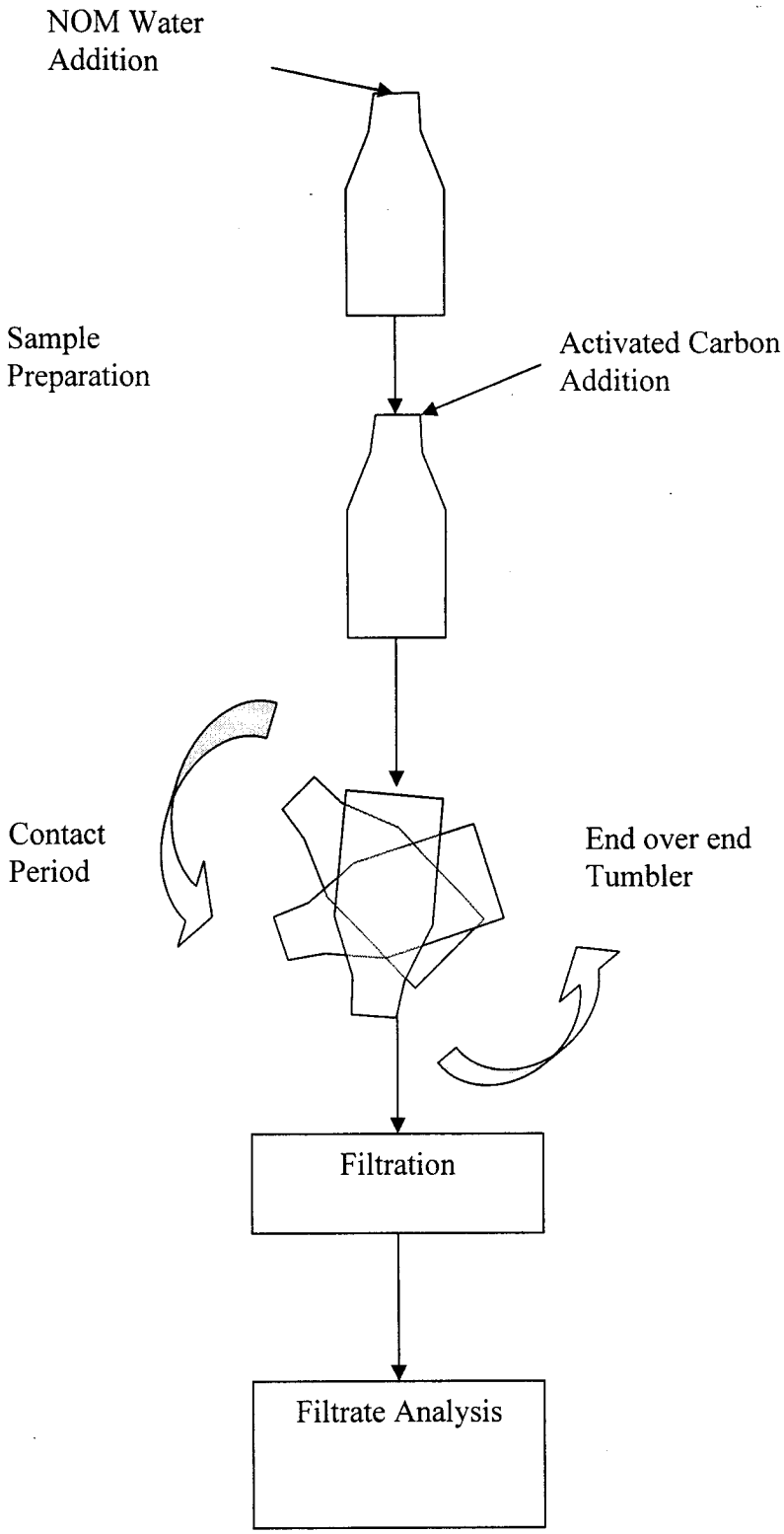

Figure 3-2 Bottle Batch Loading Method

3.4.2 Adsorption Kinetics

An adsorption kinetic experiment was performed to evaluate the length of time required to reach liquid-solid equilibrium for the batch reloading experiments. Adsorption kinetic tests were conducted for both Regina and Cincinnati water As in the adsorption isotherm experiments, the adsorption kinetic test was determined using the batch bottle-point loading method. In this experiment the AC dose of 2 g/L was used in each bottle. This dose was selected as it corresponds to the mass of 1 g of GAC used in the regeneration experiments (i.e. single layer of GAC spread over the surface of the wire mesh cathode). The GAC was measured using an analytical balance (Sartorius R200D, Germany) as quickly as possible to avoid weight gain due to moisture adsorption from the air. The weighed GAC was placed into 500 mL amber glass bottles, sealed with Teflon lined caps. The bottles were placed into the end-over-end tumbler; and then removed at various predetermined time intervals (see Appendix A for exact contact times). At the end of the contact period the liquid in the bottle was vacuum filtered to separate the GAC from the solution. The filtrate was then analysed for TOC in the UV-persulfate TOC analyser. Blanks, controls and duplicates were also evaluated.

3.4.3 pH Controlled Desorption

Electrochemical regeneration depends to a great degree on pH driven desorption. The impact of pH on NOM desorption was determined to compare with the findings of Karimi-Jashni (2001).

This test was designed to determine the effect of pH on NOM desorption. Wet field-spent GAC from Regina (0.6555 ± 0.01 g) was placed in each bottle (see Appendix A for the variation of measured mass). This was combined with buffered pH desorption solution (pH 1.0, 7.0 and 13.2). The desorbing solutions were prepared by combining buffers 1 and 2 to produce the appropriate pH solution (see Table 3.1). The bottles were placed in the end-over-end tumbler for 5 weeks to allow for equilibration. After the contact period the samples were vacuum filtered to separate the GAC for the solution. Blanks from each pH solution were also tested. The filtrates were analysed for TOC using the high temperature TOC analyser due to Cl interferences caused by the buffer solution with the UV-persulfate TOC analyser. These buffers were chosen to test the extreme pH ranges, and were chosen from Robinson (1984).

Table 3-2 Buffer Solutions

Solution pH	Buffer 1	Buffer 2
1.0	0.2 M KCl	0.2 M HCl
7.0	0.1 M Potassium di-hydrogen phosphate	0.1 M NaOH
13.2	0.2 M KCl	0.2 M NaOH

3.5 Electrochemical Regeneration Procedure

NOM-loaded GAC (0.6555 ± 0.01 g) from either Regina or Cincinnati was placed in the electrochemical reactor for 5 hours at various currents (10, 50, 100 and 200 mA).

The reactor was operated as a divided cell reactor with the GAC samples placed on top of the cathode, in the cathode compartment. In all runs, unless otherwise stated, the electrolyte was 0.1 M NaCl (see Section 3.1.3). Periodically, trapped gas was removed from under the cation exchange membrane to ensure that the electrical circuit was intact (See Appendix G for full description). At higher currents (100 and 200 mA) the gas was removed every 20 minutes. In future research, alternative reactor configurations should be investigated to eliminate the need for continuous removal of trapped gas from under the ion exchange membrane. After the regeneration cycle was completed, the regenerated GAC was then removed from the reactor and stored under refrigeration until the sample was reloaded with phosphate buffered pre-GAC water from its respective water source. The cation exchange membrane was rinsed after the regeneration and stored in a NaCl solution bath until the next regeneration cycle.

Limited electrochemical regeneration experiments were conducted with phenol-loaded Calgon F-400 GAC (batch bottle point method loading). The phenol-loaded GAC was electrochemically regenerated under the same operating conditions as described above for the NOM-loaded GAC.

3.6 Evaluation of Regeneration

The RE was evaluated with batch NOM reloading, iodine number analysis, surface area analysis, pore size distribution, and surface chemistry analysis.

3.6.1 NOM Reloading

The regenerated GAC (electrochemical and thermal) was reloaded with NOM via the bottle point method (as discussed in Section 2.6.3). Batch reloading was used to avoid some of the problems associated with column loading (i.e. large amount of GAC required, large amount of adsorbate solution required and the large number of samples required to test to plot the breakthrough). The large amount of GAC required for column loading is particularly relevant because electrochemical regeneration of GAC currently is capable of regenerating only 1 g of GAC per treatment cycle. A pilot-scale column would require approximately 5 kg of GAC and 200 m^3 of water for each test condition. This loading method would be prohibitive. Reducing the GAC particle size would decrease the amount of adsorbate solution required. However, for multiple regeneration cycles the AC particle size cannot be reduced. Previous studies by Karimi-Jashni (2001) indicated that direct contact was necessary and ground GAC would slip through the wire mesh electrode.

After completion of the desired contact times the contents of the bottles were vacuum filtered. The filters and filter apparatus were rinsed with distilled water and the first 100 ml of the filtrate was discarded to ensure that there was no contamination of the sample or losses due to adsorption on the glassware. Then the filtrate TOC was measured. The RE was defined as:

$$RE = \frac{q_r}{q_e} \times 100\% \tag{3.4}$$

Where q_e = the solid phase equilibrium concentration for the virgin GAC at the same liquid equilibrium concentration as the reloading

q_r = the solid phase concentration of the reloading.

More specifically Method 3 (equation 2.19 defined in Section 2.10.3) was used to define RE, i.e.

$$RE = \frac{(C_o - C_e)V/M}{KC_e^{1/n}} \times 100\% \quad (3.5)$$

Where K and 1/n are the Freundlich coefficients from the virgin GAC isotherm

3.6.2 Iodine Number

Iodine number is a popular means of determining the GAC RE (Karimi-Jashni, 2001). ASTM D 4607 Standard Test Method for Determination of Iodine Number of Activated Carbon was used to determine the iodine number of virgin, thermal, and electrochemical regenerated GAC from Regina and Cincinnati (ASTM, 1995). The procedure includes grinding the GAC sample to pass through a 325-mesh sieve, contacting three different doses of ground GAC with an iodine solution for 30 seconds, filtering the mixtures, titrating the filtrates to determine the concentration of iodine remaining in the solution and conducting a mass balance to calculate the iodine adsorbed by the ground GAC. The residual concentration is plotted against the amount of iodine adsorbed for the three doses. The iodine number is the mass of iodine adsorbed at the residual iodine concentration of 0.02 N. The iodine number RE was determined using the equation:

$$RE_{Iodine} = \frac{Iodine\#_{\text{Re}\,generated\_GAC}}{Iodine\#_{Virgin\_GAC}} \times 100\% \quad (3.6)$$

3.6.3 Surface Chemistry

As discussed in Section 2.4.3, the surface chemistry of AC has a great impact on adsorption capacity. In this study the surface chemistry of the thermal, the virgin and the electrochemically regenerated GAC was compared. The process for determining the surface chemistry was adapted from Boehm (1967). One gram of GAC was added to a 100 ml glass bottle (chromic acid washed). The bottles were filled with one of the following three base solutions; 0.01 N $NaHCO_3$, 0.01N Na_2CO_3, and 0.01N NaOH. The bottles were placed in the end-over-end tumbler for 24 h to allow for mixing during the contact period. The bottles were then removed from the tumbler and the contents were vacuum filtered to remove the GAC from the solution.

Using a pipette, 20 ml of the filtrate was transferred to a 100 ml beaker. The filtrate was titrated with 0.02N HCl until the pH reached 4.3. The quantity of titrant was then recorded. The above was repeated for the original base (i.e. $NaHCO_3$, Na_2CO_3, and NaOH.) solution. The quantity of base consumed (BC) by the GAC was calculated as:

$$BC = (V_B \times N) - (V_L \times N) \tag{3.7}$$

Where V_B = volume (ml) of the titrant required to achieve pH 4.3 for the original base solution (i.e. NaOH, Na_2CO_3 and $NaHCO_3$)

V_L = volume (ml) of titrant required to achieve pH 4.3 for the base solution after contact with the GAC

N = normality (N) of the titrant.

The surface chemistry parameters strong acid, weak acid and phenolic acid amounts were calculated as:

$$Strong\_Acid = BC_{NaHCO_3} \tag{3.8}$$

$$Weak\_Acid = BC_{Na_2CO_3} - BC_{NaHCO_3} \tag{3.9}$$

$$Phenolic\_Acid = BC_{NaOH} - BC_{Na_2CO_3} \tag{3.10}$$

Where BC_{XX} is the milliequilivents of base consumed of the XX base solution by the GAC.

3.6.4 Pore Size Distribution and Surface Area

The pore size distribution and surface area analysis was conducted on virgin, thermally regenerated, field-spent, and electrochemically regenerated GAC from both Regina and Cincinnati. After the regeneration cycle the samples were sent to the National Research Council Laboratories (Ottawa, Ontario) for analysis using nitrogen adsorption (ASAP 2000 Accelerated Surface Area and Porosimetry Analyzer, Micromeritics, Norcross, GA, USA). The pore size distribution and surface area analysis was conducted at the National Research Council (NRC) laboratory by NRC staff. The analysis report from NRC is included in the Appendix B.

3.7 Experimental Plan

Table 3.2 presents a list of the experiments performed in this study. Experiment numbers 6-14 required the electrochemical regeneration of GAC from Regina and

Cincinnati. The electrochemical reactor was operated at currents 10, 50, 100, and 200 mA for 5 hours.

Table 3-3 Experimental Plan

Topic	Experiment Number	Purpose	Test Factor
Adsorption Kinetics	1	Determine equilibrium time for Regina water	NOM bottle point loading
	2	Determine equilibrium time for Cincinnati water	NOM bottle point loading
Adsorption Isotherms	3	Develop Freundlich coefficients for Regina	NOM bottle point loading
	4	Develop Freundlich coefficients for Cincinnati	NOM bottle point loading
	5	Develop Freundlich coefficients for Phenol	Phenol bottle point reloading
Regeneration Efficiency	6	Investigate High pH pre-treatment for Phenol loaded GAC	Phenol bottle point reloading
	7	Investigate regeneration efficiency for Phenol loaded GAC	Phenol bottle point reloading
	8	NOM loaded regeneration efficiency for Regina GAC	NOM bottle point reloading
	9	NOM loaded regeneration efficiency for Cincinnati GAC	NOM bottle point reloading
	10	Investigate the effect of current on the iodine number of electrochemically regenerated Regina GAC	Iodine number
	11	Investigate the effect of current on the iodine number of electrochemically regenerated Cincinnati GAC	Iodine number
Surface Chemistry	12	Investigate the effect of current on the surface chemistry of Regina GAC	Iodine number
	13	Investigate the effect of current on the surface chemistry of Cincinnati GAC	Surface chemistry titration
Pore Size Distribution and Surface area Analysis	14	Investigate the effect of regeneration method on the pore size distribution and surface area of Regina and Cincinnati GAC	Nitrogen Adsorption analysis

4 Results and Discussion

4.1 Introduction

This study had two main objectives: 1) to investigate the effect of electrochemical regeneration of GAC for drinking water treatment applications, and 2) to compare electrochemical and thermal regeneration on the same basis.

This chapter discusses the results of the preliminary tests required to determine the RE (water characterisation, adsorption kinetics, adsorption isotherm, high pH desorption, phenol-loaded regeneration, and evaluation of alternative reactor parameters), and the evaluation of electrochemical and thermal REs (NOM adsorption, iodine number, pore size distribution and surface area analysis, and surface chemistry analysis).

4.2 Preliminary Experiments

4.2.1 Water Characterisation

Turbidity, hardness, pH, TOC and alkalinity tests were conducted to characterise the source water. Table 4-1 displays the results for Regina and Cincinnati pre-GAC waters. The hardness for Regina water was within 17% of the average value posted on the Regina web site. The hardness for Cincinnati GAC was within the minimum and maximum values reported for post filtration water (Summers et al., 1992). The pH values were 7.04 and 7.02 for Regina and Cincinnati, respectively. These values are also typical of water that has undergone coagulation, flocculation and filtration

(Faust and Aly, 1998). The turbidity for both sources was very low which is typical of treated water. The TDS were low for both sources. Regina's TDS was 30% higher than the average value reported by the City of Regina (see Appendix D), while Cincinnati's TDS was lower than the minimum value reported (see Appendix D). The TOC for Regina and Cincinnati was 3.0 and 1.5 mg/L, respectively. These values show that there was a significant amount of NOM present in the post – filtered water compared to distilled deionized water (See Appendix D for water quality parameters). From the higher NOM levels in Regina one may expect higher TOC loading on the Regina GAC which may result in lower RE

Table 4-1 Pre-GAC Water Characteristics for Regina and Cincinnati

	Regina	Cincinnati
Hardness (mg/L as $CaCO_3$)	164 ± 0.01	108 ± 1.33
Alkalinity (mg/L as $CaCO_3$)	182 ± 23	108 ± 1.14
pH	7.04 ± 0.23	7.02 ± 0.25
TDS (mg/L)	460 ± 0.01	110 ± 10
TOC (mg/L)	3.0 ± 0.12	1.42 ± 0.055
Turbidity (NTU)	0.198 ± 0.014	0.225 ± 0.011

4.2.2 Adsorption Kinetics

Preliminary adsorption kinetic experiments were conducted to determine the contact time required to reach equilibrium for batch loading of the virgin GAC. The results of the Regina and Cincinnati Water NOM adsorption kinetic experiments are shown in Figs 4-1 and 4-2. These figures show the reduced liquid concentration (i.e. the

percentage of initial concentration remaining in the liquid after contact with the GAC). Figures 4-1 and 4-2 demonstrate that the adsorption of NOM can be divided into two parts based on the rates of adsorption. First, there is rapid adsorption and a dramatic reduction in TOC. During the first 48 hours, almost 80% of the TOC was removed. In the second part, between 48 and 1400 hours of the experiment the, the adsorption was much slower and the TOC was only reduced by nearly 20% (of the original TOC), for Regina water. The significant rapid adsorption may be due in part to the very large carbon dose (i.e., carbon dose = 2.0 g/L). See Section 2.5.5.

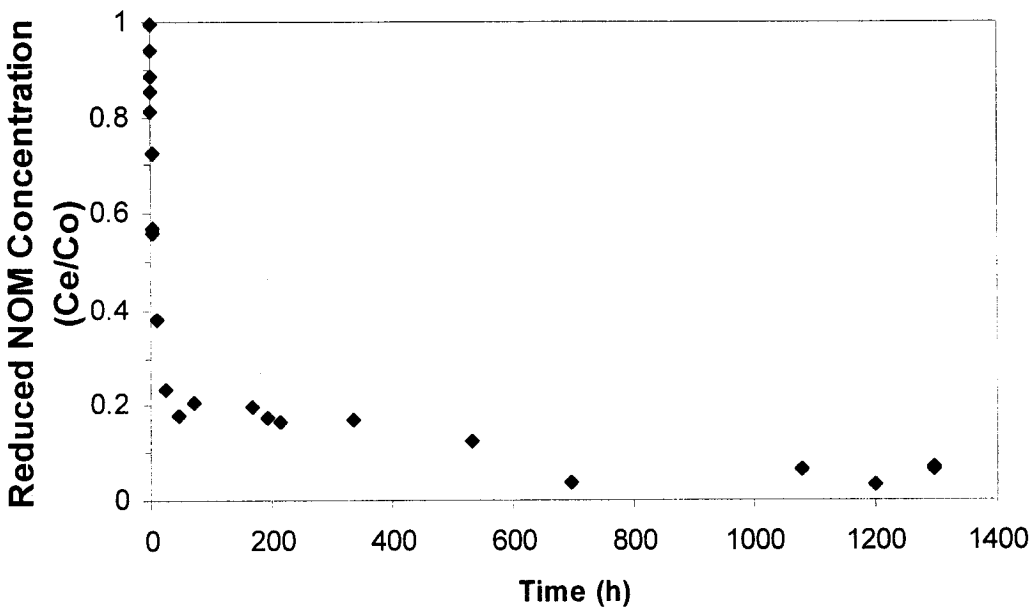

Figure 4-1 Adsorption Kinetic Data of NOM on Virgin Regina GAC versus Time (Co = 3.0 mg/L, GAC dose = 2.0 mg/L)

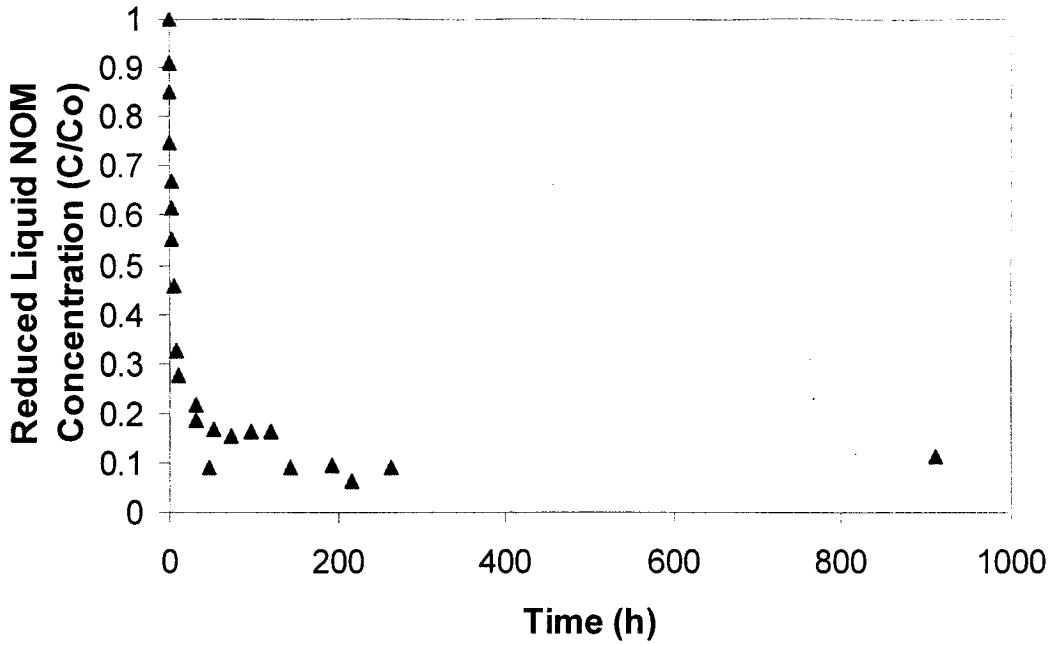

Figure 4-2 Adsorption Kinetic Data of NOM on Virgin Cincinnati GAC versus Time (Co = 1.5 mg/L, GAC dose = 2.0 mg/L)

The adsorption kinetics for Cincinnati water were similar to those for Regina water. However Cincinnati water appears to reach equilibrium a bit faster. Due to the time required to perform the electrochemical regeneration and subsequent reloading experiments it was decided that a 2-week (336 hours) adsorption time would be reasonable to approximate the time to reach equilibrium, although full equilibration for Regina's pre-GAC water takes longer. This may result in an underestimation of the regeneration efficiency.

4.2.3 Adsorption Isotherms

Preliminary batch bottle point adsorption isotherms were performed with virgin Regina and Cincinnati GAC with their respective source waters. The resulting TOC isotherms for the Regina and Cincinnati waters are shown in Figs 4-3 and 4-4. The results indicate that the isotherms are well described by the Freundlich model since

the data follow a straight line pattern within a $\log q_e$-$\log C_e$ graph for both GACs. The Freundlich coefficients and the R^2 values for the linear regression of the log-log plot of C_e vs. q_e are shown in Table 4-1. Each point represents three analysis of the same sample. The standard deviation of each sample set ranged from 1 to 4%. These Freundlich coefficients were later used to evaluate the RE of the electrochemically and thermally regenerated Regina GAC.

Table 4-2 Adsorption Isotherm Results

Source	K (L/g)	1/n	R^2	Liquid Concentration Experimental Range (mg/L)
Regina	8.86 ±1.86	1.26 ± 0.19	0.971	1.1 to 27.5
Cincinnati	8.07 ± 1.53	0.86 ± 0.19	0.953	1.6 to 10.5

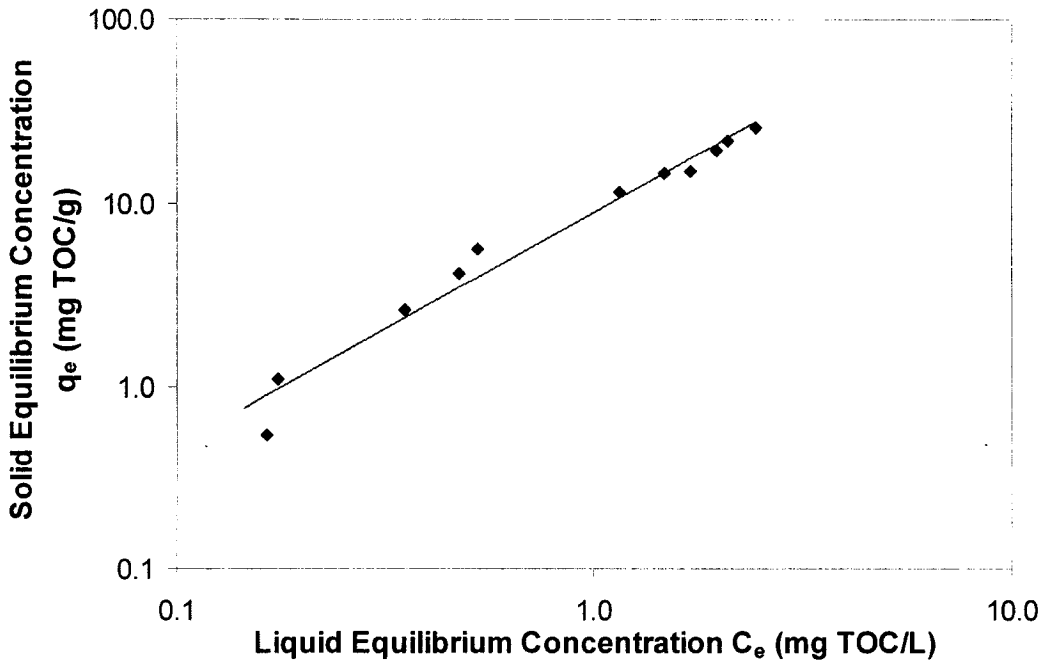

Figure 4-3 NOM Adsorption Isotherm for Regina Filtered Water on Virgin GAC

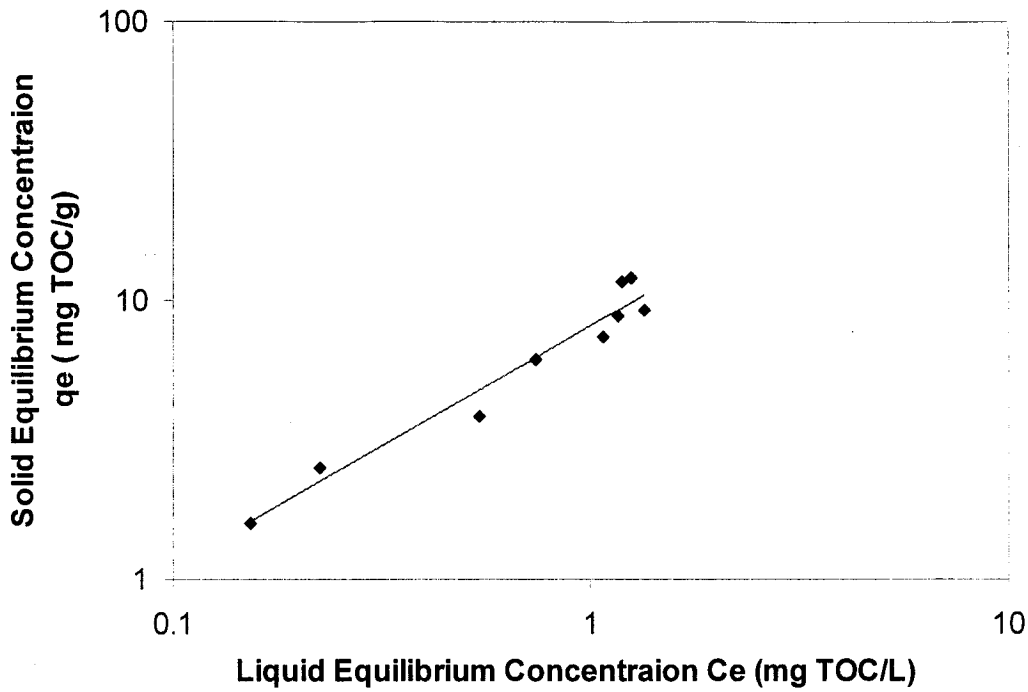

Figure 4-4 NOM Adsorption Isotherm for Cincinnati Filtered Water on Virgin GAC

Figures 4-3 and 4-4 and Table 4-1 demonstrate that the NOM adsorption capacities for both GACs were low compared to the high adsorption capacities for phenol (500 mg/g) seen in Karimi-Jashni (2001). The Freundlich coefficient K is an indicator of the adsorption capacity; higher values of K indicate greater adsorption capacity. The Freundlich K and 1/n coefficients for Regina and Cincinnati GAC are similar to those reported for commercial humic acid (Lee et al., 1981). Recently other researchers have studied Cincinnati and Regina source waters; however, they did not report isotherm data because their thermal regeneration research focused on the

NOM breakthrough characteristics (Forsyth et al., 1992; Summers et al., 1995; Hooper et al., 1996; Moore et al., 2001, and Moore et al., 2003).

The adsorption capacities within the isotherms reported in this study were quite low compared to those reported by Summers et al. (1992) (See Appendix E). The GACs of Summers et al. (1992) were identified as GAC A, B, and C, as such; the exact GAC brand and type were unavailable. The difference in the adsorption isotherms may be due to the different types of GAC, different batches of GAC, and the natural variation in the humic material in the water from season to season.

The Jacobi Carbon currently used at Cincinnati appears to have lower adsorption capacities than the GAC employed in the previous research by Summers et al., 1992. A summary of the isotherm data from Summers et al. (1992) in shown in Appendix E. Comparing the Freundlich coefficient K from the Jacobi carbon to those of Summers et al. (1992), demonstrates that the adsorption capacity was lower in this study.

It should be noted that the Freundlich equation only applies to the experimental data in the ranges of 1.1 mg/g < q < 27.5 mg/g for Regina GAC and 1.6 mg/g < q < 10.5 mg/g for Cincinnati GAC. For this reason, the reloading GAC dose for the regeneration experiments was changed from 2 to 1.3 g/L to allow the solid phase NOM concentration after re-loading to fall in the experimental range of the isotherms. GAC doses greater than 1.3 g/L resulted in solid phase NOM concentrations below the experimental range, consequently they did not agree well

with the Freundlich isotherms and they gave lower regeneration efficiencies (See Appendix E).

4.2.4 pH Controlled Desorption

Desorption experiments were conducted to confirm the effect of pH on NOM desorption. The results of the pH controlled desorption are displayed in Fig 4-5. The greatest desorption of 15.7 mg/L occurred with the pH = 13.15 desorption solution. This seems to suggest that high pH desorption is capable of regenerating NOM loaded GAC. However, due to difficulties obtaining the original loading information (breakthrough data was unavailable from Regina) of the Regina field-loaded GAC, it was not possible to determine the exact percent of the NOM desorbed at high pH. The error bars on Fig 4-6 indicate the variability in the repeats for each sample.

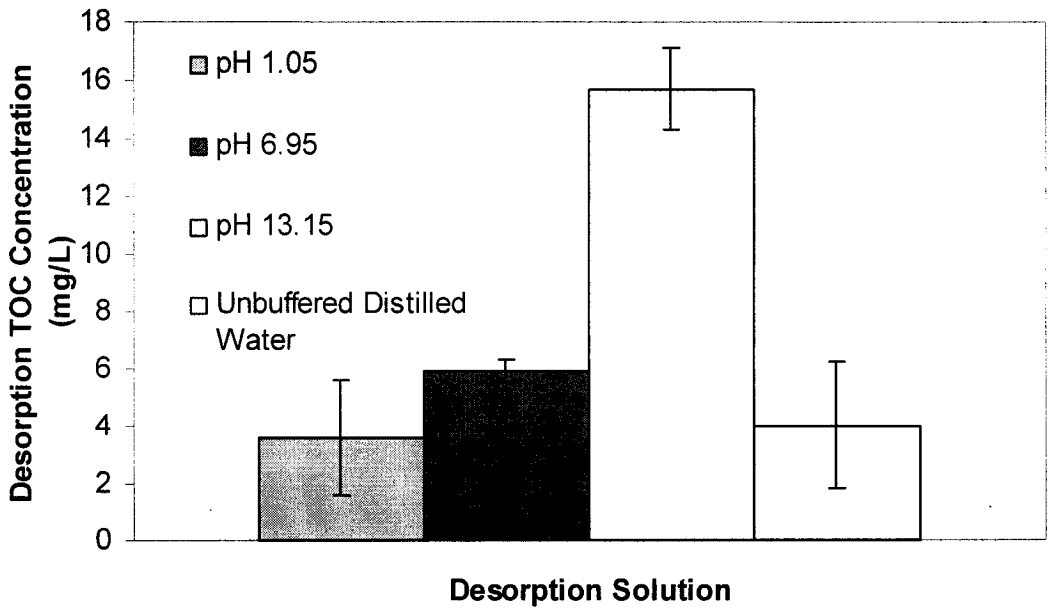

Figure 4-5 pH Controlled NOM Desorption at for Regina Field-Loaded GAC, GAC dose = 1.3 mg/L

Thus, the initial loading was estimated to be 35.37 mg/g using the Regina GAC adsorption isotherm (developed in Section 4.2.3) at an initial NOM concentration of 3.0 mg TOC/L. Based on this estimate there was 35 mg/g of TOC on the GAC prior to desorption and the desorption yielded the TOC liquid phase concentration reported in Fig 4.6. Accordingly, the RE for pH induced desorption (pH = 13.15) was about 35.9% (see Appendix F for calculations).

The RE for pH desorption was also estimated using loading data from Gammie and Giesbrech (1986). The overall NOM loading was estimated as 35 mg DOC/g. This loading information was recorded during the initial experiments to determine the feasibility of GAC use at Regina (Cecarbon 830 and Calgon Filtrasorb 300). With this information, the estimation of the NOM removal due to desorption at pH 13.15 is approximately 36% of the original NOM loaded. This suggests that high pH alone should regenerate approximately 36% of the GAC adsorption capacity (see Appendix F for calculations). This estimate admittedly may not be accurate because the GAC used by Gammie and Giesbrech (1986) was different than GAC currently used at Regina. However, it was similar to the earlier estimate. It should be noted that for nitrophenol-loaded GAC Karimi-Jashni (2001) achieved REs that were greater than could be accounted for by pH induced desorption alone.

4.2.5 Regeneration Efficiency (Phenol-Loaded)

In order to establish a benchmark for the electrochemical reactor performance electrochemical regeneration experiments with phenol-loaded GAC were conducted

(see Appendix C for isotherm data). The results of the phenol reloading for the 5 h electrochemical regeneration of F-400 GAC are shown in Fig 4-6. The RE ranged from 63 to 84% as the current increased from 10 to 200 mA. The regeneration efficiency for the non-regenerated GAC sample (0 mA) was calculated using RE method 4 (see Section 2.10.3), which are appropriate for controls and very low intensity regenerations. It indicates that there was no regeneration. These results compare well with those of Karimi-Jashni (2001). In particular, the RE of 50 mA for 5 h was only 3% lower in this study. Thus the reactor was operating as efficiently as in past research. The error bar indicates the standard deviation (± 3.5%) between duplicates for this experiment.

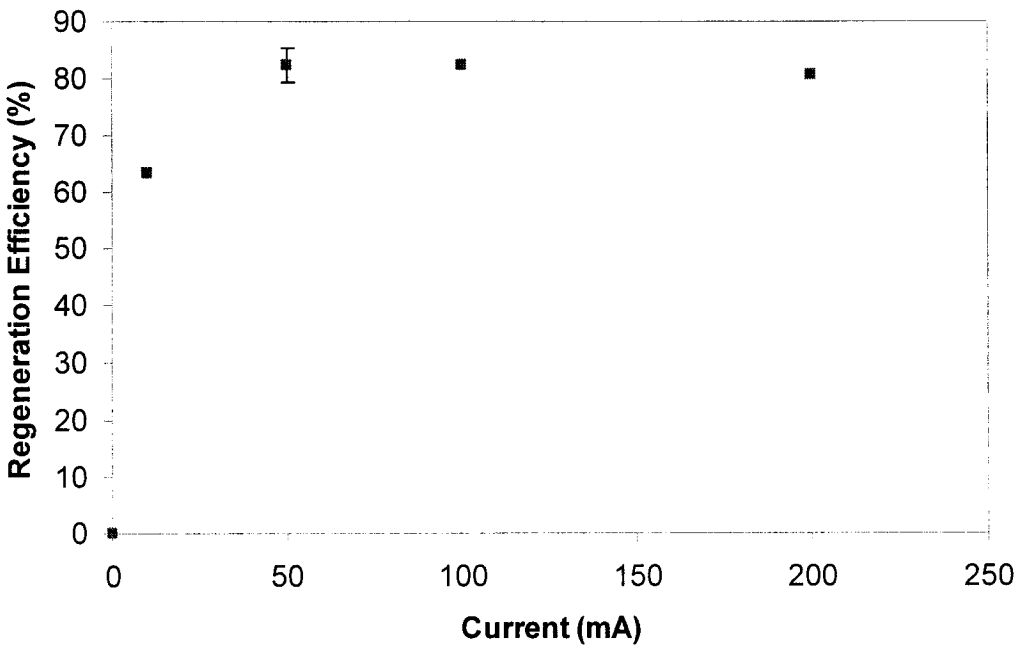

Figure 4-6 Regeneration Efficiency of F-400 GAC, Phenol-Loaded

4.2.6 Reactor Testing

Preliminary regeneration experiments were conducted on Regina field-loaded GAC to investigate the effect of electrolyte pH, and the presence of dissolved oxygen in the electrolyte on the RE. Clifford et al. (1999) demonstrated the use of high pH electrolyte and dissolved oxygen to improve the RE of phenol-loaded GAC. Their process utilized a high pH buffered high concentration Na_2SO_4 electrolyte solution and resulted in significant contaminant oxidation that was aided by the addition of bubbled O_2. Preliminary experiments were designed to investigate the potential of applying the findings of Clifford et al. (1999) to the electrochemical regeneration of NOM-loaded GAC.

Three runs were performed to evaluate the effect of using a pH buffered electrolyte and adding O_2 bubbling. All runs were performed with an undivided reactor utilizing cathodic treatment. Run 1 involved the use of 0.1 M NaCl electrolyte. Runs 2 and 3 involved the use of 1.0 M Na_2SO_4 and 1.0 M NaOH buffered to pH 14 with 1.22 cm^3/s electrolyte recycle. Run 3 had the addition of O_2 bubbling (40 cm^3/min). Figure 4-7 shows the results of the RE experiments for the reactor setup tests, the REs range from -0.2 to 8 %. The negative value indicates that the NOM concentration after GAC NOM re-loading was higher than the source water NOM concentration. Surprisingly the REs were lower with the high pH electrolyte and O_2 bubbling. Observations of the electrolyte colour (clear with no discolouration) indicated little or no NOM desorption. According to the observations of Karimi-Jashni (2001) NOM desorption should have occurred, because the pH of all of the

regeneration solutions remained above the target pH of 12 after regeneration. In run 2 and 3 the electrolyte solution started at pH 14.0 ± 0.035 and remained above pH 14 after the regeneration cycle (100 mA at 5 h).

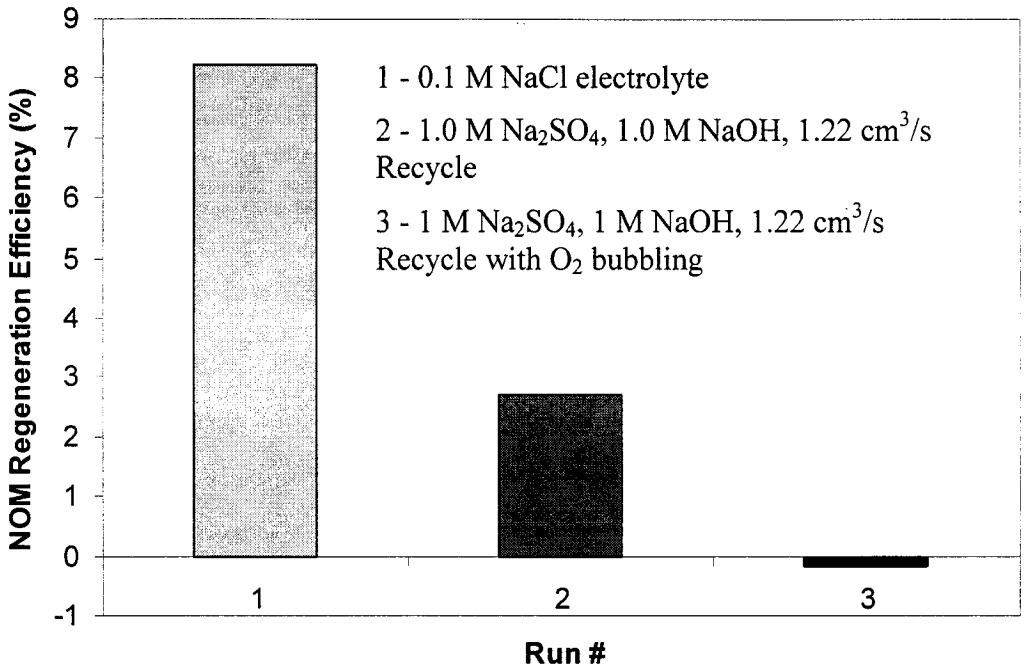

Figure 4-7 Regeneration Efficiency vs Electrochemical Run for Regina Field – Loaded GAC (undivided cell reactor, cathodic regeneration for 5 hrs and 100mA)

The high salt concentration (1.0M NaOH, and 1.0 M Na_2SO_4) of the electrolyte may have inhibited NOM desorption. Newcombe (1999) demonstrated that NOM adsorption is enhanced at high salt concentrations due to a reduction of the lateral repulsion of the adsorbed NOM. The lateral repulsion of NOM at high surface concentrations could be inhibited by the salt ions, resulting in little of no NOM desorption. With very little desorption occurring during the regeneration step there would be little space available for NOM adsorption upon reloading. The negative value for the third method indicates a higher liquid NOM concentration after

reloading ($C_{eq} > C_o$), thus desorption may have occurred in the reloading solution. The increase of the electrolyte salt concentration, the increase of the electrolyte pH and the addition of O_2 bubbling did not improve the RE of NOM loaded GAC.

4.3 Regeneration Efficiency

As discussed in the literature review, there are different methods used to determine the RE for thermal and electrochemical studies. This section compares the results of the regeneration experiments for the thermally and the electrochemically regenerated GAC from Regina and Cincinnati. The REs were evaluated in terms of NOM adsorption, iodine number analysis, pore size distribution analysis, surface area analysis and surface chemistry analysis.

4.3.1 Regeneration of NOM Loaded GAC

The results of the NOM reloading for Regina and Cincinnati GAC are presented in Figs 4-8 and 4-9, respectively. The results show that the RE increased from approximately 8 to 17% as the current was increased from 10 to 200 mA. Both GAC sources were impacted similarly by the electrochemical regeneration. The variability of the repeats was 6% of the average. Observations of the electrolyte colour, pH and TOC for Regina GAC after the regeneration period (presented in Appendix A) confirm that some NOM was desorbed. Figure 4-8 also displays the RE for Regina field-thermally regenerated GAC, which was over 100%. The Cincinnati field-thermally regenerated GAC RE was lower at 87%. This may be due to the loss of pore volume associated with thermal regeneration. It is obvious from Figs. 4-8 and

4-9 that the electrochemical REs were considerably lower than the field-thermal regeneration efficiencies.

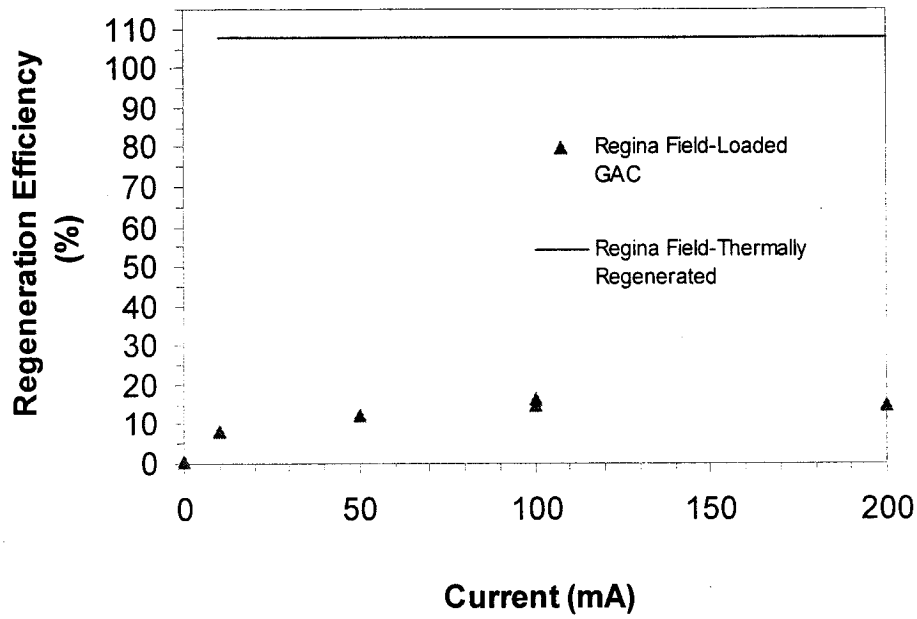

Figure 4-8 NOM Adsorption Regeneration Efficiency for Regina Field-Loaded GAC

Although the pH of the electrolyte in the cathode compartment reached the pH of 12.5 (similar to the pH of the desorption tests). The regeneration efficiencies were far lower (Fig 4.5) than the 36% achieved by the long-term desorption tests at high pH. Given that the electrochemical regenerations only lasted for 5 h and the long-term desorption tests used and equilibrium time of 1080 h, it seem that the low electrochemical REs were a result of insufficient time. This is reasonable give that the adsorption of NOM is slow and its desorption is limited and even slower (Narbaitz, 1986)

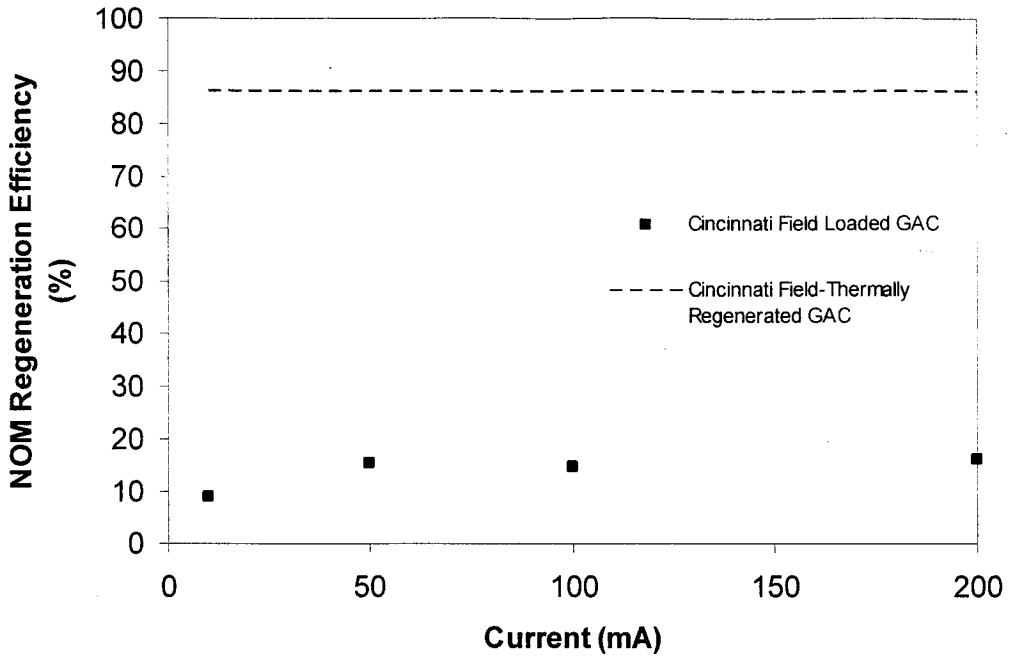

Figure 4-9 NOM Adsorption Regeneration Efficiency for Cincinnati Field-Loaded GAC

The low electrochemical REs were surprising given that previous phenol-loaded GAC regeneration experiments by Karimi-Jashni (2001) obtained REs greater than 95%. His experiments utilized batch loading of the GAC prior to the electrochemical regeneration instead of the column loading in the above tests. Thus, the effect of the loading method was investigated by batch-loading virgin Regina GAC with NOM water.

Figure 4.10 shows the effect of current on the regeneration efficiency of field-spent Regina GAC and laboratory loaded Regina GAC. As discussed earlier, the field spent Regina GAC had REs ranging from 8 to 17%, while the batch-loaded GAC has REs in the 79 to 87% range.

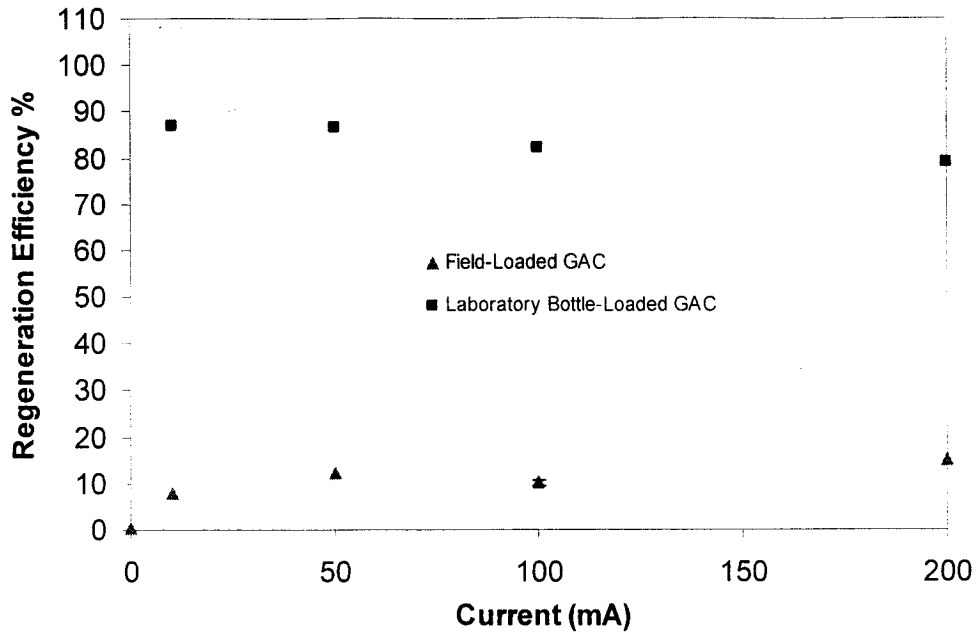

Figure 4-10 NOM Adsorption Regeneration Efficiency for Regina Field and Laboratory-Loaded GAC

The reason for the slight decrease in the RE with increasing current for lab-loaded GAC is unclear. The decline may simply be due to experimental error, with the RE 83±5%. Other possible explanations may be due to an altering of the pore size distribution or perhaps due to surface chemical changes.

The results (Fig 4-10) show a large overall increase in the RE of lab-loaded GAC compared to field-loaded GAC. The differences are so large that it is unlikely to be significantly impacted by the fact that field-loaded and lab-loaded GAC may have different initial NOM solid phase concentrations. The difference likely lies on the way NOM compounds adsorb in columns and batch systems.

NOM consists of a heterogeneous mixture of organic compounds. A fraction of these organics adsorb strongly, others adsorb less strongly, while another fraction may not adsorb at all (i.e. non-adsorbable) (McCreary and Snoeyink, 1980; Lee et al., 1981; Summers and Roberts, 1988a; Kilduff et al., 1996a; and Kilduff et al., 1996b). The strongly adsorbed fraction may adsorb irreversibly (Narbaitz, 1986; Summers and Roberts, 1988a; and Summers and Roberts, 1988b). As such the irreversible adsorption is expected to reduce the RE of electrochemical regeneration, as it is primarily driven by high pH induced desorption (Karimi-Jashni, 2001). Field-spent GAC is loaded in a column and the GAC is constantly being subjected to the strongest adsorbing NOM fraction (Carter et al., 1992). In addition, since full-scale column runs last many months the slow adsorbing NOM has a greater opportunity to migrate deeper into the pores of the GAC. In addition there is more time for oxic polymerization reactions to take place. Batch-loaded GAC is exposed to a fixed volume of water containing NOM. The strongest adsorbing NOM fraction is adsorbed to a greater extent than the weaker adsorbing fraction, but there is a limited quantity of strongly adsorbing NOM. Electrochemical regeneration seems to be able to remove the weakly adsorbed NOM fraction. Thus, in batch-loaded GAC regeneration, the weakly adsorbed NOM is removed allowing for the adsorption of more NOM upon reloading and thus, yielding a higher RE. However, field-loaded GAC contains mainly strongly adsorbed NOM and electrochemical regeneration results in very little NOM desorption and only a small fraction of the adsorption sites are available for reloading. The low REs are still somewhat surprising given that

phenol-loaded GAC has much higher adsorption capacities and a significant fraction of the phenol adsorption is irreversible (Karimi-Jashni, 2001)

4.3.2 Iodine Number

As discussed in the literature review, the iodine number is a common method to determine the RE. Iodine number analysis was performed on virgin, field-spent, electrochemically and thermally regenerated GAC to evaluate the RE and to compare with the previous research

Figures 4-11 and 4-12 show the effect of electrochemical and thermal regeneration on the iodine number for field-loaded GAC from Regina and Cincinnati, respectively. The figures show that the virgin GAC iodine numbers were over 1000, and are similar to those reported in the literature (Clark and Lykins, 1989). The manufacturer for Norit 830 GAC states that the minimum value for their GAC is 920. Figure 4-11 also shows a drop of 11, 38 and 43% for the thermally, electrochemically regenerated and spent (0 mA) for Regina GAC compared to the virgin GAC. The variability between repeats was 1%. Figure 4-12 shows a similar drop in the iodine number compared to the virgin GAC of 25, 46 and 51% for the thermally, electrochemically and spent (0 mA) Cincinnati GAC. Waer et al. (1992) also observed that field loading caused a decrease in the iodine number of approximately 30%.

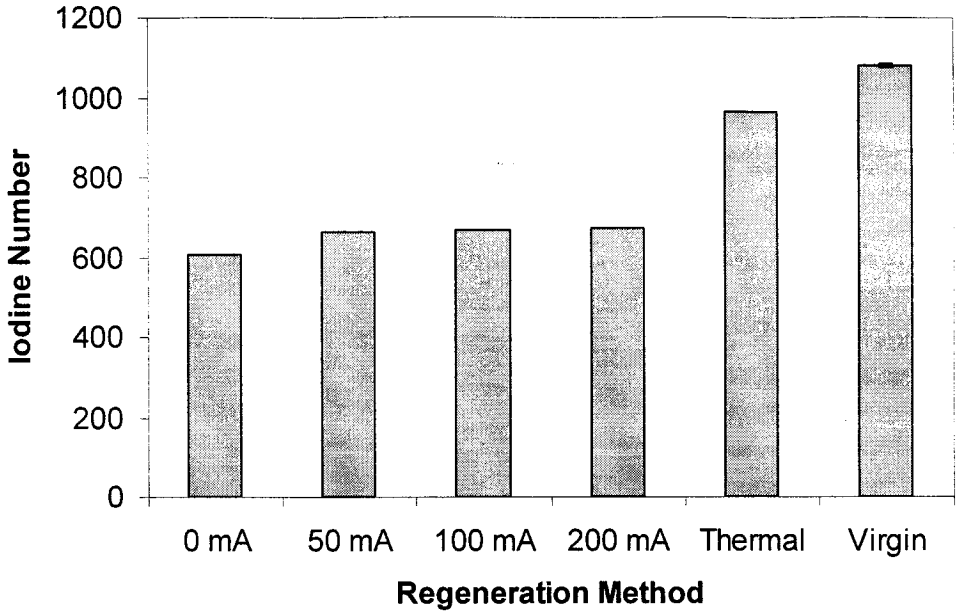

Figure 4-11 Iodine Number for Field-Loaded Regina GAC; Electrochemically Regenerated at Various Currents for 5 hrs; Field-Thermally Regenerated; and Virgin GAC

The values for the field-thermally regenerated GAC for both GAC sources were similar to those reported in the literature (Knappe et al., 1992 and Waer et al., 1992).

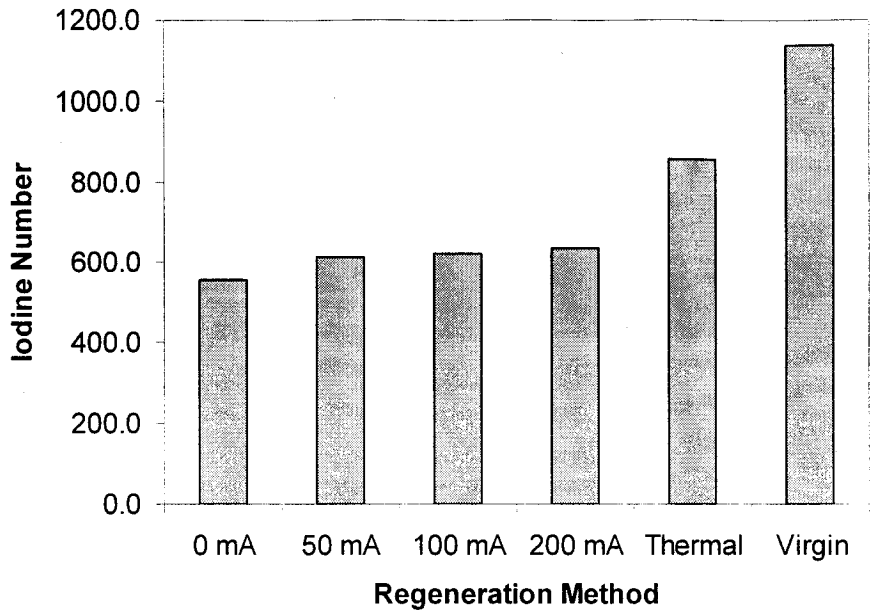

Figure 4-12 Iodine Number for Field-loaded Cincinnati GAC; Electrochemically Regenerated at Various Currents for 5hrs; Field-Thermally Regenerated; and Virgin GAC

Figure 4.13 compares the NOM adsorption RE with iodine number RE for field-loaded GAC from Regina. As the current was increased the iodine RE increased from 57 to 63% (see Section 3.6.2), while the NOM adsorption RE varies from 8 to 20%. It should be noted that the iodine RE, for NOM-loaded GAC, were lower in this study than those reported by Karimi-Jashni (2001), where the REs ranging from 70 to 75% for F-300 GAC under the same regeneration conditions.

The difference in the results of this study compared to Karimi-Jashni (2001) may be because they were different GACs or that the spent GAC may have undergone previous field-thermal regenerations, which would reduce its iodine number. As

shown, calculating the RE according to the iodine number greatly overestimates the RE for the target substances.

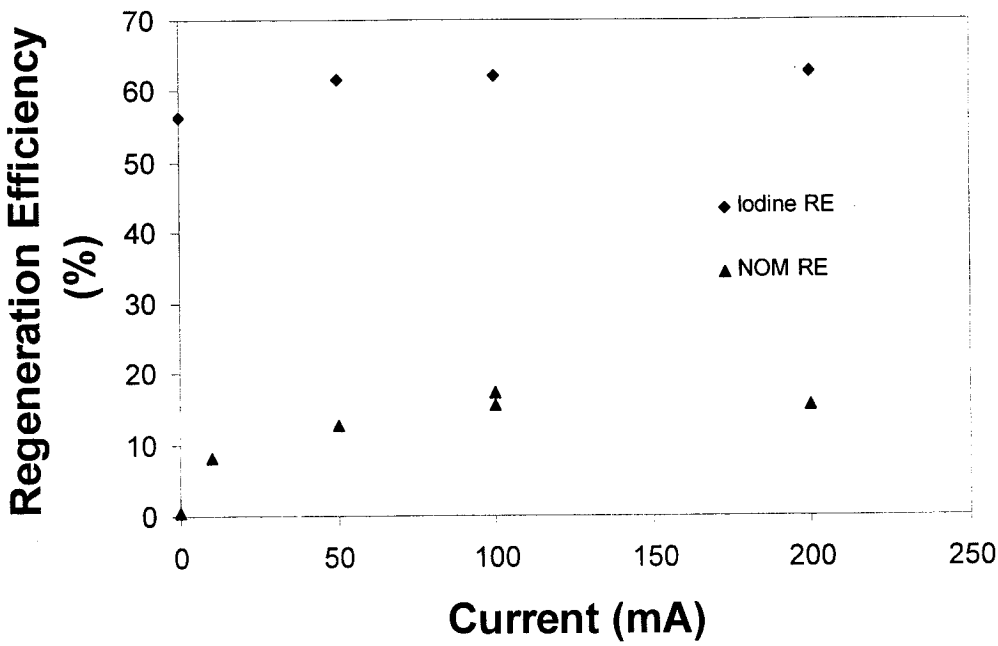

Figure 4-13 Comparison of the Regeneration Efficiency of Regina GAC at Various Currents for Iodine and NOM; Cathodic Regeneration for 5 hours

The overestimation of the RE may be due to the difference in the molecular size of iodine compared NOM. Iodine has a very small molecular size (0.22 nm) and can access deeper into the micropores as compared to NOM (ranges from 0.7 to 1.62 nm) that is adsorbed in the micro and mesopores (Newcombe et al., 1997, and Moore et al., 2001). Even with little or no regeneration of the pores containing NOM, iodine can still adsorb on other pores that are too small for NOM to access. The iodine number alone is not a good indicator of the RE for this type of application, as it measures different parameters.

4.3.3 Pore Size Distribution and Surface Area

As discussed in Section 2.4.2, pore size distribution and surface area analysis are factors that are affected by regeneration. Also, the impacts of electrochemical regeneration on these parameters have not been investigated. Therefore, virgin, field-spent, thermally and electrochemically regenerated GAC samples were sent to NRC laboratories for analysis for BET surface area and pore size distribution analysis. Figure 4-14 and 4-15 show the results of the pore size distribution (as Pore volume versus pore diameter graphs) for Regina and Cincinnati GAC, respectively. The virgin GACs (shown by the '+' sign) had a large pore volume that is mainly in the micro pore region (less than 2 nm), with little volume in the meso (2 – 50 nm) and macro (greater than 50 nm) pore regions. The thermally regenerated GACs (shown by the 'X' sign), on the other hand, have lower micro pore volume and greater meso and macropore volume. This decrease in micropore volume was also seen by other researchers (Moore et al., 2001; Moore et al., 2003).

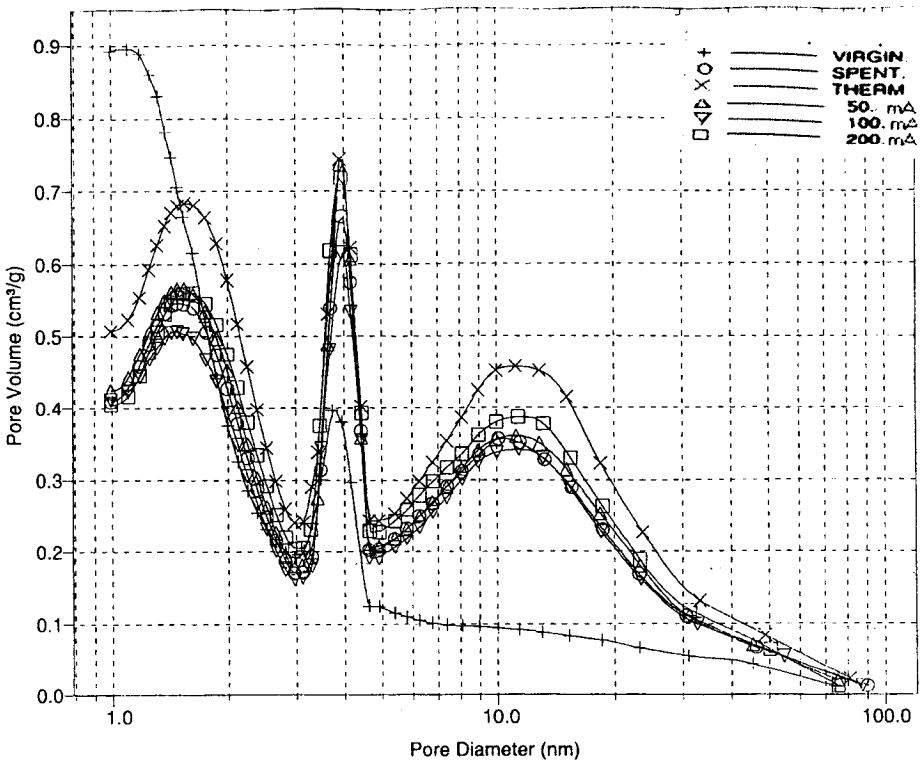

Figure 4-14 Pore Size Distribution for Regina GAC

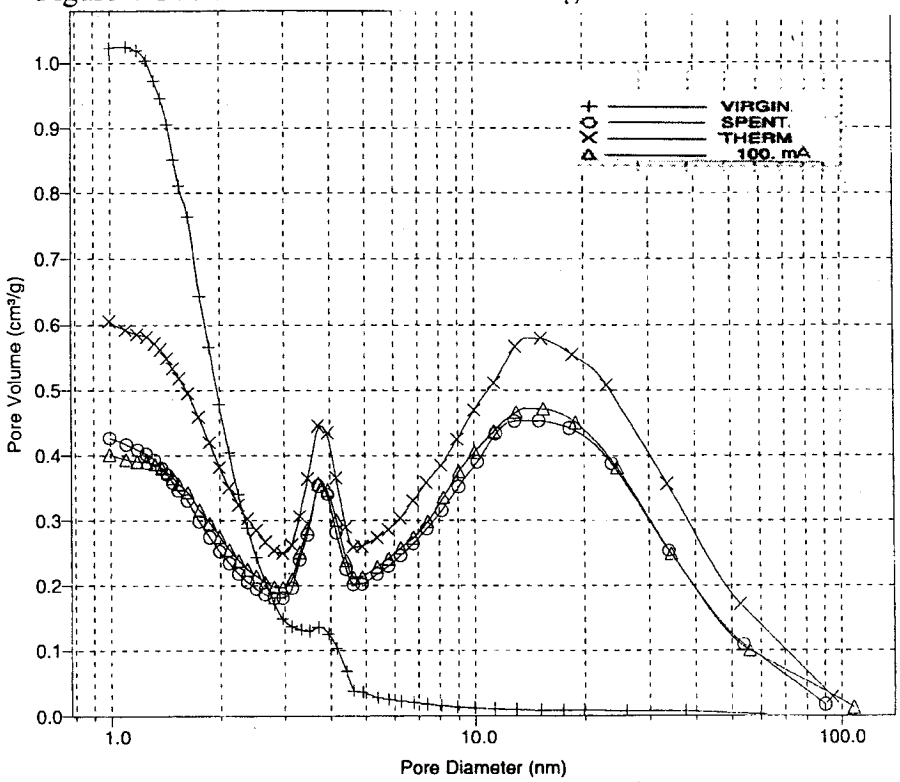

Figure 4-15 Pore Size Distribution of Cincinnati GAC

The electrochemical and the field-spent (non-treated) GACs had essentially the same pore volume distribution. However it can be seen in Fig 4-14, as the current was increased there was a slight increase in the pore volume distribution in the Regina GAC. Another interesting observation was that the shapes of the thermally, electrochemically regenerated and the field-spent GAC pore volume distributions were similar. The most likely explanation is that the spent GAC was previously thermally regenerated. Thus, it would be of interest to also study the pore size distribution of electrochemically regenerated GAC that was not previously thermally regenerated. It should be noted that both GAC sources were impacted similarly. It is worth noting that no other references have demonstrated a spike in the pore volume at approximately 4 nm. This may simply be due to the method of displaying the data; the above graphs display the pore volume cm^3/g (Moreno-Castilla et al., 1994; and Rychlicki et al., 1999), while some researchers (Korili and Gil, 2001) have chosen to display the pore volume in $cm^3/g/nm$, still others (Summers and Roberts 1987; Waer et al., 1992; Moore et al., 2003; and Ebie et al., 2001) display a cumulative pore volume, in doing so they flatten the graph (see Appendix E).

Figures 4-16 and 4-17 show the results of the Brunaur-Emmette-Teller (BET) surface area analysis for Regina and Cincinnati GACs, respectively. The results show that the virgin surface area was, as anticipated, high (996 and 990 m^2/g, respecitvely). The field-thermally regenerated GAC surface area was slightly lower (795 and 787 m^2/g). The electrochemically regenerated GAC surface area was lower still (654, 605, 654 and 559 m^2/g). The field-spent GAC (no-regeneration) surface

area was also low (614 and 556 m^2/g). When the iodine number is compared with the surface area analysis as seen in Figs 4-16 and 4-17, the iodine number closely matches the surface area for the virgin, field-spent, thermally and electrochemically regenerated GACs. Thus the iodine number was a good indicator of the surface area. This was observed for both GAC sources.

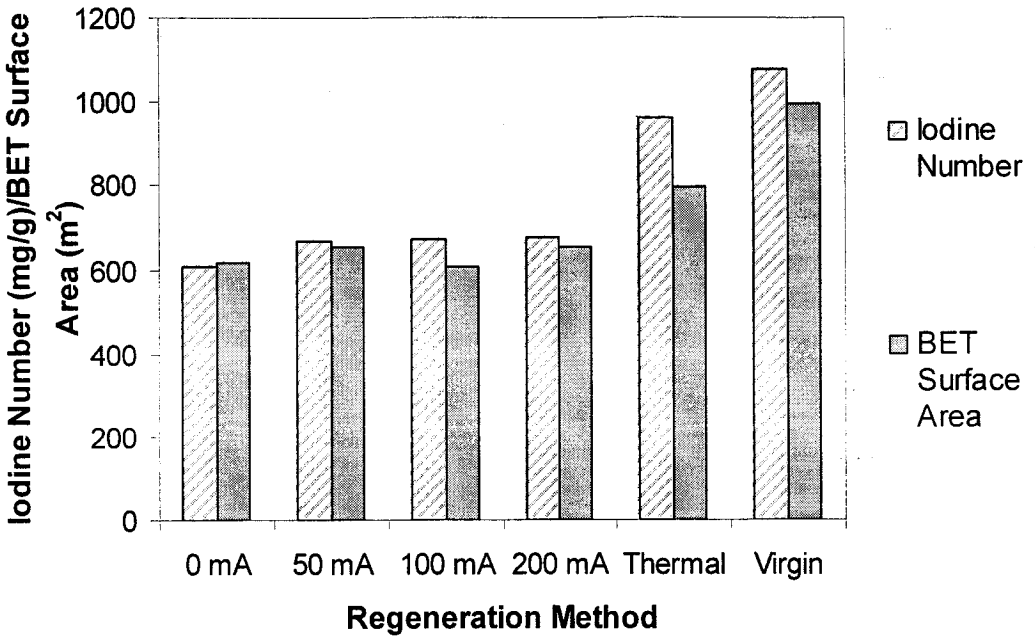

Figure 4-16 Regina GAC BET Surface Area and Iodine Number versus Regeneration Method

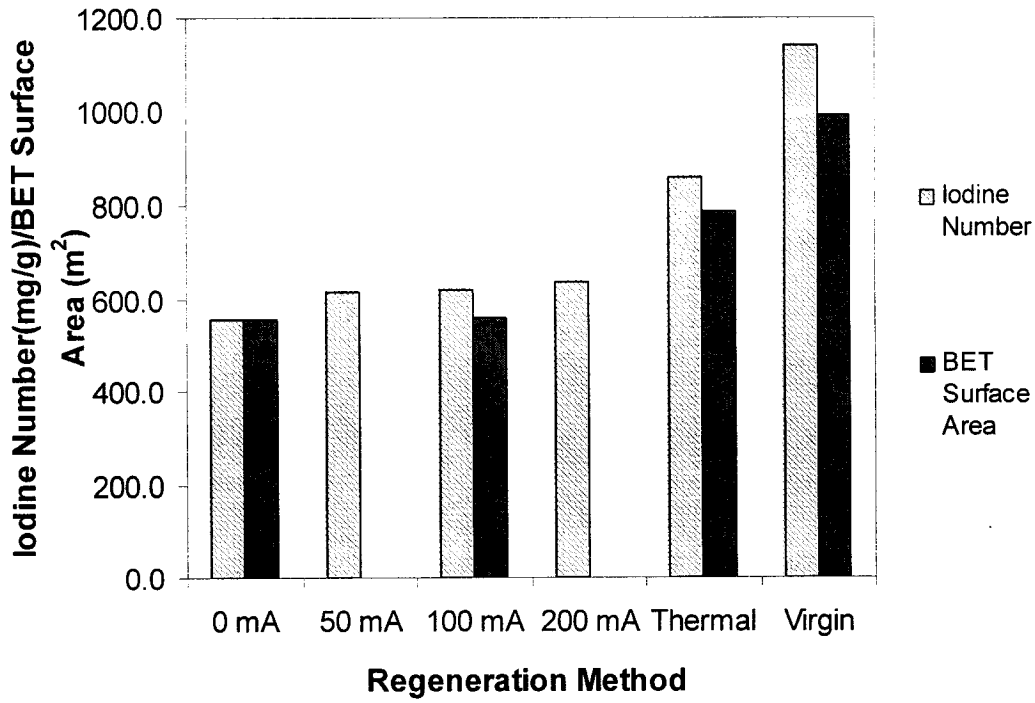

Figure 4-17 Cincinnati GAC BET Surface Area and Iodine Number versus Regeneration Method

4.3.4 Surface Chemistry

As discussed in Section 2.4.3, surface chemistry may have a significant impact on the adsorption capacity of GAC. The surface chemistry of virgin, thermally regenerated and electrochemically regenerated GAC was evaluated. The results of the surface chemistry analysis for Regina and Cincinnati GACs are displayed in Figs 4-18 to 4-23. The figures show the change in surface acid concentration with the addition of current. A negative value for the current indicates cathodic regeneration. A negative value for the surface acid concentration indicates that the regenerated GAC was less acidic that the base solution. The error bars shown on each figure indicates the variability of the repeats for each sample.

The surface acid groups were divided into strong acid, weak acid and phenolic acid groups. Figures 4-18 and 4-19 demonstrate that the strong acid group's concentrations decreased slightly with electrochemical treatment for both Regina and Cincinnati GAC at 100 mA. In Fig 4-18 it also appears that the surface acidity decreases as the current is increased from 100 to 200 mA for the Regina GAC. The surface acidities of thermally regenerated GAC for both Regina and Cincinnati were only slightly lower than the virgin GACs.

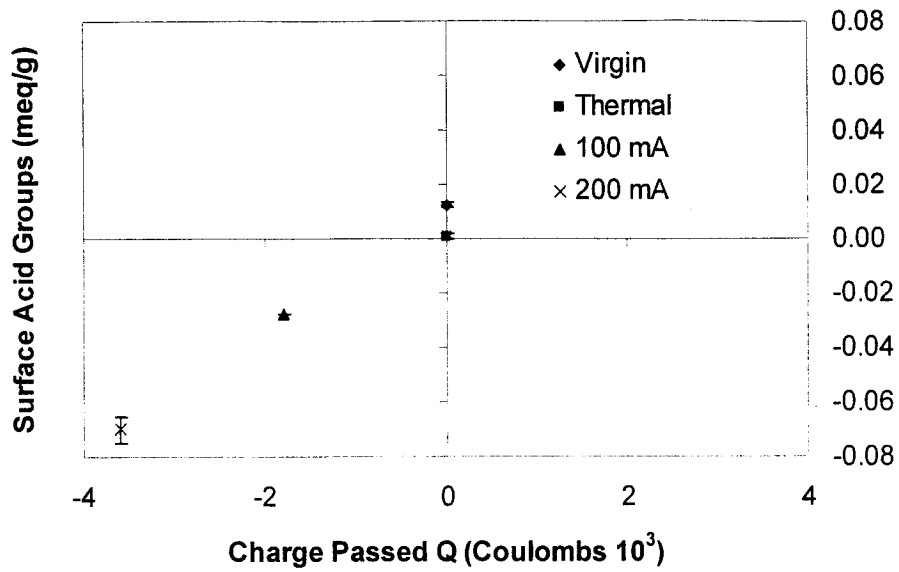

Figure 4-18 Effect of Current Intensity on the Strong Surface Acid Groups for Field-Loaded Regina GAC

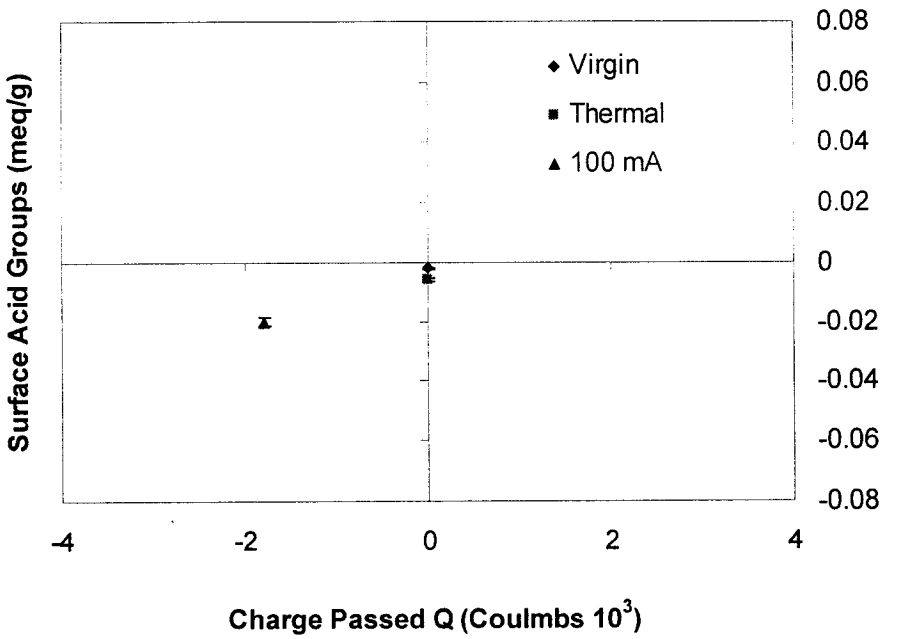

Figure 4-19 Effect of Charge on the Strong Surface Acid Groups for Field-Loaded Cincinnati GAC

In Figs 4-20 and 4-21 the weak acid group concentrations for the virgin and electrochemically regenerated GAC have overlapping confidence values; therefore there is essentially no change in the weak acid concentration due to electrochemical treatment, for both Regina and Cincinnati GAC. The same could be said for the thermally regenerated GACs for both sources.

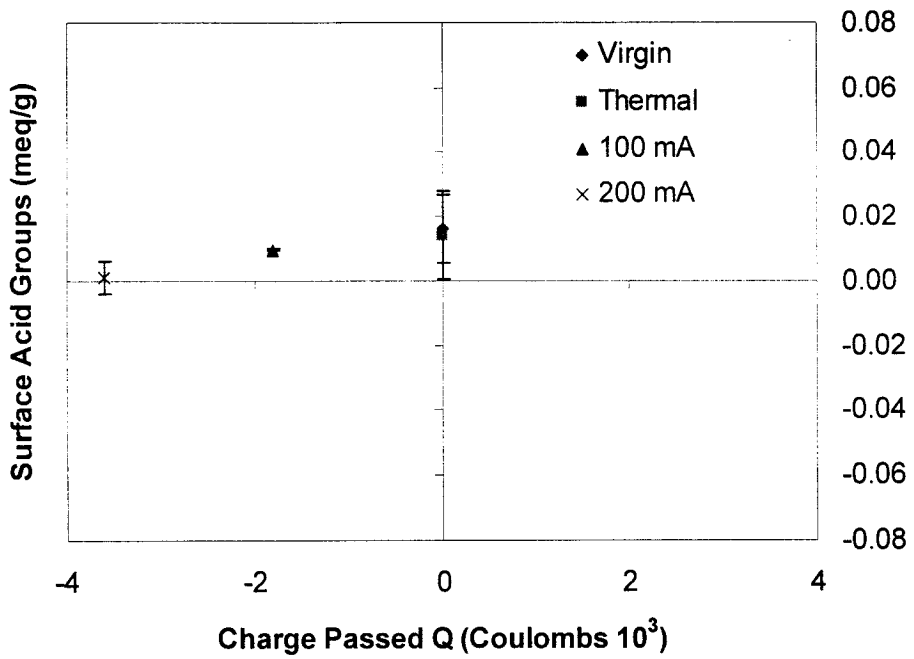

Figure 4-20 Effect of Charge on the Weak Surface Acid Group for Field-Loaded Regina GAC

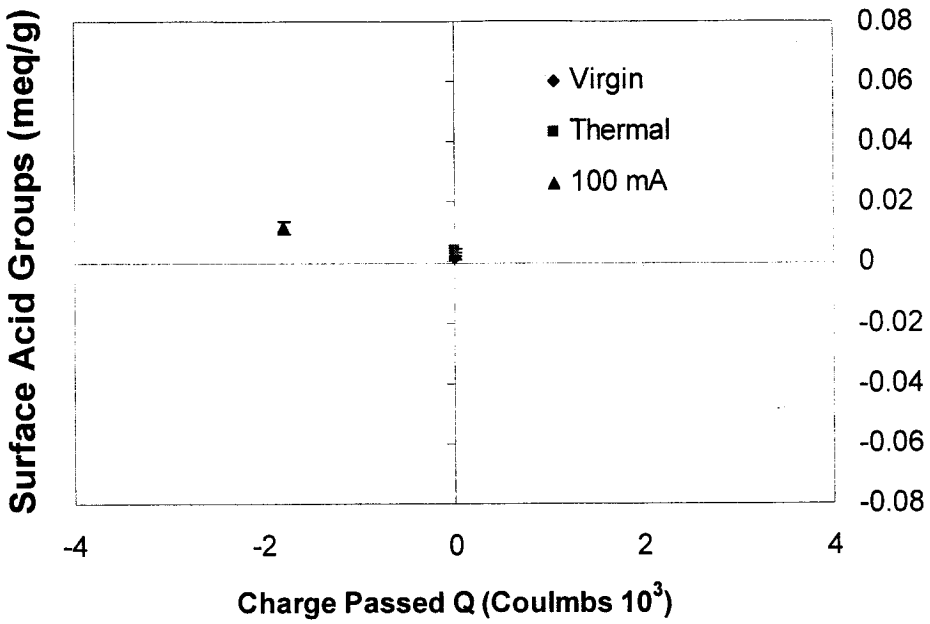

Figure 4-21 Effect of Current Intensity on the Weak Surface Acid Groups for Field-Loaded Cincinnati GAC

Figure 4-22 shows that the phenolic acid groups on the electrochemically regenerated and virgin Regina GAC have overlapping error bars, thus their values are essentially the same. However there is a slight decrease in the thermally regenerated phenolic acid groups for Regina GAC. In Fig 4-23 the Cincinnati GAC had a slight decrease in phenolic acidity for the thermal and a slight increase in the phenolic acid group for the electrochemically regenerated GAC.

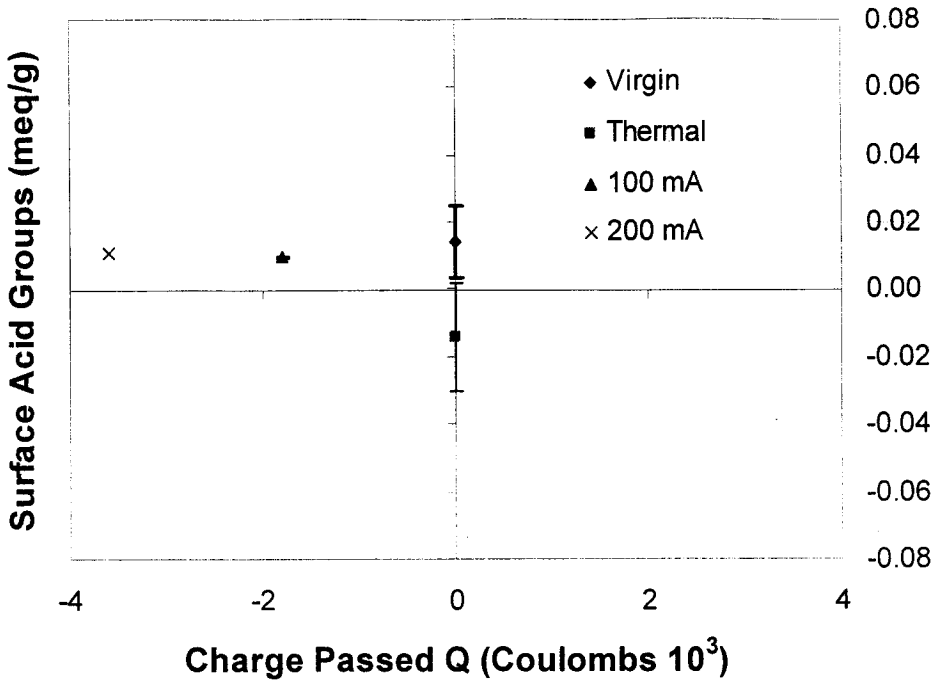

Figure 4-22 Effect of Current Intensity on the Phenolic Acid Groups for Field-Loaded Regina GAC

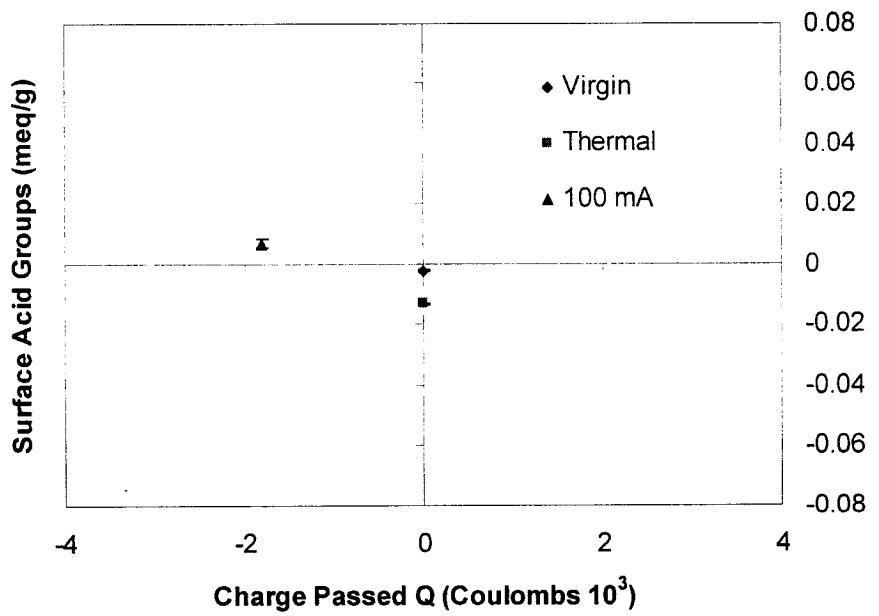

Figure 4-23 Effect of Current Intensity on the Phenolic Acid Group for Field-Loaded Cincinnati GAC

These results show a slight overall decrease in surface acidity due to cathodic regeneration which agrees with the findings of Metha and Flora (1997). However, the magnitudes of the decreases in some cases were approximately 10 fold smaller than those reported by Metha and Flora (1997). This may be due to the difference in test conditions. Metha and Flora (1997) performed the Boehm titrations on electrochemically treated virgin GAC and the electrochemical treatments were of longer duration (12 vs 5 h). This study investigated electrochemically treated spent GAC that may have undergone previous thermal regenerations. These differences may be the source for the difference in magnitude of the two studies.

These results may suggest that the change in surface chemistry is responsible for the decrease in adsorption. However, Coughlin and Ezera (1968) reported an increase in phenol adsorption capacity with a decrease in surface acid groups. Those findings were disputed by Metha and Flora (1997); they reported a decrease in the phenol adsorption capacity with cathodic treatment. Karimi-Jashni (2001) also observed a decrease in adsorption capacity with cathodic regeneration. He theorized that the decrease was due to hydroxide ions trapped in the pores of the GAC. To counter this he added 0.05 M of phosphate buffer to the reloading solution. Since this same buffering procedure was implemented in all NOM reloading in this study, the change in surface chemistry would not be the sole reason for the dramatic reduction in RE. Salvador and Jimerez (1999) demonstrated that changes in the textural

characteristics had more of an impact on the adsorption capacity than small changes in the acid-base characteristics on the GAC surface.

5 Conclusions and Recommendations

5.1 Conclusions

1. Electrochemical regeneration was ineffective for the regeneration of field-loaded GAC.
2. Batch pre-loading of regenerated GAC with NOM solution yields much higher regeneration efficiencies but they are not representative of what can be achieved by column systems. Thus, for GAC systems treating waters whose main organic contaminant is NOM, loading and reloading to assess regeneration efficiency should be conducted via column loading.
3. Iodine number was not a good indicator of the electrochemical regeneration efficiency.
4. Surface chemistry analysis showed that electrochemical regeneration caused a slight decrease in the surface acidity. It does not seem plausible that such small changes could cause the large drop in adsorption capacity.
5. Electrochemical regeneration did not appear to change the pore size distribution of the spent-GAC which probably explains the substantial loss in adsorption capacity.
6. Thermal regeneration impacted the pore size distribution and surface area with a loss of microporosity and an increase in meso and macro porosity.
7. GAC from both sources impacted similarly by electrochemical regeneration.

5.2 Recommendations for Future Work

1. Investigate the effect of time on the regeneration efficiency for an undivided reactor. An undivided reactor is recommended because of the large gas generation and the expected problems caused by gas accumulation below the ion exchange membrane
2. Investigate the effect of loading on laboratory column-loaded GAC for either NOM or phenol on the electrochemical regeneration efficiency.
3. Investigate the effect of electrochemical regeneration on the surface area and pore size distribution on laboratory column-loaded GAC (phenol or NOM), to eliminate effect of previous regenerations seen in field-loaded GAC.

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7 Appendices

Appendix A

Table A-1 Regina GAC Isotherm Data

										y	x	xy	x^2
Bottle #	Wt of Bottle (g)	Wt of Bottle + Water (g)	Volume (L)	GAC (g)	Actual Mass of GAC (g)	V/M	C_e (TOC mg/L)	% Standard Deviation	q_e (mg/g)	Log (q_e)	Log(C_e)		
							3		3				
10	293.7	812.7	0.519	0.0021	0.0026	200.39	2.452	0.013	25.6	1.4087	0.3895	0.548757	0.15174
1	285.2	756.9	0.472	0.0119	0.0101	46.56	2.110	0.012	21.9	1.3401	0.3243	0.434583	0.105172
2	272.2	746.3	0.474	0.0172	0.0148	32.08	1.975	0.031	19.4	1.2877	0.2957	0.380712	0.087412
3	270.7	749.4	0.479	0.0247	0.0278	17.21	1.716	0.019	14.9	1.1725	0.2345	0.274911	0.054975
4	306.4	840.3	0.534	0.0367	0.0399	13.38	1.483	0.018	14.7	1.1669	0.1710	0.199561	0.029249
5	281.7	752.2	0.471	0.0597	0.0586	8.04	1.157	0.022	11.4	1.0582	0.0634	0.067097	0.004021
6	272.7	751.1	0.478	0.1264	0.1742	2.75	0.525	0.013	5.6	0.7516	-0.2799	-0.21039	0.078357
7	283.4	754.9	0.472	0.2576	0.2395	1.97	0.473	0.031	4.1	0.6179	-0.3250	-0.2008	0.105596
8	267.9	749.5	0.482	0.4315	0.4136	1.16	0.352	0.008	2.6	0.4140	-0.4540	-0.18795	0.206072
9	279.1	753.7	0.475	1.0822	1.0183	0.47	0.175	0.009	1.1	0.0495	-0.7560	-0.03741	0.571491
10	302.6	839.3	0.537	2.5993	2.3427	0.23	0.164	0.013	0.6	-0.2569	-0.7857	0.201804	0.617303
11	296.2	829.3	0.533	4.0000	4.0180	0.13	0.144	0.038	0.3	-0.4906	-0.8404	0.412287	0.706327
12	272.5	750.4	0.478	-	0.0026	187.43	-		-				
13	282.5	754.3	0.472	-	0.0129	36.58	-		-	-	-	-	-
14	277.5	755.4	0.478	-	0.0039	123.16	-		-	-	-	-	-
15	303.1	836.4	0.533	-	0.5043	1.06	-		-	-	-	-	-
										9.0102	-1.1221	1.4709	2.0114
										a	0.947632		
										b	1.25993		
										n	11		
										k=	8.864051		

Table A-2 Cincinnati GAC Isotherm Data

										y	x	xy	x^2
Bottle #	Wt of Bottle (g)	Wt of Bottle + Water (g)	Volume (L)	GAC (g)	Actual Mass of GAC (g)	V/M	Ce (TOC mg/L)	% Standard Deviation	qe (mg/g)	Log (qe)	Log(ce)		
51	274.6	808.8	0.534		0.00546	97.84	1.3555		9.245769	0.9659	0.1321	0.127601	0.01745
36	268.7	750.8	0.482	0.0079	0.00762	63.27	1.260	0.031	12.04196	1.0807	0.1003	0.108346	0.010051
55	277.3	809	0.532		0.01191	44.64	1.187	0.032	11.72561	1.0691	0.0746	0.079728	0.005561
41	271.4	808.8	0.537	0.0172	0.01726	31.14	1.166	0.033	8.832453	0.9461	0.0668	0.06322	0.004465
42	275.4	810.3	0.535	0.0247	0.0267	20.03	1.078	0.019	7.446279	0.8719	0.0328	0.028559	0.001073
44	275.6	808.7	0.533	0.0597	0.06122	8.71	0.742	0.022	6.169227	0.7902	-0.1299	-0.10264	0.016871
45	270.4	804.3	0.534	0.1264	0.12611	4.23	0.541	0.039	3.850825	0.5856	-0.2672	-0.15646	0.071398
46	275.7	808.8	0.533	0.2576	0.26021	2.05	0.224	0.040	2.512767	0.4002	-0.6507	-0.26039	0.42344
47	269.4	802.9	0.533	0.4315	0.43606	1.22	0.153	0.024	1.587374	0.2007	-0.8167	-0.1639	0.667048
48	277.8	808.2	0.530	1.0822	1.09359	0.49	0.140	0.022	0.63542	-0.1969	-0.8539	0.168161	0.729097
49	275.6	807.7	0.532	2.5993	2.52042	0.21	0.139	0.004	0.276889	-0.5577	-0.8586	0.478809	0.737108
										6.9104	-1.4580	-0.2759	1.2174
										a	0.907113		
										b	0.859788		
										n	9		
										k=	8.074454		

Table A-3 Regina GAC Kinetic Study

Sample #	GAC Mass (g)	V/M Ratio	Time (h)	Ce	% Standard Deviation	Ce/Co
35	1.0666	0.44002	0.3	3.18	2.48	1.00
47	0.9374	0.56914	0.6	3.02	2.58	0.94
36	1.0373	0.46476	1	2.73	3.06	0.85
45	0.9359	0.57053	1	2.83	3.42	0.88
38	0.9464	0.56077	1.5	2.60	2.40	0.81
44	0.9377	0.56849	2	2.32	1.64	0.73
37	1.0047	0.49643	3	1.79	2.13	0.56
42	0.9345	0.57242	4	1.83	3.01	0.57
43	0.9368	0.56908	5	1.82	1.98	0.57
46	0.9364	0.56932	9.5	1.21	5.55	0.38
61	0.9300	0.57766	26.5	0.75	3.70	0.23
56	0.9433	0.56175	48	0.57	2.30	0.18
51	0.9350	0.57134	73	0.67	2.90	0.21
53	0.9428	0.56234	168	0.63	2.52	0.20
50	0.9439	0.56131	192	0.56	3.38	0.18
58	0.9367	0.56921	216	0.53	2.38	0.16
55	0.9390	0.56618	336	0.55	1.75	0.17
39	0.9417	0.56493	531	0.40	2.55	0.13
40	0.9326	0.57491	696	0.12	4.21	0.04
54	0.9388	0.56703	1080	0.20	1.81	0.06
57	0.9440	0.56113	1200	0.10	1.96	0.03
49	0.9413	0.56530	1296	0.22	7.81	0.07
48	0.9448	0.56147	1296	0.22	2.03	0.07
59	0.9334	0.57299	1296	0.20	0	0.06
52	0.9362	0.57051	-	-		-
41	0.9284	0.57887	-	-		-
60	0.9344	0.57235	-	-		-

Table A-4 Cincinnati Kinetic Study

Sample #	GAC Mass (g)	V/M Ratio	Time (h)	Ce	Ce/Co
	-	-	0	1.5	1
10	0.9598	0.5408	0.3	1.32	0.88
19	1.0599	0.4449	0.6	1.24	0.82
11	1.0399	0.4581	1.0	1.08	0.72
24	1.0126	0.4720	1.5	0.97	0.65
15	1.0451	0.4581	2.0	0.89	0.59
21	1.0522	0.4510	3.0	0.80	0.53
18	1.0459	0.4575	4.0	0.66	0.44
24	1.0461	0.4569	7.5	0.48	0.32
19	1.0618	0.4441	9.5	0.40	0.27
14	1.0532	0.4502	30.5	0.27	0.18
15	1.0445	0.4583	31.5	0.31	0.21
64	1.0404	0.4622	48.0	0.13	0.09
20	1.0382	0.4638	52.0	0.24	0.16
17	1.0611	0.4434	72.0	0.23	0.15
26	1.0472	0.4563	96.0	0.24	0.16
25	1.0589	0.4456	120.0	0.24	0.16
13	1.0566	0.4464	144.0	0.14	0.09
68	1.0452	0.4556	144.0	0.13	0.09
64	1.0420	0.4615	192.0	0.14	0.09
71	1.0393	0.4632	216.0	0.09	0.06
65	1.0256	0.4760	264.0	0.13	0.09
67	1.0682	0.4400	912.0	0.16	0.11

Table A-5 Regina Field-Spent GAC Regeneration Efficiency

Regina
Field-Spent GAC Reloading

#	Adsorbate Volume (L)	Current (mA)	Coloumbs	GAC Mass (g)	Ce	qe (Mass Balance)	qe Freundlich (mg/g)	RE	RE4	Catholyte pH
38	0.5307	10	180	1.14	3.09	0.10	36.65	0.27	-0.04	11.30
49	0.5321	50	1080	1.14	3.16	0.07	37.72	0.18	-0.08	11.90
53	0.5302	100	1800	1.14	2.72	0.27	31.32	0.86	0.11	12.00
55	0.5317	200	2115	1.14	2.22	0.50	24.22	2.08	0.32	12.00
59	0.5348	-	-	-	3.301					
32	0.4798	10	180	0.6711	1.18	0.88	10.93	8.0	51.2	11.18
40	0.53614	50	900	0.6518	1.03	1.14	9.17	12.4	61.2	12.06
52	0.53412	100	1800	0.6621	0.92	1.20	8.01	15.0	67.4	12.30
53	0.5302	100	1800	0.6494	0.88	1.24	7.60	16.4	69.8	12.45
56	0.52992	200	3600	0.6429	0.93	1.22	8.14	14.9	66.9	12.73
54	0.53233	-	-	-	2.409					

Table A-6 Regina Bottle-Loaded GAC Regeneration Efficiency

Regina Batch-Loaded GAC	Bottle Volume	Current mA	Coloumbs	GAC Mass (g)	Ce	qe (Mass Balance)	qe langmuir	RE3	RE4
32	0.4798	10	180	1.08	0.20	1.22	1.89	64.35	98.07
32	0.4798	10	180	1.08	0.24	1.20	2.41	49.83	96.55
33	0.4714	50	900	1.07	0.22	1.20	2.14	56.00	97.31
39	0.5320	100	1800	1.06	0.23	1.36	2.24	60.42	97.46
41					2.93				
55	0.53167	10	180	0.60061	0.32	1.79	2.06	87.1	88.6
41	0.53742	50	900	0.60416	0.32	1.80	2.08	86.5	88.0
39	0.53198	100	1800	0.60256	0.33	1.77	2.15	82.4	83.4
33	0.47137	200	3600	0.60171	0.31	1.59	2.01	79.1	79.0
control	2.340571			2.892733					

Table A-7 Cincinnati Field-Loaded GAC Regeneration Efficiency Data

Sample Number	Volume (L)	Current (mA)	GAC Mass	Ce (mg/L)	Qe (mg/g)	Freundlich q	RE3	Catholyte pH
21	0.4746	10	0.82231	0.6119	0.512549	5.28955	9.689849	-
25	0.4718	50	0.83846	0.4064	0.615419	3.7202636	16.54235	12.00
26	0.4779	100	0.87976	0.4089	0.592654	3.7399367	15.84662	12.35
20	0.4816	200	0.85016	0.3915	0.627893	3.6026565	17.4286	12.67
15				0.9942				
17				0.9497	0.97195			

Table A-8 Regina GAC Thermally Regeneration Data

Thermal Regenerated GAC

Bottle #	Volume (L)	Mass	Ce	Qe	Freundlich	RE3	RE4
39	0.5320	1.20206	0.13	1.27	1.14	111.25	113.20
58	0.5332	1.20192	0.13	1.27	1.11	115.12	113.20
59	0.5348	1.20280	0.13	1.28	1.13	113.20	113.20
55	0.5317	1.20011	0.13				113.20

Table A-9 Regina Field-Spent (Non-Regenerated) Reloading Data

Bottle #	Volume (L)	Mass	Ce	Qe	Freundlich	RE3
33	0.47137	1.14	3.13	-0.06	51.19	-0.11
41	0.53742	1.14	2.48	0.25	38.64	0.64

Table A-10 Regina GAC Regeneration Observations

Current (mA)	Colour	Catholyte pH	Catholyte TOC
50	yellow	11.92	34.24
100	yellow	12.33	82.29
200	yellow	12.47	69.83

Table A-11 Cincinnati Thermally Regeneration GAC Data

Sample Number	Volume (L)	Current (mA)	GAC Mass	Ce (mg/L)	Qe (mg/g)	Freundlich q	RE3
34	0.4808	0.6021	-	0.1351	1.090002	1.442903	75.5423
64	0.4808	0.6033	-	0.1173	1.102057	1.2778204	86.24507
68	0.4762	-	-	1.115			

Table A-12 Alternative Regeneration Method Data

Undivided Cell Reactor

Sample Number	Volume (L)	Current (mA)	GAC Mass (g)		Ce (mg/L)	q	Freundlich	RE	Catholyte pH
60	0.5348	100	0.6541	1	0.921	-0.75	8.0	8.2	12.40
50	0.530	100	0.6623	2	1.305	-1.04	12.4	2.7	14.00
53	0.530	100	0.6218	3	1.762	-1.50	18.1	-0.2	13.95

1 NaCl BP GAC undivided Cell no recycle
2 BP GAC 1 M Na2SO4, 1 M NaOH 0.5 Recycle
3 BP GAC 1 M Na2SO4, 1 M NaOH 0.5 Recycle with O2 bubbling

Table A-13 Regina GAC Iodine Number Analysis Data

GAC Mass (g)	Titrant Volume (mL)	X/M	C	Iodine No.
Regina Virgin GAC				
0.83989	17.375	1431.02592	0.03807	
1.21744	9	1044.6345	0.01972	
1.09232	10.1	1155.890355	0.02213	
		3631.550776	0.079919	
				1079.819
Thermal				
0.9917	14.925	1093.320613	0.029519	
1.1133	10.875	1005.86737	0.021509	
1.2034	9.75	938.7711216	0.019284	
		3037.9591	0.0703	
				964.5796
Field spent GAC 200 mA				
1.1147	17.875	953.1033171	0.035501	
1.2268	15.75	881.295939	0.031281	
1.2989	14.7	839.5090934	0.029196	
		2673.90835	0.095978	
				677.0101
Field spent GAC 100 mA				
1.1058	18.15	958.5800778	0.036048	
1.2264	15.75	881.5833806	0.031281	
1.3355	14.3	819.144662	0.028401	
		2659.30812	0.09573	
				671.747
Field spent GAC 50 mA				
1.166	16.95	918.1696861	0.033664	
1.3321	14.305	821.2022967	0.028411	
1.2391	15.8	868.8222894	0.03138	
		2608.194272	0.093456	
				664.8679
Field spent GAC No Regeneration				
0.9418	21.75	1087.573687	0.043018	
1.1171	18.8	940.1106719	0.037184	
1.2261	16.4	873.734349	0.032437	
		2901.4187	0.1126	
				609.206

Table A-14 Cincinnati GAC Iodine Number Analysis Data

	GAC Mass (g)	Titrant Volume (mL)	X/M	C	Iodine No.
Virgin					
	0.9981	8.6	1150.387	0.017177	
	1.1602	0.55	1051.225	0.001099	
	1.376	2.9	871.2054	0.005792	
			3072.817	0.024068	
					1138.971
Thermal					
	1.0079	16	1074.054	0.031957	
	1.1283	13.6	978.3166	0.027164	
	1.2688	10.825	889.39	0.021621	
			2941.76	0.080742	
					857.3869
Field spent GAC 200 mA					
	1.069	19.95	932.5192	0.037829	
	1.3206	15.75	781.6477	0.029865	
	1.7344	9.9	623.5727	0.018773	
			2337.74	0.086467	
					637.3119
Field spent GAC 100 mA					
	1.0466	20.3	949.6604	0.038493	
	1.4002	14.65	743.8297	0.02778	
	1.7279	10.43	623.3345	0.019778	
			2316.825	0.08605	
					620.0243
Field spent GAC 50 mA					
	1.1943	18.2	851.0582	0.034511	
	1.3023	16.05	794.3872	0.030434	
	1.5717	12.6	676.7152	0.023892	
			2322.161	0.088838	
					614.819
Iodine # Field spent GAC 0 mA					
	1.0159	22.5	964.8543	0.042665	
	1.4588	15.55	712.0527	0.029486	
	1.6803	12.55	633.2289	0.023797	
			2310.136	0.095948	
					556.0473

Table A-15 Iodine Number Regeneration Efficiency

Regina GAC

Regeneration Method	Iodine Number	Iodine RE
0 mA (Spent)	609.2	56.4
50 mA	664.9	61.6
100 mA	671.7	62.2
200 mA	677.0	62.7
Thermal	964.6	89.3
Virgin	1079.8	100.0

Cincinnati GAC

Regeneration Method	Iodine Number	Iodine RE
0 mA (Spent)	556.0	48.8
50 mA	614.8	54.0
100 mA	620.0	54.4
200 mA	637.3	56.0
Thermal	857.4	75.3
Virgin	1139.0	100.0

Table A-16 Regina GAC Wet Volume Calibration Data

Crucible #	Wet volume teaspoons	Wet GAC + Cruible Mass	Dry GAC + Crucible Mass	Crucible Mass	Wet GAC	Dry GAC
55	0.25	10.80000	10.55686	10.29918	0.50082	0.25768
45	0.5	11.06484	10.40633	9.7171	1.34774	0.68923
35	0.75	11.87298	10.95833	10.0027	1.87028	0.95563
37	1	12.67826	11.36654	9.98186	2.6964	1.38468
41	0.25	12.56945	12.24587	11.9109	0.65855	0.33497
With Packing of GAC material into the 1/4 and 1/2 measuring teaspoons						
37	0.75	12.8032	11.22578	9.98242	2.82078	1.24336
35	0.75	12.33538	11.05147	9.98707	2.34831	1.0644
45	0.75	11.91428	10.82281	9.71768	2.1966	1.10513
41	0.75	14.37306	13.05889	11.9119	2.46116	1.14699
55	0.75	12.42021	11.9956	10.29899	2.12122	1.69661
					Average	1.13997
					Average Dev	0.055205
					% AVESTD	4.842671
					Std Dev	0.076732
				95%	Confidence	0.067257
					sample size = 1.13997+/- 0.225	
55	1	11.88009	13.27653	10.29882	1.58127	2.97771
41	1	13.45045	14.84986	11.91127	1.539177	2.938587
35	1	11.53121	13.0444	9.98707	1.54414	3.05733
45	1	11.41968	13.01901	9.7179	1.70178	3.30111
37	1	11.60884	13.25312	9.9826	1.62624	3.27052
					Average	3.109051
					Average Dev	0.141411
					% AVESTD	4.548361
					Std Dev	0.167289
				95%	Confidence	0.146632
					sample size = 3.109051+/- 0.146632	

Table A-17 Regina Electrochemically Regenerated GAC Wet Calibration

bottle #	Crucible	Wet Volume (tsp)	mass of crucible (g)	wet GAC+ crucible	dry GAC + crucible	dry GAC
32	41	0.5	11.9112	13.9721	12.5823	0.6711
40	37	0.5	9.9827	12.1860	10.6345	0.6518
52	35	0.5	9.9890	12.2951	10.6511	0.6621
53	1	0.5	9.9521	12.1383	10.6015	0.6494
56	55	0.5	10.2994	12.6158	10.9423	0.6429

Average	0.65546
Average Dev	0.008912
% AVESTD	1.359656
Std Dev	0.011142
Confidence	0.009766

sample size = 0.6555 +/- 0.0098

Table A-18 Surface Functional Group Analysis Data

Regina GAC					
Current Applied (C * 10^3)		Strongly acid	Weak acid	Phenolic	Overall Decrease
0	Virgin	0.012471	0.016161	0.014035	
	Average	0.012015	0.014953	0.012936	
	Stdev	0.001109	0.008996	0.01084	
0	Thermal	0.000838	0.014216	-0.01422	0.0418
		0.000291	0.015084	-0.01727	
	Stdev	0.000851	0.013794	0.016023	
-3.6	200 mA	-0.06992	0.000999	0.010931	0.1007
	Average	-0.06994	0.00125	0.011461	
	Stdev	0.004953	0.004953	0	
-1.8	100mA	-0.02742	0.009731	0.009712	0.0506
	Average	-0.02742	0.009601	0.009944	
	Stdev	0	0.000185	0.000378	

Cincinnati GAC					
Current Applied (C * 10^3)		Strongly acid	Weak acid	Phenolic Acid	Overall Decrease
0	Virgin	-0.00186	0.001631	-0.00219	
	Average	-0.0018	0.001565	-0.00219	
	Stdev	0.000251	0.000578	0.000317	
0	Thermal	-0.00578	0.003957	-0.01311	0.0125
	Average	-0.00617	0.004348	-0.01311	
	Stdev	0.000552	0.000736	0.000336	
-1.8	100 mA	-0.02004	0.011567	0.006978	-0.0009
	Average	-0.02004	0.011567	0.006978	
	Stdev	0.001405	0.002111	0.001411	

Table A-19 Phenol-Loaded GAC Analysis Data

Multi-Layer Phenol Regeneration With High pH Pre-Treatment

	Bottle #	Sample Mass	Time (Hrs)	Current Applied (Columbs)	Cathode pH	Leaching solution pH	Ce (mg/L)	Freundlich qe (mg/g)	Qe Reload (mg/g)	RE3	RE1
	8	5.0699	4.5	1600	12	12.4	64.28	83.92111	90.30532	78.26244	96.47881
	6&7	15.05682	4.5	1600	11.7	12	67.93	88.68639	82.44246	70.41784	95.03735
	1&5	20.06555	4.5	1600	12	12	85.025	111.0049	86.20983	69.41447	93.36015
*	4	10.02935	4.5	1800	12.3	-	72.4	94.52222	87.47453	73.47411	94.76916

* Sample was not pre soaked with NaOH instead the regeneration solution was swiched from NaCl to NaOH

Phenol Single layer Regeneration

Bottle #	volume L	Mass GAC g	V/M	Current	Inital Loading Phenol (mg/l)	qe (mg/g)	Reloading Phenol (mg/l)	qe (mg/g)	RE 1	RE3
31	0.51847	1.20483	0.430326	0	56.4	96.33252	187.6083	41.40575	42.98212	28.97773
14	0.47413	1.2045	0.393632	10	40.31556	94.44957	93.06	75.09234	79.50522	63.21295
10	0.519	1.20105	0.432122	50	47.60056	100.5369	75.16083	90.16956	89.688	80.29853
22	0.5367	1.20233	0.446383	50	58.00583	99.21021	73.07194	94.07788	94.82681	84.40334
21	0.47458	1.2019	0.394858	100	44.14083	93.23328	61.60917	87.74483	94.1132	82.3406
30	0.51915	1.2019	0.431941	200	49.06278	99.86326	74.62556	90.36304	90.48677	80.62248

							y	x	xy	x^2	
Bottle #	volume (L)	Mass GAC g	V/M	TOC	Phenol Ce	qe (cc adjusted)	Log (qe)	Log(ce)			Q Freundlich
16	0.53391	0.0513	10.4076	205.3	268.0306	127.2715	2.104731	2.428184	5.110675	5.896079	156.9667
26	0.47786	0.2168	2.204151	164.4	214.6333	144.6495	2.160317	2.331697	5.037205	5.436812	148.0442
27	0.53333	0.44351	1.202521	127.1	165.9361	137.476	2.138227	2.219941	4.746737	4.928138	138.3418
24	0.47795	0.85537	0.558764	58.15	75.91806	114.1785	2.057584	1.880345	3.868969	3.535698	112.5898
23	0.53314	0.629	0.847599	95.19	124.2758	132.2115	2.121269	2.094387	4.442758	4.386456	128.1978
23	0.53314	0.629	0.847599	98.86	129.0672	128.1503	2.10772	2.110816	4.449008	4.455544	129.4817
25	0.47184	1.0134	0.465601	43.55	56.85694	104.0163	2.017102	1.754784	3.539577	3.079265	104.3337
12	0.53311	1.19965	0.444388	37.98	49.585	102.5089	2.010761	1.69535	3.408945	2.874213	100.6396
15	0.47872	1.21505	0.393992	28.87	37.69139	95.5698	1.980321	1.576242	3.121465	2.484539	93.6255
20	0.48156	1.43533	0.335505	20.82	27.18167	84.90873	1.928952	1.434276	2.76665	2.057148	85.90102
20	0.48156	1.43533	0.335505	21.83	28.50028	84.46633	1.926684	1.454849	2.803034	2.116586	86.97962
19	0.47153	-	-	220.7	288.1361	-	-	-	-	-	-
13	0.47169	-	-	208.5	272.2083	-	-	-	-	-	-
17	0.4705	-	-	214.8	280.4333	-	-	-	-	-	-
18	0.47845	-	-	0.0783	0.102225	-	-	-	-	-	-
11	0.47634	1.9885	0.239547	1.657	2.163306	-	-	-	-	-	-
							20.44894	18.55269	38.18435	35.3544	
							a	1.55619			
						1/n=	b	0.263414			
							n	10			
							Cn	0.2			
						k=	10^a	35.99068			

Appendix B
Porosity by Nitrogen Adsorption

Provided by Steve Argue, National Research Council

The Micromeritics ASAP 2000 Accelerated Surface Area and Porosimetry Analyzer was calibrated for pressure and manifold volume prior to analyses. A nitrogen adsorption standard, pelletized silica-alumina was run to ensure that the instrument was providing accurate results.

Sample tubes were cleaned with soap and water and then with acetone and allowed to thoroughly dry. The tubes were then placed onto the thermal desorption ports of the analyzer and evacuated while being heated to 120 ^{O}C. When the instruments base pressure of 1 umHg was achieved the tubes were back filled with helium and weighed.

Samples of carbon were analyzed as received by adding approximately 500 mg to 750 mg to the sample tubes. The samples were placed onto the thermal desorption ports of the instrument and evacuated at 120 ^{O}C until at least the base pressure of 1 umHg was achieved. In some instances the samples were degassed for a longer period of time while they were waiting to be analyzed.

The samples were back filled with helium after thermally desorbing and then re-weighed. The sample mass was calculated by subtracting the empty sample tube weight from the weight of the sample tube with sample. The sample tube was then transferred to the analysis port of the instrument and the appropriate method files for nitrogen adsorption/desorption were invoked.

Appendix C
Phenol Regeneration

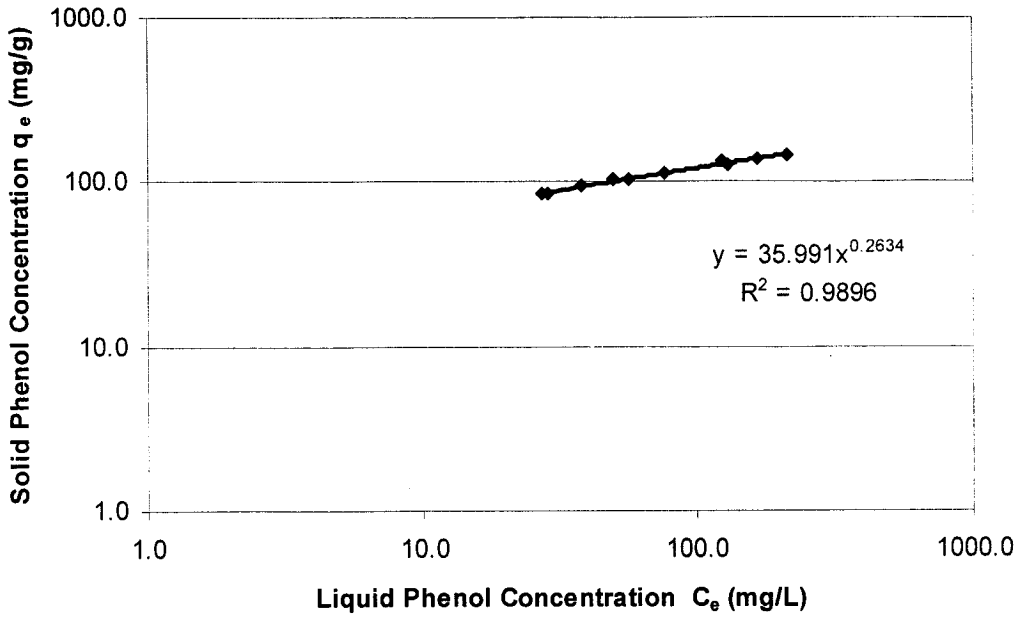

Figure C-1 Adsorption Isotherm for Phenol on Virgin F-400 GAC

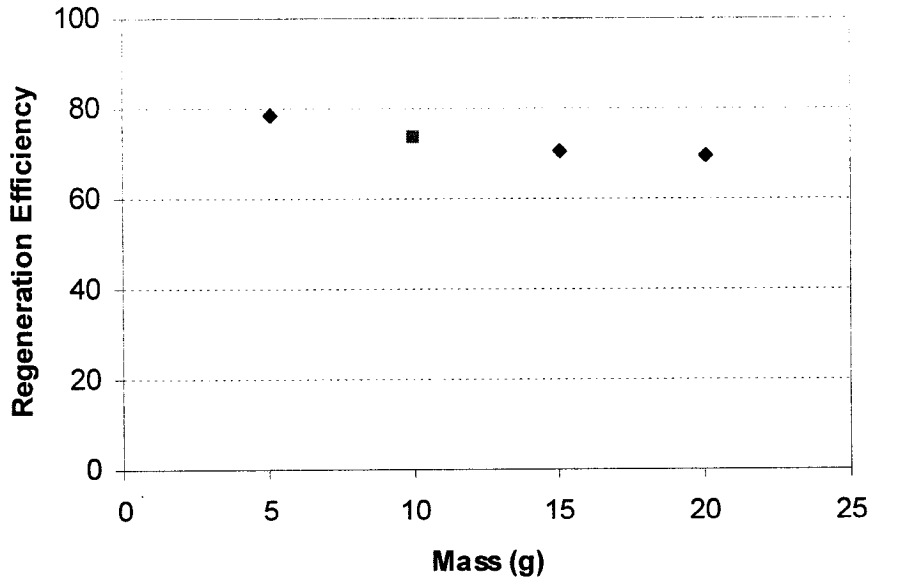

Figure C-2 Effect of Multi-Layer Regeneration on the Regeneration Efficiency of Phenol-Loaded F-400 GAC

Appendix D Water Quality Characteristics

Table D-1 Regina Water Quality Parameters (Source: www.regina.ca)

Regina Water Quality Parameters

Parameter	Testing Result Annual Average	Saskatchewan Environment Water Quality Objective
Sodium (Na)	36.2	<300.0
Sulphate (SO_4)	125.8	<500.0
Total Dissolved Solids (TDS)	329	<1500
Manganese (Mn)	<.0003 (High 0.0013)	<0.05
Nitrate (NO_3)	Low <0.004 (High 0.064)	<45.0
Potassium (K)	3.55	No Standard
Hardness	198.2 (13.9)	<800
Iron (Fe)	<.003 (High<0.10)	<0.30
Magnesium (Mg)	21.1	<200
Calcium (Ca)	44.4	No Standard
Chloride (Cl)	14.7	<250
Fluoride (Fl)**	0.15	<1.50

** No fluoride is added to Regina water. Fluoride measured is naturally occurring

Table D-2 Cincinnati Water Quality Parameters (Source: www.gcww.org)

Cincinnati Water Characteristics

Regulated Contaminants subject to a Maximum Contaminant Level (MCL), Action Level (AL) or Treatment Technique (TT)*					
Substance (units)	Maximum Allowed MCL*	(MCLG*)	Highest Compliance Level Detected	Range of Detections	Typical source of contamination
Fluoride (ppm)	4	4	1.09	0.91-1.09	May come from erosion of natural deposits. Additive to promote strong teeth
Nitrate (ppm)	10	10	1.96	0.73-1.96	Runoff from fertilizer use, leaching from septic tanks, sewage, erosion of natural deposits
Total Trihalomethanes (ppb)	80	na	32.9	20.2-46.3	Byproduct of drinking water disinfection, measured in distribution system
Haloacetic Acids (ppb)	60	na	8.73	5.76-12.4	Byproduct of drinking water disinfection, measured in the distribution system.
Gross Beta (pCi/L)	50	0	nd	nd	Decay of natural and man-made deposits (EPA considers 50 pCi/L to be the level of concern)
Turbidity (NTU)	TT1 <1 NTU Max and TT2 <0.3 NTU 95% of the time	na na	0.11 100% <0.3 NTU	0.04-0.11	Soil runoff
Lead[c] (ppb)	AL=15	0	*90th percentile* 5	nd-22.6 (1 out of 112 samples tested were > AL)	May come from erosion of natural deposits. There is no detectable lead in our water as it leaves the treatment plants. Since corrosion of household plumbing is a source of contamination, GCWW tests water samples collected at customer taps, as required by the Safe Drinking Water Act to ensure safe water.
Copper[c] (ppm)	AL=1.3	1.3	*90th percentile* 0.0382	nd - 0.128 (0 out of 112 samples > AL)	
Total Organic Carbon (ppm)	TT[b]	na	2.64	1.50 - 3.49	Naturally present in the environment.
Total Chlorine[c] (ppm)	MRDL=4	MRDLG=4	0.93	0.91-0.95	Water additive used to control microbes.

Appendix E

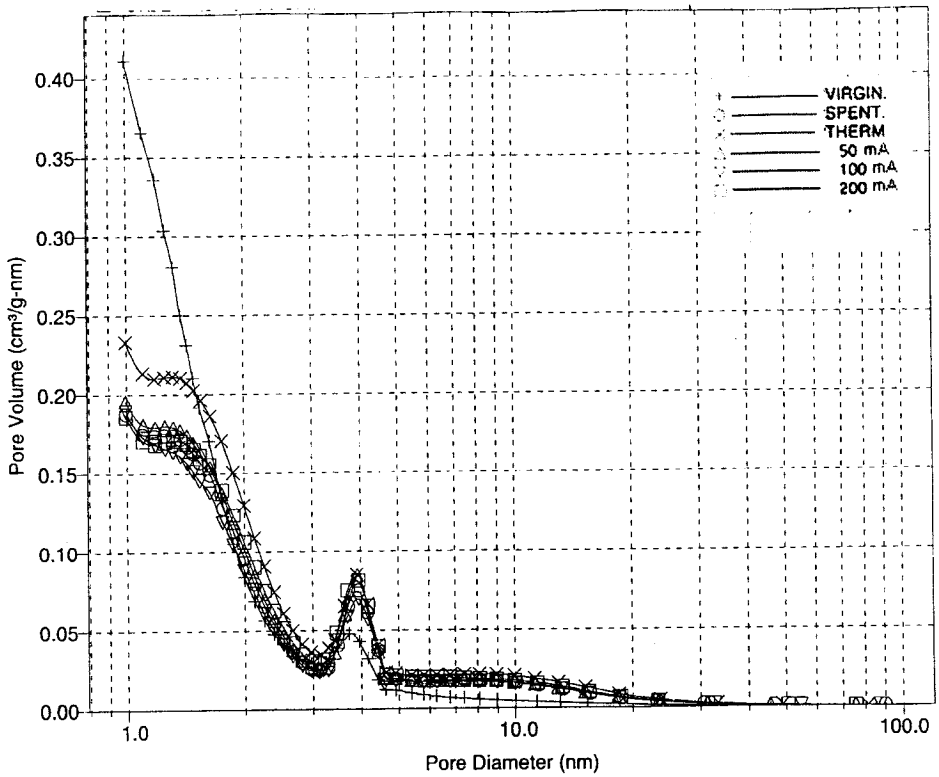

Figure E-1 Regina GAC Pore Volume versus Pore Diameter

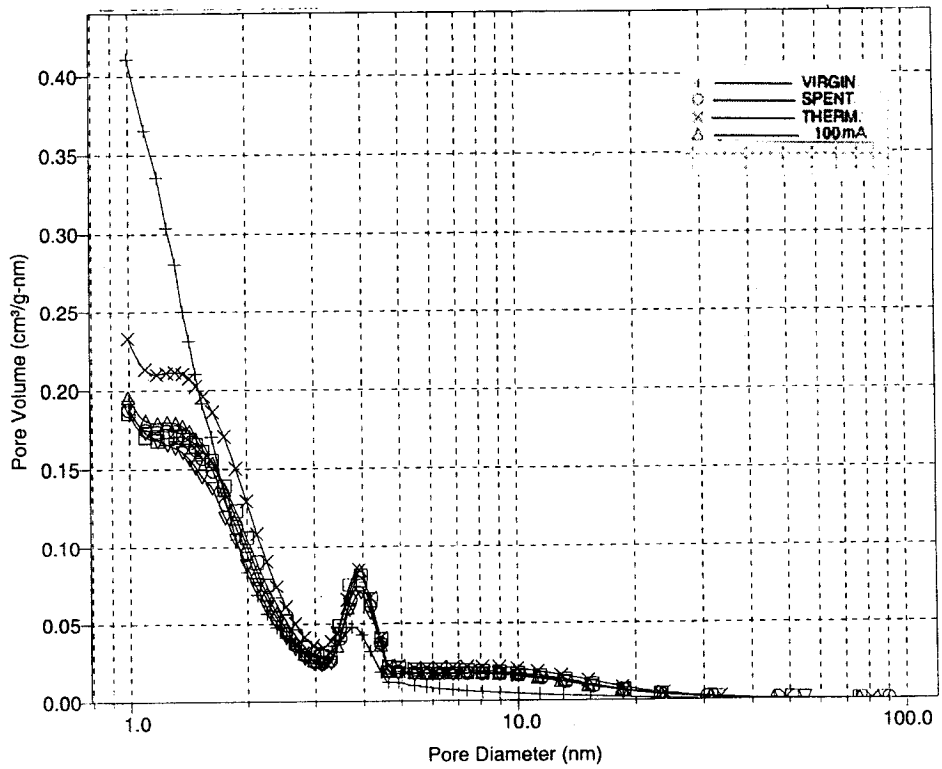

Figure E-2 Cincinnati Pore Volume versus Pore Diameter

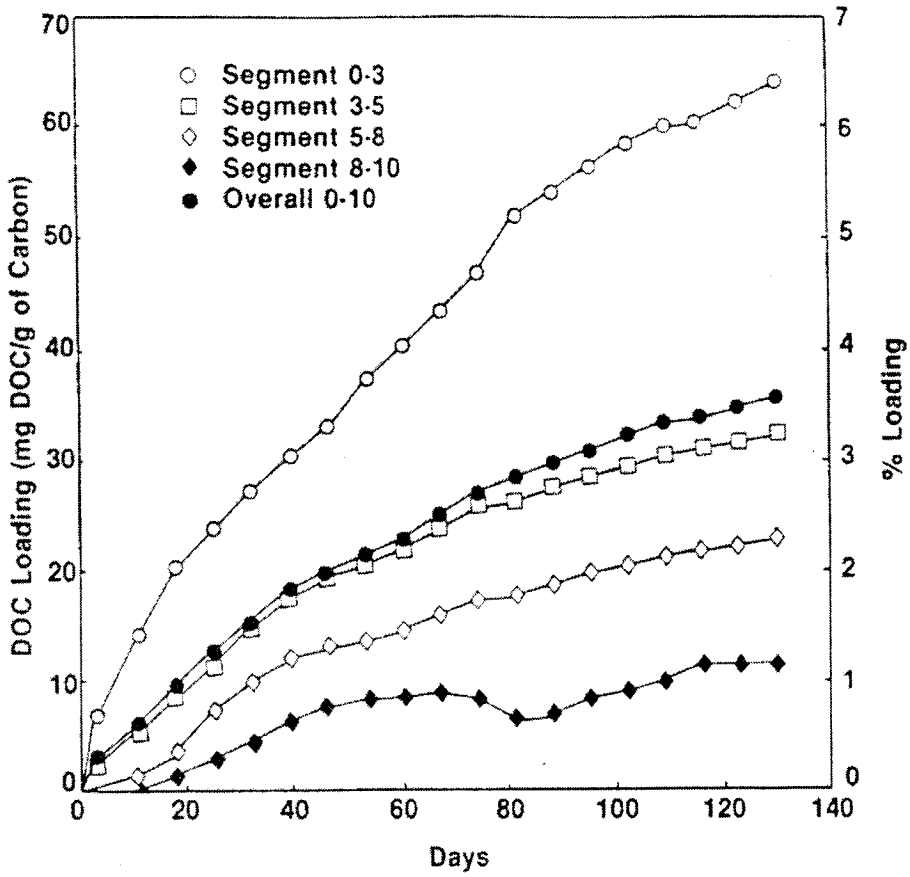

Figure E-3 Cumulative DOC Loading for Regina GAC (source: Gammie and Giesbrecht, 1986)

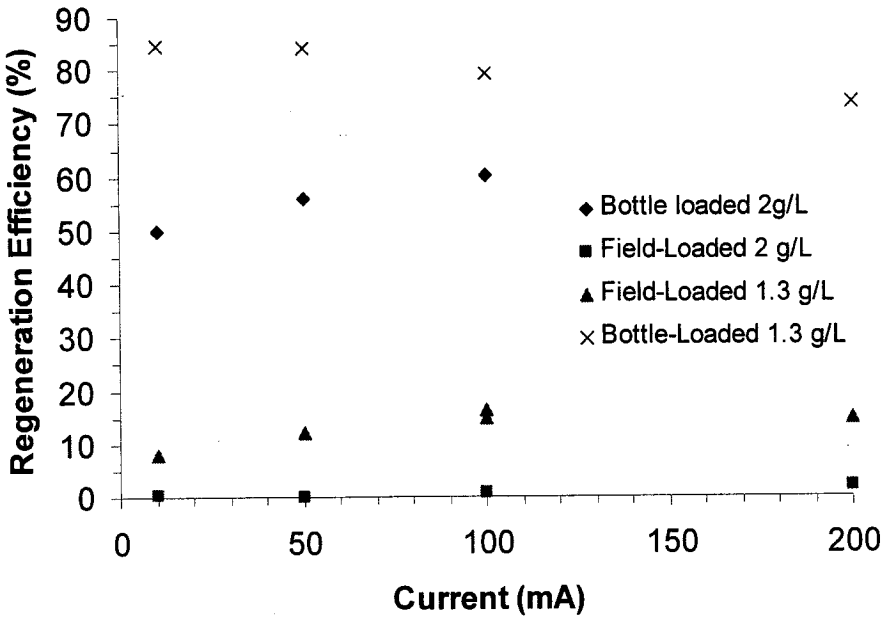

Figure E-4 Effect of Current on Regeneration Efficiency for Different Reloading Doses for Regina Bottle and Field-Loaded GAC

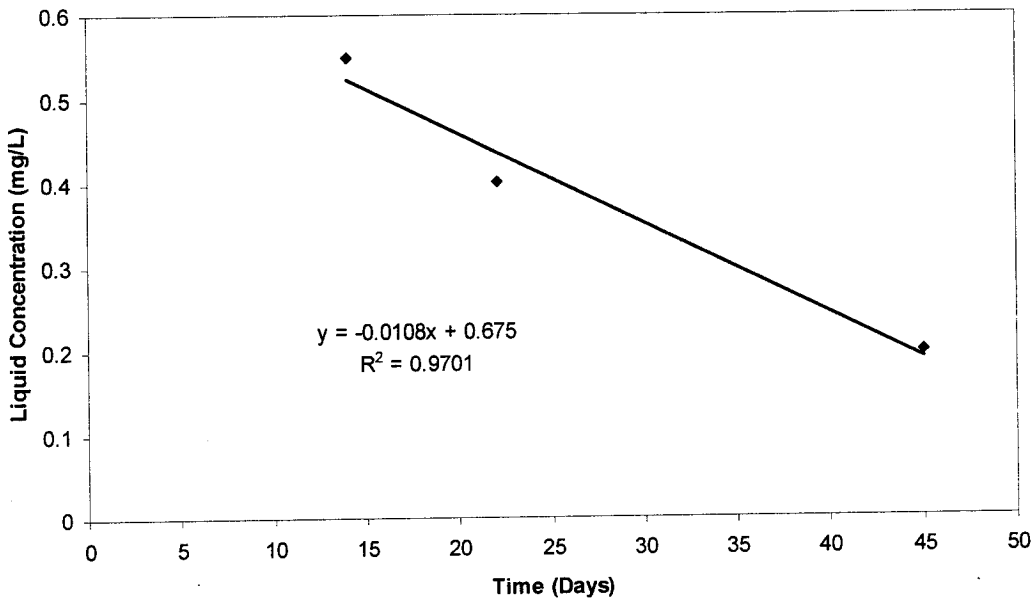

Figure E-5 Liquid Concentration versus Time for Regina GAC (model of the effect of time on the liquid concentration for the Regina kinetic test)

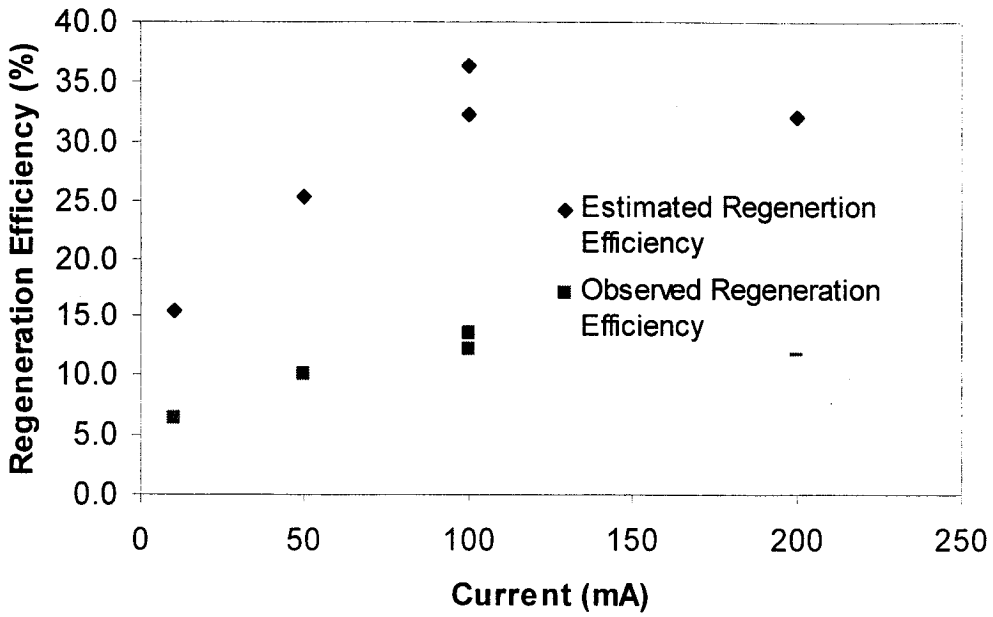

Figure E-6 Estimated and Observed Regeneration Efficiencies for Regina GAC versus Current Applied

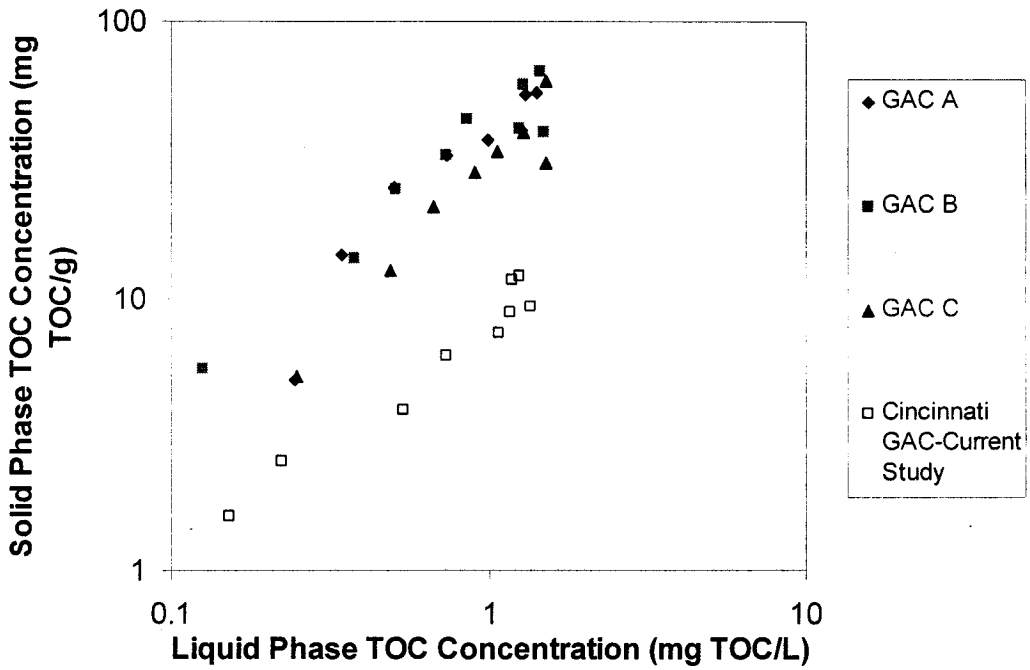

Figure E-7 Comparison of Cincinnati GAC Isotherms (adapted from Summers et al., 1992)

Table E-1 Cincinnati Isotherm Coefficients

	K (L/g)	1/n	R^2
GAC A	39.25±12.05	1.16±0.38	0.902
GAC B	40.02±8.3	0.94±0.25	0.931
GAC C	15.05±8.04	1.18±0.33	0.926

Appendix F

Calculations:

Regeneration efficiency for pH controlled desorption.

$$q_R = \frac{V}{M}\left(C_f - C_{initial}\right)$$

=0.530(15.71-0)/0.655

= 12.71 mg/g

$$q_{Int} = K\left(C_f\right)^{1/n}$$

$= 8.86(15.71)^{1.26}$

=35.37 mg/g

$$RE = \frac{q_R}{q_{\text{int}}} \times 100$$

= 12.71/35.37*100

= 35.9%

Regeneration Efficiency with estimated value from Reference

The estimated capacity from Figure E-5 is 35 mg/g

q_R is the same as above, 12.71 mg/g

$$RE = \frac{q_R}{q_{\text{int}}} \times 100$$

= 12.71/35*100

= 36%

Appendix G
Electrochemical Reactor Gas Removal System

During the electrochemical regeneration gas was evolved from both the cathode and anode. The ion exchange membrane trapped the cathodic gas and it would accumulate under the membrane. This accumulated gas would eventually cause the electrochemical circuit to be interrupted. Periodic removal of the gas was then required. The configuration of the gas removal system was shown in the Fig G-1. Gas was removed via a Teflon tube with a 5 cc gas syringe. A few minutes were required, with the removal of several syringe volumes, to re-establish the electrochemical connection. This procedure was repeated as often as necessary.

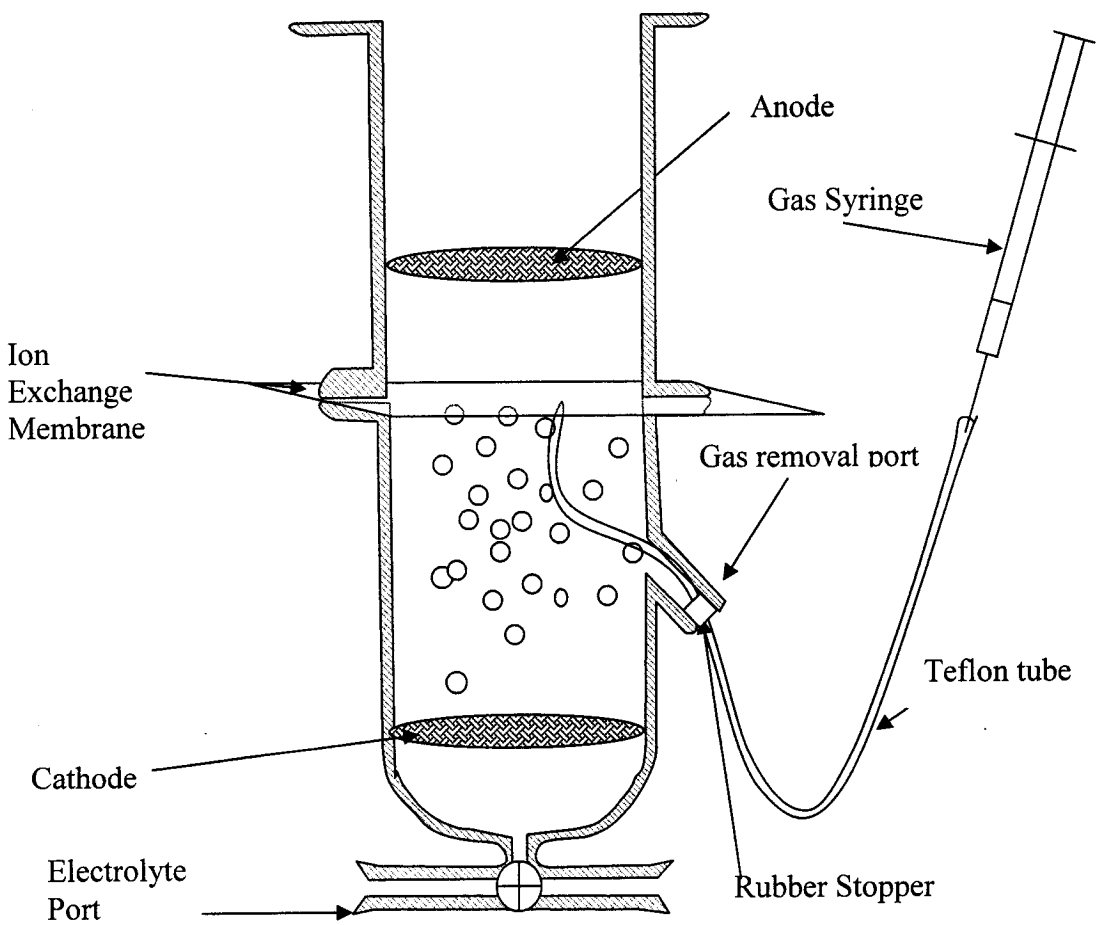

Figure G-1 Gas Removal System

Appendix G
Electrochemical Reactor Gas Removal System

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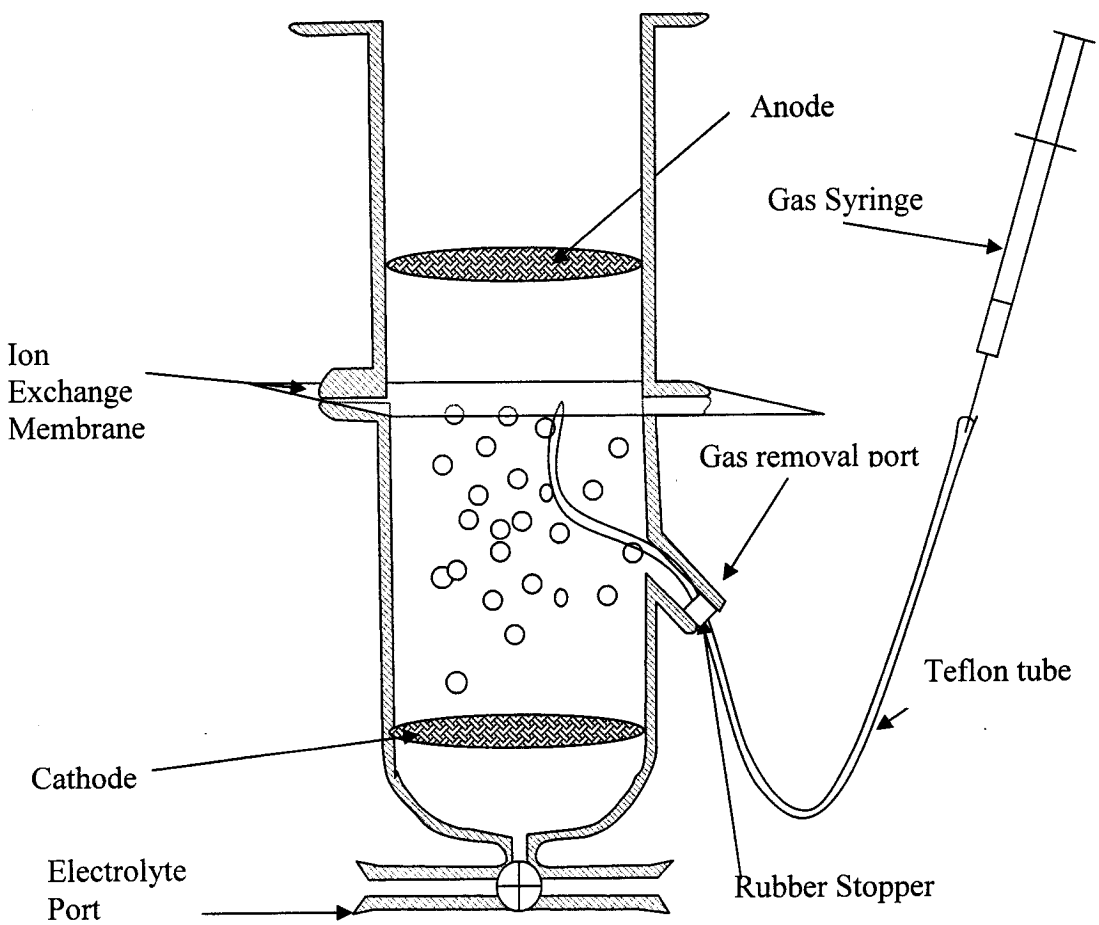

Figure G-1 Gas Removal System