Competitive Adsorption between Atrazine and Humic acid onto NYEX® 1000 and its Electrochemical Regeneration

by

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Abstract

Activated carbon (AC) has been extensively used as an adsorbent for the removal of target contaminants from water. However, it has a number of limitations. First, through competition with background organic compounds the ACs capacity to remove the target compounds can be decreased by up 70%. This is attributed to competitive adsorption and pore blockage by the background organics. Second, AC have a finite adsorption capacity so granular activated carbon (GAC) in adsorbers needs to be periodically regenerated or replaced. Third, the conventional thermal GAC regeneration technique results in the loss of 10 to 12% of the carbon mass in each regeneration cycle. As a result, there has been significant lab-scale research on alternative GAC methods that avoid such a significant carbon mass loss. Unfortunately, they have not been as effective as thermal regeneration. NYEX® is a newly-developed graphitic intercalated compound adsorbent capable of removing different types of contaminants and which can be completely regenerated electrochemically without a loss of adsorbent mass. The objectives of this thesis are to determine, if like with activated carbon, the adsorption of trace target contaminants on NYEX® is impacted by the presence of background organic compounds, and to quantify the impact of competitive adsorption has on the electrochemical regeneration.

Experiments were conducted using atrazine, as a model toxic target contaminant, and humic acid as a model background organic matter. Bottle-point batch isotherm tests of single solute solutions were performed using two different approaches. The constant adsorbate solution-varying adsorbent dose isotherms for humic acid yielded unreasonable data for the high equilibrium liquid phase concentrations data points, it is speculated this was caused by competition with compounds leaching from the adsorbent. The varying adsorbate solution concentration-constant adsorbent dose humic acid isotherms yielded reasonable results and was adopted for all the remaining experiments. The humic acid isotherm yielded Freundlich model coefficient values that were statistically the same as those of an earlier study. A NYEX® bi-solute (atrazine and humic) isotherm experiment showed that the humic acid decreased the atrazine adsorption capacity by an average of 37%, which is of the same order of magnitude one would expect for the same experiment using activated carbon. Given that NYEX® lacks the large network of internal pores of AC, pore blockage by the humic acid should not be significant yet there still was a significant decrease in the atrazine adsorption. The literature on activated carbon adsorption isotherms involving target contaminants and background organic matter generally does not report on the adsorption of humic acid within these experiments, however two studies indicate that the adsorption capacity of the background acids in only slightly impacted by the competition. So, it was surprising that the bi-solute loading of NYEX® yielded 98% lower humic adsorption capacities. The dominance of atrazine in the competitive adsorption tests is attributed to its higher molar concentration in the test solutions and the higher diffusivity of atrazine.

Batch regeneration tests were performed using a reactor with similar construction to the reactor used by Brown et al. (2004a). Electrochemical regeneration yielded regeneration efficiencies of up to 170% indicating the NYEX® 1000 was improved by the electrochemical processing. Hydrogen ions could have bonded to the NYEX® and improved the adsorption capacity of atrazine, which is a weak base, and decreased the adsorption capacity of humic acid. Multiple regeneration cycles of the atrazine-humic acid loaded NYEX® 1000 and atrazine-only loaded NYEX® 1000 were performed, they showed

that the presence of the humic acids did not decrease the long-term atrazine adsorption capacities. Thus, the long-term atrazine adsorption on NYEX® followed by the NYEX® electrochemical regeneration is not impacted by the presence of humic acid, i.e., the improvements in the NYEX® compensate for the competitive adsorption decrease in adsorption capacity. This phenomenon should be investigated further in future research.

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Nomenclature

C_{01}	Initial liquid phase contaminant concentration for the first cycle (mg/L)
C_{02}	Initial liquid phase contaminant concentration for the reloading (mg/L)
C_{e}	Equilibrium liquid phase concentration (mg adsorbate/L)
C_{e1}	Equilibrium liquid phase concentration for the first cycle (mg/L)
C_{e2}	Equilibrium liquid phase concentration for the second cycle (mg/L)
$C_{Control}$	Solute concentration in the control bottle (mg adsorbate/L)
K_{FREUND}	Freundlich coefficient for the isotherm with virgin NYEX® (mg/g/(mg/L)$^{1/nFREUD}$)
K_{LANG}	Langmuir coefficient for the isotherm with virgin NYEX® (L/mg adsorbate)
M	Mass of NYEX® used in the batch test (g)
M_{2}	Mass of NYEX® used in the batch reloading test (g)
mg/L	Parts of solute per million quantities of solvent (unit mass/unit volume)
n	Freundlich model exponent (unitless)
pKa	Acid dissociation constant
PR_{S}	Standard percent regeneration method (%)
PR_{2}	Percent regeneration method 2 (%)
PR_{3}	Percent regeneration method 3 (%)

µg/L	Parts of solute per billion quantities of solvent (unit mass/unit volume)
q_2	Solute equilibrium solid phase concentration at the end of the reloading cycle (mg/g)
q_e	Equilibrium solid phase concentration (mg contaminant / g of adsorbent),
q_{ee}	Regenerated adsorbent solid phase concentration that is in equilibrium with the same liquid phase concentration as produced by the initial loading cycle (mg/g)
q_{e1}	Solid phase concentration of virgin adsorbent (mg/g)
q_{e2}	Solid phase concentration of adsorbent after the readsorption cycle (mg/g)
q_{e11}	Solid phase concentration of virgin adsorbent after the readsorption cycle (mg/g)
q_m	Maximum (monolayer) adsorption of the solid phase contaminant (mg adsorbate/g adsorbent)
q_r	Adsorption capacity of regenerated adsorbent after the reloading (mg/g)
V	Volume of contaminated water in the equilibrium vessel (L)
V_2	Volume of contaminated water used in the reloading cycle (L)
RE	Regeneration efficiency (%)
$Var(q)$	Variance for the isotherm loading (mg adsorbate /g NYEX$^{®}$)
$\sigma_{C_{Control}}$	Standard deviation of the solute concentration of the control samples
σ_{C_e}	Standard deviation of the equilibrium liquid solute concentration

σ_V	Standard deviation of the liquid volumes
σ_M	Standard deviation of the adsorbent mass

Abbreviations

AC	Activated carbon
ATZ	Atrazine
BET	Brunauer-Emmet-Teller theory
CGAC	Commercial granular activated carbon
DBP	Disinfection by-products
DOC	Dissolved organic carbon
DWT-PAC	Powdered activated carbon made from demineralised waste tea leaves
GAC	Granulated activated carbon
GIC	Graphitic intercalated compound
HPLC	High-performance liquid chromatography
KHP	Potassium hydrogen phthalate
MTBE	Methyl tert-butyl ether
N_2	Nitrogen gas
NOM	Natural organic matter
PAC	Powdered Activated Carbon
PNP	p-nitrophenol
PVC	Polyvinylchloride

PZC	Point zero charge
SEM	Scanning electron microscope
T	Temperature
TOC	Total organic carbon
THM	Trihalomethane
USGS	United states geological survey
UV	Ultraviolet light
WT-PAC	Powdered activated carbon made from waste tea leaves
WTP	Water treatment plant

CHAPTER 1: Introduction

Adsorption is a powerful contaminant separation technology that can be used to remove many different compounds including toxic contaminants and hard to oxidize compounds. In adsorption, the contaminants (i.e., adsorbates) are transferred from one medium (liquid or gas) into an interface; generally, this is the surface of solid adsorbent. The most commonly used adsorbent is activated carbon (AC), which is a highly porous manufactured material with a very large internal surface area (~ 1000 m^2/g) (Crittenden et al. 2012). The contaminants attach themselves to sorption sites on the vast internal surface area of the activated carbon via a number of different mechanisms. One of the key features of activated carbon is that it is non-selective, it can be used to remove most organic compounds and a number of heavy metals. This makes this technology very versatile. Accordingly, it is extensively used in water treatment, industrial wastewater treatment and groundwater remediation. A second important feature is that granular activated carbon (GAC) column adsorbers can remove 100% of the target contaminant for a period of time (Sontheimer et al. 1988). This is something that most competing technologies cannot achieve and it can be extremely important in the treatment of waters containing highly toxic compounds. This technology also has a number of limitations. First, due to the nonspecific adsorption, GAC simultaneously removes many contaminants which compete for the available adsorption sites (Ding 2010; Pelekani and Snoeyink 2000; Singh and Yenkie 2004). This competitive adsorption will reduce the removal capacity of the target solutes. The extent of the reduction will depend on the characteristics of the solutes, their size, chemical structure and their relative concentration within the water matrix. In water treatment and groundwater remediation applications, the naturally occurring organic matter, including humic and fulvic acids, present in the water can severely decrease the adsorption capacity of target toxic compounds (Kilduff et al. 1996; McCreary and Snoeyink 1980). It has been theorized the natural organic matter (NOM) competes for adsorption sites and it blocks access to some internal pores. Second, AC's capacity to remove contaminants is limited by the finite number of adsorption sites within the AC. As the adsorption sites on the AC become saturated, the contaminant removal of GAC adsorbers decrease and at some point, the GAC needs to be replaced with virgin or regenerated GAC. Due to the relatively high cost of virgin GAC, GAC regeneration can reduce costs. However, the cost of regeneration facilities is also quite high and it is only feasible if the carbon usage rate is high. So small water treatment plants (WTPs) will generally purchase more virgin GAC instead of regenerating it. Some WTPs with large GAC usage rates find it economical to have GAC regeneration units on-site, while many WTPs have their GAC regenerated at regional regeneration facilities, or by AC manufacturers (Chowdhury et al. 2013; Moore et al. 2003; Narbaitz and McEwen 2012). To avoid contamination problems, water treatment plants (WTPs) are only allowed to use virgin GAC or regenerated GAC originating from their plant (Chowdhury et al. 2013).

Currently, thermal regeneration processes are used almost exclusively for the regeneration of GAC, however this results in the loss of 10-12% of the GAC (AWWA and ASCE 2013; San Miguel et al. 2001). Due to this, there has been a great deal of research on alternative methods for the regeneration of GAC, these include chemical, biological, microwave, and electrochemical approaches (Chan et al. 2018; Lu et al. 2011; Narbaitz and Karimi-Jashni 2009; Yagmur et al. 2017). Our group has studied cathodic electrochemical GAC regeneration and found it to be quite effective for GAC loaded with phenol and p-nitrophenol (Karimi-Jashni and Narbaitz 2005a; b; Narbaitz and Cen 1994; Narbaitz and Karimi-Jashni 2009, 2012), but not effective in regenerating GAC originating from two full-scale WTPs were the principal adsorbate was NOM (Narbaitz and McEwen 2012).

Dr. Roberts and his colleagues have developed an alternative adsorption-electrochemical regeneration system using a graphitic intercalated compounds (GIC) called NYEX® (Asghar et al. 2013; Brown et al. 2004b; a; Hussain et al. 2014; Liu et al. 2016; Mohammed 2011). Although NYEX® has few internal pores and a low surface area (~ 1-2 m^2/g), it is highly conductive (Mohammed 2011). This system has shown to be effective for removing many different sorbed contaminants from the NYEX® and destroying them, including NYEX® 100 loaded with atrazine (Brown et al. 2004a) and humic acid-loaded NYEX® 1000 (Asghar et al. 2013). Given that NYEX® 1000 was chosen because it was hypothesized that its removal of trace toxic contaminants would be less impacted by the competitive adsorption with NOM. Thus, the objectives of this thesis are: a) to investigate the adsorption behaviour of humic acid (as a model NOM compound) and a model trace organic contaminant on NYEX® 1000; b) to evaluate on the competitive adsorption of a model toxic contaminant (atrazine) with a humic acids; and c) to investigate the impact of the humic acid competitive adsorption on the NYEX®-atrazine electrochemical regeneration efficiency. Atrazine was selected as the model trace toxic contaminant in this study because it is one of the most commonly used herbicides in North American agriculture and it was the most commonly detected pollutant in surface waters by the USGS in 2001 and exceeded in some cases the concentration required (0.2 ppb) to feminize frog populations (Duris et al. 2004; Gilliom et al. 2006). Atrazine is therefore classified as a Group III (possibly carcinogenic to humans) by Health Canada (Health Canada 1993) and banned in the European Member States in 2004 for the potential of groundwater contamination (Health Canada 2015).

CHAPTER 2: Literature review

This chapter discusses the relevant literature regarding adsorption mechanisms, activated carbon characteristics, factors affecting activated carbon adsorption, equilibrium sorption capacities and their modeling, and methods for regenerating spent activated carbon. The latter includes a discussion of the conventional thermal regeneration methods, research on alternative regeneration methods (including electrochemical regeneration) as well an alternative sorbent that can be effectively regenerated electrochemically.

2.1 Adsorption mechanisms

Adsorption is considered the mass transfer of the adsorbates (contaminants) from a solvent (liquid or gas) to an interface where it accumulates, the interface is generally a solid material called the adsorbent. Dissolved species in the liquid phase are transported by diffusion to the surface of the adsorbent and for porous adsorbents further inward into the various adsorption sites within the pores (Crittenden et al. 2012). The contaminants are held in these sites by physical attraction to the surface or by chemical attraction. These mechanisms are more commonly referred to as physical adsorption and chemical adsorption. Physical adsorption is considered reversible, in most cases involving chemical adsorption mechanisms the adsorption is not reversible since the compound and the adsorbent surface react with one another and become irreversibly bound. Physical adsorption is preferred to chemisorption in most cases since the adsorbents can be more easily regenerated and possibly reused. When the contaminants are primarily chemisorbed, the adsorbent needs to be regenerated by intensive methods, such as thermal regeneration, or discarded. The development of many different types of adsorbents has been due to attempts to expand the use of adsorbents. The most common type of adsorbent used in water and wastewater treatment applications is activated carbon.

2.2 Activated Carbon

Activated carbon (AC) is a porous carbonaceous adsorbent that is created from carbonaceous raw materials subjected to high temperatures in the absence of oxygen to create a highly porous structure and to “activate” the adsorbent. The raw carbonaceous material can be from many sources, such as various types of coal, wood, coconut shells, hemp, etc. The material is heated to high temperatures in the absence of oxygen to carbonise it without it being converted to ash, and then heated further while exposed to steam, other gases or liquid chemicals to activate the pores (Van Vliet 1991). Each manufacturer has their own proprietary manufacturing process, that differ in the temperatures used, the temperature rise rate, and the activation agents used. Activated carbon is comprised of turbostratic crystallites (Sontheimer et al. 1988). The crystallites are similar to graphite, layers that are parallel to each other, except they are randomly oriented and extensively interconnected by carbon cross links. This type of interconnectivity leads to voids between the linkages. The voids between the crystallites comprise the pore volume and they can vary in size (Sontheimer et al. 1988). Based on their size pores are classified as macropores ($50\text{ nm} < d_p$), mesopores ($2\text{ nm} < d_p < 50\text{ nm}$), and micropores ($d_p < 2\text{ nm}$) (Crittenden et al. 2012). AC is a primarily a physical adsorbent meaning it adsorbs due to physical attraction caused by nonspecific mechanisms such as van der Waal’s forces between the positive surface of the pores on the carbon and the negatively charged adsorbate (Crittenden et al. 2012). The van der Waal’s forces form relatively weak bonds between both the adsorbent and the adsorbate. This attraction can be reversed when exposed to the appropriate conditions such as heat. For example, in thermal AC regeneration the spent carbon is exposed at the temperatures ranging from 800 °C and 1000 °C, the pores expand and release the adsorbate from the attached pore structure (McLaughlin 2005). Thus, the regenerated carbon can be reused in treatment. Thermal regeneration also regenerates AC loaded with chemisorbed contaminants, they may be volatilized (making the adsorption site available) or carbonized on the internal surfaces of the activated carbon (Sontheimer et al. 1988). The following subsections discusses the factors affecting activated carbon adsorption, the determination of the equilibrium adsorption capacities as well modeling them.

2.3 Factors affecting adsorption

The adsorption process can be affected by many factors: the raw material of the adsorbent, size/molecular weight and charge of the adsorbate, the adsorbent pore size distribution, overall adsorbent surface area, the surface charge, etc. (Li et al. 2002; Sontheimer et al. 1988). Factors such as the raw material of the adsorbent are important as it may impact the activated carbon's surface area, predominant pore size, etc. For instance, activated carbons manufactured from liquorice residues can have a surface area of 114 m^2/g while activated carbons prepared from pistachio shells can a surface area of 1184 m^2/g (Yeganeh et al. 2006). Most commercial activated carbons have surface areas in the order of 1000 m^2/g. The adsorbent surface area is particularly important as adsorption is a surface phenomenon, thus the magnitude of the adsorption capacity is to a certain extent a function of the adsorbent's surface area. The following sub-sections will discuss in detail the impact of particle size and pH on adsorption capacities, other factors such temperature can also impact the magnitude of the adsorption.

2.3.1 Adsorbent Particle Size

Particle size for an adsorbent is an important factor in the rate of adsorption. Smaller particle sizes promote an increased adsorption rate and causes the adsorbent to reach its capacity more rapidly than if it was of a larger particle size (Chowdhury et al. 2013). Granular activated carbon (GAC) is the larger variant of AC and can have a mean particle size from 0.5 to 3 mm. The second classed size of AC is powdered activated carbon (PAC), its mean particle size ranges from 20 to 50 µm. It should be noted that practically all of the surface area of AC is within the internal pores, therefore the surface area per unit mass of GAC and PAC is essentially the same. Accordingly, the adsorption capacity of GAC and PAC are the same (Sontheimer et al. 1988). The key advantage of PAC is that it has much faster kinetics, as the rate of adsorption is proportional to the inverse of the particle diameter squared. The systems using PAC have a number of advantages and disadvantages.

PAC in water treatment is generally added at the coagulation stage and removed through sedimentation, although sometimes the separation is via filtration (Crittenden et al. 2012). To implement PAC additions only a PAC slurring system and a feed pump need to be added to the treatment plant, so the capital costs of PACs addition systems are much lower than compared to GAC contactors because no additional treatment units are required (Chowdhury et al. 2013). This is a benefit smaller plants who have a limited budget (Chowdhury et al. 2013). If, as in many water treatment plants, the PAC is only added seasonally to combat algal/cyanobacterial-related taste and odour problems, the operational cost of PAC is not high (Crittenden et al. 2012). If PAC systems are used on a continuous basis it will lead to a larger AC consumption rate than GAC columns, which result in higher operating costs. In addition, if high contaminant removals are required (>80% removal) the

PAC usage rates will be very high (Sontheimer et al. 1988). Other PAC operating concerns include the dirtiness of the PAC slurring preparation systems, and the larger amount of sludge wastes produced. The PAC in the sludge cannot be regenerated (Chowdhury et al. 2013).

On the other hand, GAC columns have a number of advantages. First, due to their flow configuration the GAC achieves higher contaminant loadings that can be achieved by PAC contact systems. Second, GAC column adsorbers can achieve up to 100% contaminant removal for a period of time, this is critical for the removal of toxic compounds and PAC contact systems cannot achieve 100% removal (Sontheimer et al. 1988). Third, GAC can be economically regenerated, on-site or at regional facilities (Sontheimer et al. 1988). However, the GAC in GAC column contactors can operate for months to years before it becomes saturated and needs to be replaced or regenerated. The service life of the GAC depends on the contaminant being targeted, the concentration of the contaminant, the level of removal required, the size of the column and column system configuration (i.e., single column operation, columns in-series, off-phase parallel columns). For the removal of NOM, the GAC service life will be in the order of months, while for taste and odour applications the service life is often longer than four years. For on-site regeneration facilities to be economically feasible the GAC usage rate has to be greater than 140 000 kg/yr (Sontheimer et al. 1988). Accordingly, many plants simply replace the GAC with virgin GAC when the capacity is reached. Due to the different contaminants, the concentration of the contaminant, the different degrees to which they adsorb, levels of removal required for a particular application and the economics, some water treatment plants use PAC contact systems and others use GAC column systems. Given their greater effectiveness and the possibility of regenerating the GAC, GAC column systems are theoretically preferable.

2.3.2 pH

pH defined by the Bronsted-Lowry theory is the mixture of positively charged hydrogen ions and negatively charged hydroxide ions in solution (Crittenden et al. 2012). This balance of positive and negative ions greatly affects the water chemistry in a sample and also possibly affects the mechanics of adsorption. Shi et al. (2012) studied the impact of pH on saxitoxin adsorption on activated carbon, saxitoxin is a toxin secreted by some blue-green algae. When the pH was below 7, the adsorption capacity of the PAC dropped significantly. As the pH increased from 5.7 to 7.05, 8.7 and 10.7 (for a 2 hours of mixing time), the percent saxitoxin removal increased from <10 to 48, 51, and 77%, respectively (Shi et al. 2012). However, this pattern seems to change in the adsorption of different compounds showing the opposite of this behaviour (Guedidi et al. 2013; Lee et al. 2007; Ward and Getzen 1970). The inconsistency of this result has to do with AC's point zero charge (PZC) of the adsorbent and the adsorbate species involved. The point zero charge is the pH where the AC is electrostatically neutral. At a pH below this level, the surface of the AC becomes positively charged and at a level higher than this pH the surface of the AC becomes negatively charged. The pH could also affect the adsorbate in solution, this is because some adsorbates are transformed into ionized sister species. Ionization can occur when the pH increases above or below the pKa value of the adsorbate and ionize to another species. For instance, Karimi-Jashni & Narbaitz (2005b) were observed solution ionization when adsorbing phenol. When the pH rose above the phenol pKa value of 9.99, the adsorption capacity of the F-400 GAC dropped significantly, by pH of 13 it dropped 75%

(Karimi-Jashni and Narbaitz 2005b). This is because above a pH of 9.99 phenol increasingly ionizes to phenate and has negative charge instead of a neutral charge. The intramolecular repulsion by the negative charges causes the phenol molecules to repulse each other and desorb off of the surface of the GAC (Cooney 1999). This would infer the importance of controlling and/or monitoring the pH during the adsorption tests. Next, the experiments used to quantify the maximum adsorption capacity will be discussed.

2.4 Equilibrium Adsorption Capacity Experiments

Adsorption experiments can be conducted to determine the overall capacity and determine the favourability of adsorption of the adsorbent for a specific contaminant. This also helps estimate the activated carbon usage rate in full-scale applications. Adsorbents only have a limited surface area per unit mass, a particular pore size distribution and charge, therefore, single solute equilibrium studies must be conducted to determine its maximum adsorption for the specific contaminant-specific activated carbon combination in question. Equilibrium studies with AC have been performed on a variety of different contaminants that are considered hazardous to human health (Dobbs and Cohen 1980). It should be emphasized that the adsorption capacity for a given contaminant for different types of activated carbons will be different. In order to assess different commercial activated carbon products, adsorption isotherms should be conducted for each of these products. The isotherm data can be very useful to determine the quantity of a specific AC required to treat a water that has a large concentration of a specific contaminant. Once the volume of water/wastewater is known the mass of AC required for a PAC contact system can be estimated using the q_e (mg adsorbate/g adsorbent) in equilibrium with the system's liquid phase effluent contaminant concentration (Crittenden et al. 2012; Sontheimer et al. 1988).

In the case of a GAC column adsorbers, the mass of GAC required is based on the q_e (mg adsorbate/g adsorbent) in equilibrium with the contaminant's feed concentration (Crittenden et al. 2012; Sontheimer et al. 1988).

Batch equilibrium tests are generally performed to determine the maximum adsorption capacity or loading of a target contaminant, the capacity equals the mass of contaminant adsorbed per gram of adsorbent. As the equilibrium tests are performed at a constant temperature they are referred to as isotherms or isotherm tests. The simplest way to conduct isotherm tests is by the bottle-point tests at room temperature. Bottle-point isotherms tests are experiments conducted by contacting adsorbate solutions with the adsorbent within multiple bottles until equilibrium is reached, then the liquid solutions are separated and their solute concentrations are measured. This final concentration is referred to as the equilibrium liquid phase concentration (C_e). The loading or equilibrium solid phase concentration, q_e, is calculated conducting contaminant mass balances of these bottle batch tests and rearranging it, i.e.,

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

Where q_e is the equilibrium solid phase concentration (mg contaminant / g of adsorbent), C_o is the initial (or control) liquid phase concentration (mg contaminant/ L), V is the volute of solute solution (L), and M is the mass of the adsorbent (g). Temperature is also significant as it can change the adsorption capacity of adsorbents, this parameter must be kept constant during all experimentation to accurately determine the maximum adsorption capacity at the relevant temperature.

There are two different methods of conducting the bottle-point isotherm tests. The first method is to use the same solution (so C_o is constant) and to change the mass of the adsorbent in each bottle. The second approach is to use the same amount of adsorbent in all the bottles and change the initial solute concentration of the solutions added to the various bottles. The second approach has been used in many laboratory studies using single adsorbate (i.e., single solute or contaminant) solutions (Asghar et al. 2013; Brown et al. 2004a). However, the constant solute / changing adsorbent dose is the most practical approach in real applications because they may involve many solutes and one cannot readily modify the feed concentration of all solutes and pH-impacting ions.

If the adsorbing material is not suited for a variable adsorbent dosage isotherm, such in cases were large adsorbent doses are required, then one would use a constant adsorbent dose and vary the concentration of the solute. In addition, the range over which the solute concentrations can be accurately measured needs to be considered. Given the adsorption capacity of the selected adsorbent and the adsorbent mass used in the batch experiments, will influence the selected initial solute concentrations. Of course, the equilibrium solute concentrations will be lower than the initial ones. So, in order to quantify the initial and equilibrium solute concentrations with the selected analytical technique the samples may have concentrated or diluted. Dilution would appear to be the simplest approach since concentration would require another piece of equipment such as a centrifugal vacuum or concentrators. In addition, if one varies the solute concentration, one needs to carry at least one control bottle for every solute concentration used and the final concentrations in the solutions in these bottles would need to analyzed, i.e., it requires more analytical resources. For drinking water applications, it is better to study the adsorption using a constant solute concentration and a variation in the dose since this approach saves the difficult tasks of manipulating all the components of the water matrix. Once the isotherm data is generated it should be plotted as q_e versus C_e graph, which is referred to as the isotherm graph. Then, the data should be modeled.

2.5 Single Solute Adsorption

Single solute equilibria isotherms tend to show a specific pattern of adsorption when plotted. Isotherms with a convex shape (Figure 2.1a), the denomination as favourable relates to the fact that once the mass transfer zone develops within a column it remains constant in size as it proceeds downstream in the column with time. Unfavourable isotherms have concave shape (Figure 2.1b), and they are considered unfavourable because within a GAC column the mass transfer zone increases in size as it proceeds down the column with time (Sontheimer et al. 1988). The trend shown in Figure 2.1(a) serves as a good indicator to the adsorbent’s favourability to the adsorbate. Ayotamuno et al. (2006) showed the adsorption of petroleum hydrocarbons from contaminated groundwater was unfavorable adsorption, while Hamdaoui & Naffrechoux (2007) found the adsorption of phenol was favourable. Most of the priority pollutants studied by Dobbs and Cohen (1980) and others are adsorbed favourably. In the favourable isotherm data, it can be seen a distinct increase in q_e at the higher values of C_e to determine the maximum adsorptive capacity. The majority of the isotherm data available is for single solutes.

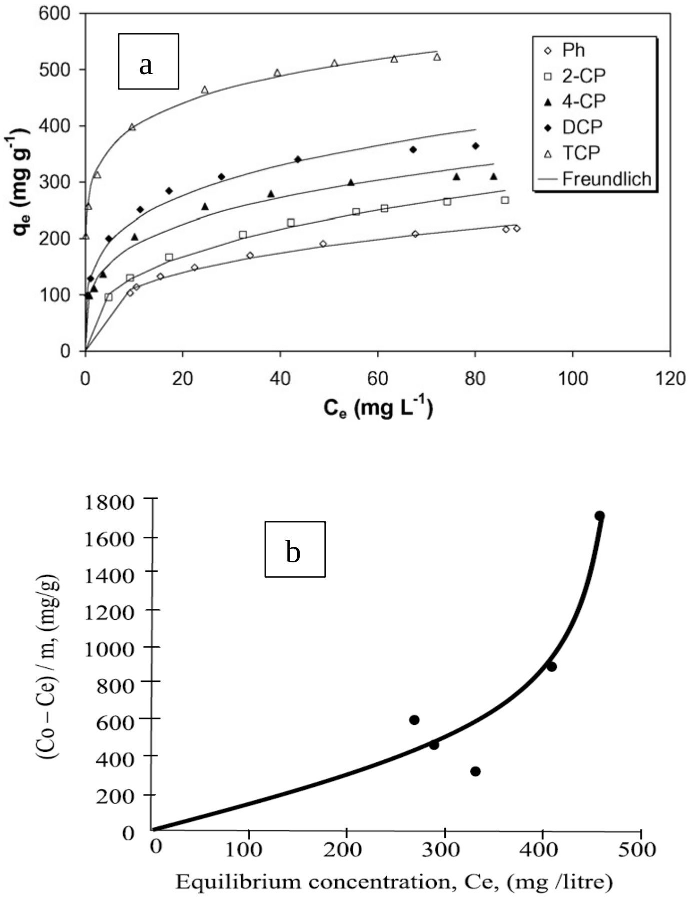

Figure 2.1: Comparison between (a) an favorable (Hamdaoui and Naffrechoux 2007) and (b) unfavorable isotherm (Ayotamuno et al. 2006)

2.5.1 Single solute isotherm modeling

Isotherm models are equations that describe the isotherm test data, these equations can be used for preliminary carbon usage calculations, for comparisons among different activated carbons, and for calibrating mass transfer models. There are many different types of models that are appropriate depending on the circumstance (Foo and Hameed 2012; Hamdaoui and Naffrechoux 2007). The most common models used for modelling the adsorption of individual compounds are the Langmuir model and the Freundlich model. These models are the standard of isotherm modelling because they only have two adjustable parameters so it is relatively simple to determine the coefficient values and their values are generally not highly correlated.

2.5.1.1 Langmuir Model

The Langmuir model, developed by Irving Langmuir in 1916, was one of the first isotherm models (Sontheimer et al. 1988). It assumes uniformity in the adsorbent, uniformity in the energy of adsorption of the sorption sites, adsorption at one site does not interfere with the adsorption in the adjacent sites, and the maximum loading that can be achieved is a monolayer. The Langmuir model equation is:

$$q_e = \frac{q_m \cdot K_{LANG} \cdot C_e}{1 + K_{LANG} \cdot C_e} \tag{2.2}$$

Where q_m is maximum (monolayer) adsorption of the solid phase contaminant (mg adsorbate/g adsorbent); and K_{LANG} is the Langmuir constant (L/mg adsorbate). Accordingly, the Langmuir describes data well that reaches a plateau value at a certain equilibrium solid phase concentration demonstrated in Figure 2.2. Thus, if experimentally the data reaches a plateau level of capacity, it is likely that the Langmuir model will describe the data well.

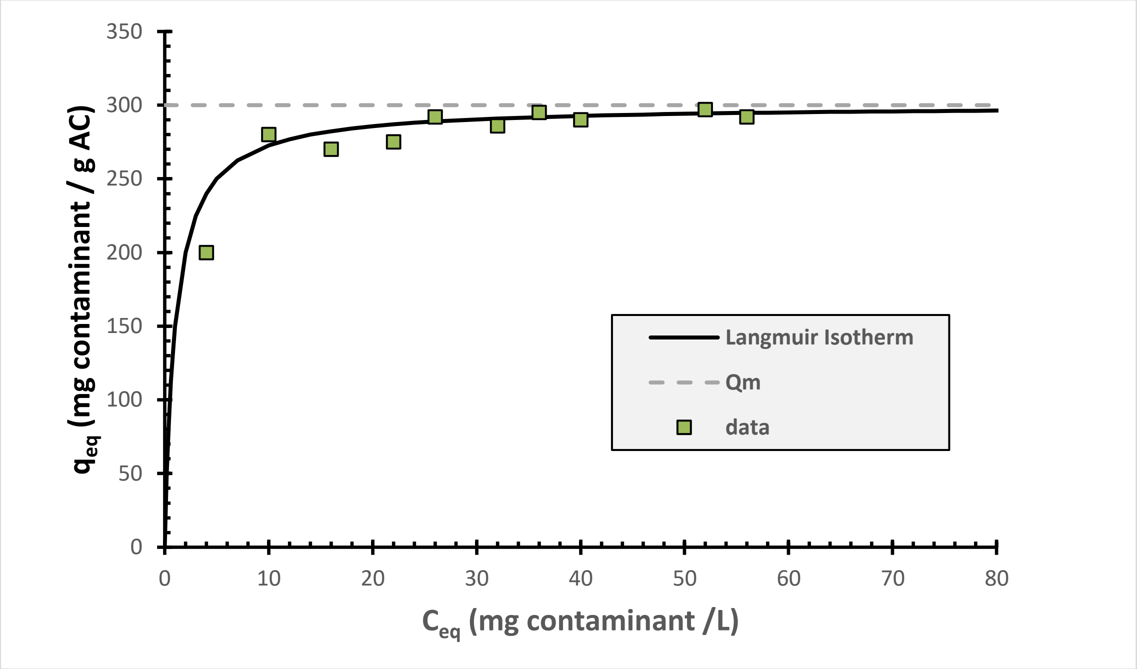

Figure 2.2: Sample data described well by a Langmuir isotherm model (Narbaitz 2019)

The Langmuir model can be linearized by two different means. The first one, which is more accurate for low concentrations, is obtained by inverting Equation 2.2, that is

$$\frac{1}{q_e} = \frac{1}{C_e q_m K_{LANG}} + \frac{1}{q_m} \tag{2.3}$$

If the data is described by a straight line in a $1/q_e$ versus $1/C_e$ graph, it is described well by the Langmuir model. This can be demonstrated by the methyl *tert*-butyl ether (MTBE) data in Figure 2.3. The values of the Langmuir coefficients can be obtained based on the slope and intercepts of the plot. Alternatively, linear regression can be used to obtain the values of the Langmuir coefficients, this approach has the added advantage that it also yields the confidence intervals of the coefficient values.

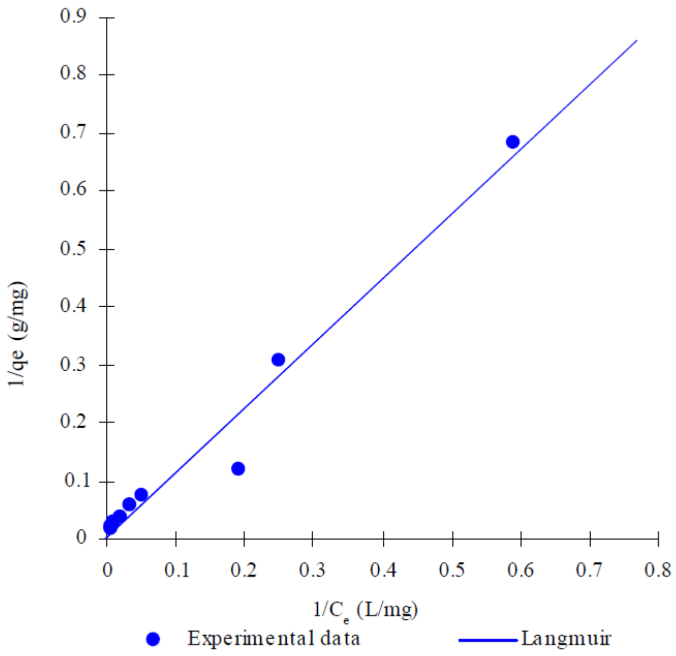

Figure 2.3: Langmuir linearization of GAC adsorbing MTBE (Chen et al. 2010)

It should be noted that the least squares regression minimizes the sum of the squares of the errors, accordingly it gives a greater weight to the data points of larger magnitude. Therefore, for the above Langmuir model linearization (i.e., $1/C_e$ and $1/q_e$), the regression gives greater weight to the larger $1/q_e$, that is the smaller q_e. Accordingly, as this linearization may not fit the higher q_e data so well, so the regressed q_m value will not be determined as accurately. The limits of the model become clear when the liquid phase concentration is low, so the values of $1/C_e$ and $1/q_e$ are high. A common alternative approach is to use an alternative linearization of the Langmuir model, this is achieved by multiplying by C_e to obtain

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_{LANG} q_m} \tag{2.4}$$

Based on this equation, the suitability of the Langmuir model can be tested by plotting the data in a C_e/q_e versus C_e graph, if data yield a straight line the Langmuir model is adequate. As C_e increases, q_e will also increase to account for the inaccuracy at higher concentration values. As explained by Sontheimer et al (1988) if the range of the experimental data is rather small both linearization should work equally well, however when the experimental data covers a large concentration range the two linearizations will yield different fits. For such cases, they recommend using nonlinear regression.

2.5.1.2 Freundlich Model

Freundlich model is an empirical two-parameter model, it was later found to describe an adsorbent with adsorption sites whose energy of adsorption follow an exponential distribution (Yang 1998). As such, it describes adsorption on heterogeneous adsorbents and activated carbon is considered to have heterogenous adsorption characteristics. The Freundlich isotherm model is

$$q_e = K_{FREUND} C_e^{1/n} \tag{2.5}$$

Where K_{FREUND} is the Freundlich constant and n is the Freundlich adsorption exponent (unitless). The units of K_{FREUND} depend on the units of q_e and C_e, for example if the units of C_e are mg of contaminant/L and those of q_e are mg contaminant/g adsorbent then the units of K_{FREUND} are $\frac{mg\ contaminant}{g\ adsorbent} \cdot \left[\frac{L}{mg\ contaminant}\right]^{1/n}$. In practice, the Freundlich model is better suited to model heterogeneous adsorbents such as activated carbon since there are multiple layers of adsorption sites and more than one adsorbate can adsorb onto the same site (Crittenden et al. 2012). This statement contradicts one of the assumptions made by the Langmuir equation where only one adsorbate molecule can occupy one adsorption site (Crittenden et al. 2012). The Freundlich model has been extensively used in describing adsorption onto activated carbon because it often models the data better than the Langmuir model because at the applicable lower liquid phase concentrations the adsorption capacities do not plateau (Yang 1998). The model can be linearized by applying log transformations to yield

$$\ln(q_e) = \frac{1}{n}\ln(C_e) + \ln\,(K_{FREUND)}) \tag{2.6}$$

Figure 2.4 shows a MTBE adsorption data set modelled using the linearized Freundlich equation (Chen et al. 2010). The value of 1/n equals the slope of this line and K_{FREUND} equals the value of q_e at the liquid phase concentration (C_e) value of 1. For the MTBE data discussed earlier, the Freundlich model describes the higher concentrations and loadings of MTBE better plotted the Langmuir model (Chen et al. 2010).

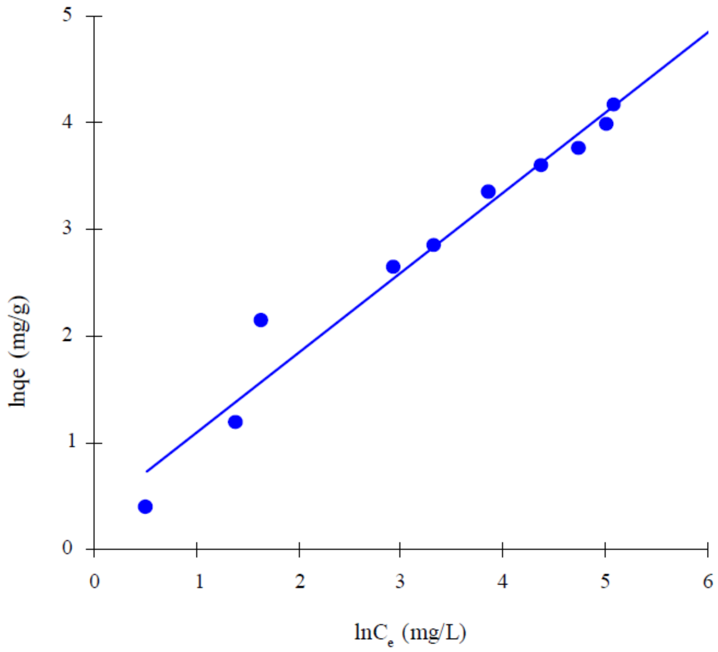

Figure 2.4: Freundlich modelling of GAC adsorbing MTBE (Chen et al. 2010)

Depending on the behaviour of the adsorbent-adsorbate combination, one model may be better suited then the other. If higher concentrations are being explored and the q_e values reach or approach a constant level, then the Langmuir would be a more appropriate model.

2.5.2 Competitive Adsorption

In industrial wastewaters multiple contaminants are involved (Dobbs and Cohen 1980), this is also the case for contaminated groundwater at hazardous waste sites. If activated carbon is used when there are multiple contaminant species present in the water the contaminants will try to compete for the adsorption sites on the pores of the adsorbent. This phenomenon is more commonly known as multicomponent or competitive adsorption. Most waters have a multitude of solute species that will engage in this behaviour. The extent to which the adsorption capacity of a given target pollutant is decreased by the competition depends on the adsorbability of the other compounds present and their concentration within the water in question.

The highest concentration organic compound found in drinking water plants (and some groundwater remediation sites) is natural organic matter (NOM). NOM is present in almost every natural water body as well as in groundwaters. NOM is the result of decomposition of organic matter that would be found in a lake, river or land. This includes decomposing vegetation, microbial and algal remains, and decomposing animal matter that originate from the water body or enters it with runoff or wastewater discharges. NOM is a heterogeneous mixture of organic acids and is normally dominated by humic and fulvic acids (Chowdhury et al. 2013).

Water treatment plants need to account for the NOM when treating the raw water because of a number of reasons. Practically all water treatment plants in North America use chlorine for primary disinfection and/or post-disinfection. If NOM is not removed before the disinfection stage, the resulting reaction with chlorine can produce harmful disinfection by-products (DBPs) (Chowdhury et al. 2013). Trihalomethanes (THMs) are the most prevalent family of DBPs that are produced from chlorine reacting with organic matter. Trihalomethanes have been proven to lead to cancer if the subject is exposed for long periods of time to concentrations above the maximum contaminant level (CDC 2014). The main current method of avoiding the formation of DBP formation is maximizing NOM removal through enhanced coagulation prior to chlorination. Through higher coagulant doses, enhanced coagulation can remove up to 50% of the NOM, but the remaining NOM will still produce DBPs. The DBP formation may be further minimized by using alternative disinfectants. In some cases, further NOM removal is required because enhanced coagulation is not sufficiently efficient for the particular water, then AC adsorption is sometimes implemented for this purpose (USEPA 1999)

Incorporating a GAC filter layer within the multi-media filtration step is a possibility, however a dedicated a GAC post-filter adsorber with significant depth is required in order to achieve large removals of NOM (Chowdhury et al. 2013). Given that GAC's adsorption capacity is somewhat limited for this type of applications, the GAC may have to be replaced (or regenerated) relatively frequently (0.3 to 1 years). This makes the GAC a rather expensive option for NOM removal and may not be the most appropriate choice (Sontheimer et al. 1988).

In drinking water treatment, GAC is most frequently used for the removal of taste and odour compounds, and it is occasionally used to cleanup contaminated groundwater sources. In both cases, the target contaminants are in trace levels (µg/L or ηg/L) but these waters still contain mg/L of NOM. And while we may not be directly interested in the NOM removal, this NOM can impact the performance of the GAC. This is because: a) NOM competes with the target contaminant(s) (which is present in significantly smaller concentrations) for adsorption sites; b) the NOM is adsorbed onto the pores chemically irreversibly; and c) the NOM can block entrance to pores (Crittenden et al. 2012; Ding 2010; Kilduff et al. 1996; Narbaitz and McEwen 2012). NOM-linked competitive adsorption phenomena reduced the adsorption capacity of 1,1,2 trichloroethane by over 50% (Narbaitz and Benedek 1994). Ding (2010) studied the competitive adsorption of atrazine and NOM onto various types of PACs, as shown in Figure 2.5, the atrazine adsorption capacity of W20 PAC drops by about 85% when NOM is present (Ding 2010).

This may result in restricting access to unused micropores due to these molecules blocking larger pores (Narbaitz & Benedek 1994).

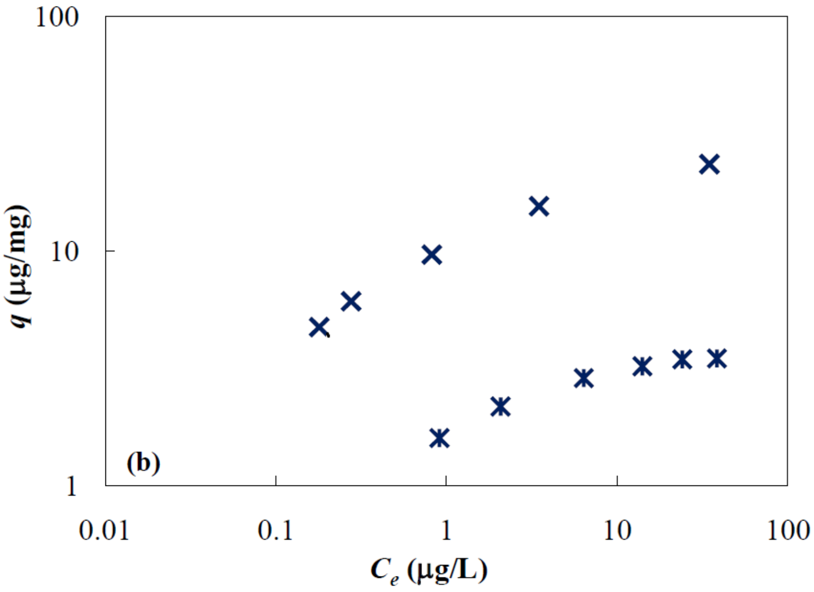

Figure 2.5: Adsorption isotherms of atrazine in the presence of NOM on PACs (✱) at $C_{o,atz}$ = 50µg/L in comparison to non-competitive isotherms (×) at $C_{o,ATZ}$ = 100µg/L (Ding 2010)

Regardless of the type of contaminants being remove at some point the GAC column effluent will reach a maximum acceptable contaminants level and the GAC will have to be replaced by virgin GAC or regenerated GAC.

2.6 Activated Carbon Regeneration Methods

This section will discuss the calculation of the adsorbent regeneration efficiency followed by a discussion of alternative regeneration methods.

2.6.1 Regeneration Efficiency

Regeneration efficiency (RE) is a metric of how effective a regeneration method is in recovering the adsorbent's original sorption capacity. The general approach is to conduct a batch loading tests, like those in an isotherm, with the water to be treated, followed by the activated carbon regeneration and finally a batch reloading using the same water and procedure. There are several ways to determine the percentage regeneration efficiency value. The general method is calculated by determining the ratio of the adsorption capacity of the regenerated carbon (q_{e2}) over the adsorption capacity of the virgin carbon (Narbaitz and Cen 1997; Sun et al. 2017). Mathematically this can be described as

$$PR_S = \frac{q_{e2}}{q_{e1}} * 100\% = \frac{(C_{02} - C_{e2})V/M}{(C_{01} - C_{e1})V/M} * 100\ \% \tag{2.7}$$

Where PR_S is the standard percent regeneration efficiency; q_{e2} is the solid phase concentration of adsorbent after the reloading (readsorption) cycle (mg contaminant/g adsorbent); q_{e1} is the solid phase concentration of the virgin adsorbent after the initial loading cycle (mg contaminant/g adsorbent); C_{01} is the initial or control liquid phase contaminant concentration for the first cycle (mg contaminant/L or µg contaminant/L); C_{02} is the initial liquid phase contaminant concentration for the reloading cycle (mg contaminant/L or µg contaminant/L); C_{e1} is the equilibrium liquid phase concentration for the first cycle (mg contaminant/L or µg contaminant /L); C_{e2} is the equilibrium liquid phase concentration for the second cycle (mg contaminant/L or µg contaminant/L); M is the mass of adsorbent used in the batch test (g); and V is the volume of contaminated water in the equilibrium vessel (L).

There can be several alternative methods of evaluating the regeneration efficiency (Narbaitz and Cen 1997). An alternative approach is based on using the loadings of the regenerated GAC and the virgin GAC that correspond to the same equilibrium liquid phase concentration (C_{e1}). In this approach

$$PR_2 = \frac{q_{ee}}{q_{e1}} * 100\% \tag{2.8}$$

Where PR_2 is percentage regeneration efficiency by method 2; q_{ee} is the regenerated adsorbent's equilibrium solid phase concentration (mg contaminant/g adsorbent) that is in equilibrium with the equilibrium liquid phase concentration achieved during the initial loading cycle (C_{e1}). However, if one conducts the batch reloading experiment using the same conditions as the original loading experiment (including the same mass of GAC) the resulting equilibrium liquid phase concentration (C_{e2}) is unlikely to be the same as that during the initial loading step. In order to obtain q_{ee} several reloading experiments with slightly different initial conditions are required followed by interpolation. Accordingly, this is a trial and error approach which requires substantial time and effort to determine q_{ee}. Narbaitz and Cen (1997) proposed a somewhat analogous approach that requires less experimental effort, that can be used when the adsorption is described by a Freundlich isotherm. It uses the isotherm of the virgin GAC to estimate the loading of the virgin adsorbent (q_{e11}) at the equilibrium liquid phase achieved during the reloading step. The equation for this approach is as follows

$$PR_3 = \frac{q_{e2}}{q_{e11}} * 100\% = \frac{(C_{02} - C_{e2})V/M}{K_{FREUD} C_{e2}^{\frac{1}{n}}} * 100\ \% \tag{2.9}$$

Where PR_3 is percentage regeneration efficiency by method 3.

The second and third approaches (i.e., PR_2 and PR_3) seem to be more fair evaluations of the regeneration efficiencies, because they use more consistent liquid phase concentration basis. PR_3 has been used by Narbaitz and coworkers (Karimi-Jashni and Narbaitz 2005a; b; Narbaitz and Karimi-Jashni 2009), but by few others. This is presumably because the higher values obtained using PR_S make their regeneration methods appear to be better.

2.6.2 GAC Regeneration Methods

The conventional GAC regeneration method for GAC used in water and wastewater treatment applications is thermal regeneration (Chowdhury et al. 2013; Crittenden et al. 2012; Moore et al. 2003). Due to some limitations there has been extensive research into alternative GAC regeneration methods. The following subsections discuss conventional thermal GAC regeneration as well as some of its proposed alternatives.

2.6.2.1 Conventional Thermal Regeneration

Thermal regeneration is the standard method used in regenerating spent activated carbon, it uses both conductive and convective heat transfer to regenerate GAC. The regeneration consists of three main steps: drying, vaporization, pyrolysis, and selective oxidation (Chowdhury et al. 2013; Sontheimer et al. 1988; Van Vliet 1991). Each step has a gradual escalation in temperature to obtain the desired effect. Drying usually occurs by the time the AC reaches 200^{O}C and as the temperature rises it also helps desorb highly volatile adsorbates. Afterwards, the vaporization step, that occurs at 200^{o}C to 500^{o}C, further degrades the volatile adsorbates into fragmented compounds. Then, pyrolysis occurs at 500^{o}C to 700^{o}C with the use of steam, it is necessary to destroy the fragmented compounds remaining on the activated carbon. This will form some carbon residues on the surface of the activated carbon. Selective oxidation at 700^{o}C or higher is required by steam, carbon dioxide and/or other oxidizing substances to oxidize the carbon residue (Van Vliet 1991). At these conditions, the carbon residue is more reactive than the AC being treated, a small portion of the AC will be gasified along with the carbon residue (Chowdhury et al. 2013). Temperature at this stage is a key parameter in avoiding the carbon residue to a structure similar to that of the activated carbon. This process is called graphitization and when the carbon residue is treated in this manner the resulting compound will be equally as resistant to deterioration as the activated carbon being treated. Therefore, temperatures closer to 700 ^{O}C work better than higher temperatures (Van Vliet 1991). These temperatures are used as general guidelines since each AC manufacturer has their own process when regenerating different types of AC. When the regeneration is complete, steam or hot gases are used to remove the carbonaceous residue on the adsorbent. The gases carry this material as a flue gas to be treated further. Conventional thermal regeneration is an energy intensive process.

While GAC adsorbers at water treatment plants are primarily intended for the removal of taste and odour compounds or possibly trace levels of toxic compounds, the presence of significantly concentrations of NOM in the water causes the NOM to be primarily loaded with NOM. Thermal regeneration provides the intense heat necessary to volatilize NOM and carbonize the NOM that cannot be desorbed. Regeneration efficiencies of GAC loaded with NOM can reach up to 99% with thermal regeneration (Cannon 1993; Cannon et al. 1997; Moore et al. 2003; Narbaitz and McEwen 2012). However, the regenerated carbon does lose 10-12% of its mass when thermally regenerated and may be inferior in performance as compared to virgin GAC (AWWA and ASCE 2013; Cannon 1993; Cannon et al. 1997; Moore et al. 2003; San Miguel et al. 2001). The value of the GAC mass losses is due to the thermal regeneration itself plus the transportation of the adsorbent from the adsorber to the regeneration system and then back to the adsorber.

Because of the high energy requirement and significant loss of GAC mass, there has been significant laboratory-scale research on alternative methods of GAC regeneration in an attempt to overcome these deficiencies. The majority of this work has involved the regeneration of GAC loaded with model single synthetic organic compounds, such as phenol. The alternative methods include microwave regeneration, chemical regeneration, and electrochemical regeneration. The following subsections discuss some of key findings of this research.

2.6.2.2 Microwave Regeneration

Microwave regeneration uses microwave radiation in the form of electromagnetic energy where this energy is then converted into heat by a medium that can conduct a charge (i.e., water). Microwave research during the Second World War led to numerous developments in the 1950s. In the 1970s, Japanese companies developed a more affordable version of the microwave oven that was first invented in 1951 by the Raytheon Company (Yuen and Hameed 2009). This has led to research on other applications of microwaves, of particular interest is the use of microwaves in the regeneration of AC. Strictly speaking, this is also a thermal regeneration process, however the different nature of the heating mechanism may result in different regeneration efficiencies.

The high voltage frequency produced by microwaves create a dipole moment and changes the direction of their pole to the opposite of the applied field (Yuen and Hameed 2009). This creates agitation in the molecules and that agitation will generate heat. Microwave regeneration is considered one of the most uniform methods of regeneration of GAC since the heat transfer is occurring on a molecular level and provides an even transfer of the microwaves into the water molecules in the AC. In contrast, conventional thermal regeneration occurs primarily by conduction, this leads to greater heating of the outer parts of the GAC particles and less heating of the inner parts of the GAC particles (Sun et al. 2017; Yagmur et al. 2017).

Yuen and Hameed (2009) conducted bench-scale studies involving the preparation and regeneration of GAC. They claimed the main advantages of this approach are greater particle interior heating, higher heating rates, greater operational control of heating, no direct contact of the heating materials, and reduced equipment size and waste (Yuen and Hameed 2009). Theoretically, microwave heating does not damage the carbon unlike methods with indirect heating and consumes less energy (Yuen and Hameed 2009). Yuen & Hameed (2009) claim regenerated carbon by this method shows is unaltered and unaffected by the regeneration.

Other researchers such as Ania et. al. (2005) who performed a study on the effects of thermal and microwave regeneration on the pore structure of ACs. They found that there is a large drop in surface area (50% lower in N_2 adsorption) after each microwave regeneration cycle (Ania et al. 2005). Yagmuir et al. (2017) studied the effects of microwave regeneration of AC loaded with different phenolic compounds. They used a commercial activated granular activated carbon (CGAC), a powdered activated carbon produced from waste tea leaves then activated by microwaves (WT-PAC) and a powdered activated carbon produced from demineralised waste tea leaves then activated by microwaves (DWT-PAC). The reactor configuration was very similar to a conventional microwave oven (Figure 2.6). In order to provide venting of the gas, nitrogen was circulated and there was an infrared pyrometer to measure the temperature within the crucible. After production, the AC was loaded in batch tests using 400 mg/L phenol or 400 mg/L of p-nitrophenol (PNP) solutions, the AC removed 90% of these compounds. The regeneration cycle used a microwave oven at a frequency of 2.45 GHz for 30 seconds. Their results showed that the capacity of the CGAC, which was produced through a conventional thermal method, to reabsorb after microwave regeneration increased to a higher level than virgin CGAC (Figure 2.7) and the higher capacity was maintained after subsequent regeneration cycles. Accordingly, it may be that microwave heating appears to be able to reach some internal pores that the conventional thermal method did not manage to initially activate. The CGAC achieved higher phenol removals than the experimental ACs activated and regenerated using microwaves (Yagmur et al. 2017) (Figure 2.7). However, the phenol-removal capacity of the experimental activated carbons was maintained through several cycles of microwave regeneration, thus microwave regeneration was 100% efficient. These regeneration efficiency results seem to contradict the large percent losses in adsorbent area reported by Ania et al (2005).

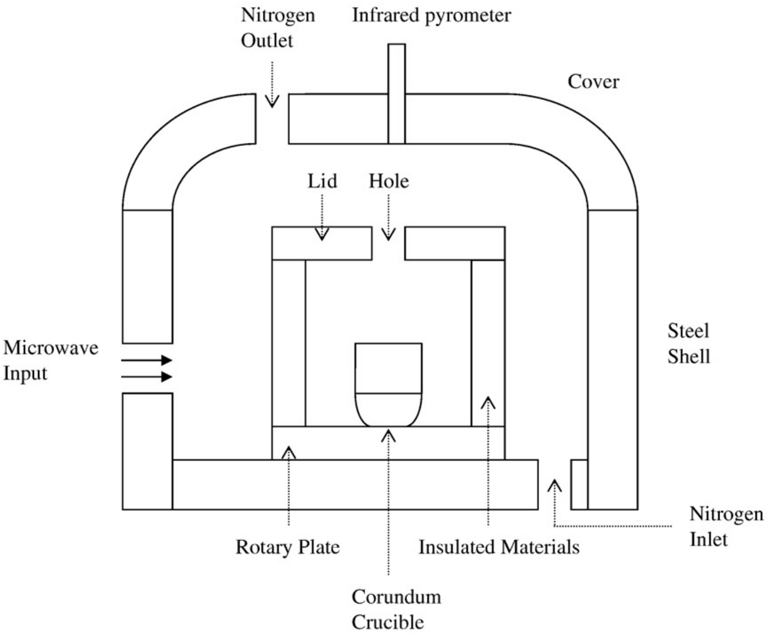

Figure 2.6: Diagram of a microwave heating system (Yagmur et al. 2017)

Figure 2.7: Percent phenol removal in batch tests using virgin and microwave regenerated activated carbons (Yagmur et al. 2017)

The differences in phenols removals of the CGAC and the microwave prepared materials may be more related to the AC pore size distribution of the activated carbons as they were prepared from different raw material and activated differently. Yagmur et al. (2017) concluded that superior removal can be achieved by preparing the activated carbon by thermal activation process and regenerating it via microwave regeneration. However, the comparisons were not fair. First, because the raw materials of CGAC and the other two activated carbons were different. And secondly, there was no comparison of the impact of thermal and microwave regeneration. So, their conclusions seem premature. The microwave regeneration method was completed in minutes, which is a much shorter time than the days required to regenerate the AC by conventional thermal regeneration techniques (AWWA and ASCE 2013). On the other hand, the microwave regeneration was conducted in the bench-scales tests and when it is scaled-up to handle the large batches of GAC will take significantly longer than the 30 second microwave regeneration step. This is because at water treatment plants one must also consider the time required to transport the GAC, drain the GAC, microwave process the GAC and transport the GAC back to the adsorber.

There is also the consideration of the regeneration of GAC loaded NOM, that adsorbs irreversibly onto the pore structure of the AC. Zhang et. al. (2018) evaluated microwave regeneration (T = 97 ^{o}C after 90 seconds in the microwave oven) with a 210 second regeneration time, they observed that the maximum regeneration efficiency was less than 7%. (Zhang et al. 2018). This would mean that microwave regeneration would not be able to desorb effectively humic acids by itself. This is a crucial requirement for any regeneration method for water treatment applications since humic acids compose a majority of all organic matter adsorbed on the GAC.

2.6.2.3 Chemical Regeneration

Chemical regeneration is the use of chemical solvents or oxidants to desorb and possibly degrade the adsorbed compounds on the surface the adsorbent, so as to free the adsorption sites for the next adsorption cycle. Chemical regeneration has the potential benefits of being performed in situ or on site rather than having to invest in an onsite thermal regeneration facility. Adsorbates can potentially be recovered during regeneration if that is desired or profitable. The main categories of regenerants are organic and inorganic solvents. Investigating the various mechanisms of adsorption will lead to information as to how well GAC loaded with different compounds will be regenerated based on their properties. It has been proven that organic solvents with high solubility are better at regeneration than inorganic solvents with high oxidation potentials (Leng and Pinto 1996). Also, solvents with smaller molecular weights tend to be more effective at regenerating than solvents with higher molecular weights (Lu et al. 2011). This may be because the smaller molecules are more effective at reaching all of the smaller pores of the adsorbents than regenerants with a larger molecular size (Leng and Pinto 1996). Also, some regenerants are more effective at regenerating a specific type of adsorbent than others. For instance, sodium hydroxide was shown at being very effective at desorbing phenol as found by Himmelstein et al. (1973). Although, investigation as to whether the residual phenolic by-products (from the regeneration) remain adsorbed in the subsequent adsorption phase has yet to be considered. The main by-product formed after regeneration was sodium phenate (Himmelstein et al. 1973).

Lu et al. (2011) investigated the regeneration of AC loaded with two different colored dyes (i.e., peach red and mustard yellow dyes) using a variety of chemicals. The effectiveness of the regeneration depended on the composition and concentration of the regenerants. For instance, 60% of acetone in 40% of water was more effective at desorption than pure acetone. This phenomenon can be explained by the regenerant themselves, acetone as a pure solution has a lower degree of wettability than when it is mixed with water. Wettability is a compound's ability in the liquid phase to adhere to a solid surface when in the presence of other liquids. Regeneration using chemicals was impacted by a variety of factors such as solubility (Leng and Pinto 1996). The effectiveness of the regeneration particularly impacted the solubility of the adsorbate in the regenerant solution. The higher degree of solubility for the dyes would have a higher driving force for desorption of the dyes. Lu et al. (2011) evaluated the effects of regenerating the desorption efficiencies of red and yellow dyes with over 80% desorption efficiencies for yellow dyes at 100% methanol concentration. They claimed that it can be an acceptable alternative for thermal regeneration If the regenerant (i.e. methanol) be used to regenerate the GAC is cost effective (Cooney et al. 1983; Lu et al. 2011). Although, the reloading of dyes into the AC would be challenging since the chemicals would ultimately alter the structure of the adsorbents. Many researchers try to make the case for chemical regeneration saying that the chemicals used are fairly volatile and can be removed with a distillation column (Cooney et al. 1983). Although chemical regeneration may be feasibly for GAC used in industrial wastewater applications, it is not accepted for drinking water applications because of the potential for residual regenerant to leach from the regenerated GAC into the treated drinking water. The potential for savings that may be achieved by using inexpensive chemical regenerants is outweighed by the need for additional treatment process to safeguard the public.

2.6.2.4 Electrochemical Regeneration Methods

Electrochemical regeneration is the process of using an electrochemical cell to regenerate an adsorbent. Electrochemical cells can either harness chemical reactions to produce electricity or facilitate reactions with the induction of an electrical current (Bard and Faulkner 2001; Sillanpää and Shestakova 2017). These reactors usually have two chambers or cells filled with electrolyte and contain an electrode, the cells are connected through conductive wires and electrolyte bridges. The wires and electrolyte bridges are the conductors that complete the circuit of the cell. By applying an electrical current, the cell hydrolyses the water and H^+ & OH^- ions are formed at the anode and cathode, respectively (Asghar et al. 2013; Brown et al. 2004b; a; Hussain et al. 2014, 2015). The anode is the oxidizing electrode and it generates very strong oxidizing agents, such as hydroxy radicals (OH^o) and chlorine (when the electrolyte contains chloride). In electrochemical GAC regeneration systems, these ions interact with adsorbed compounds and rapidly reduce or oxidize them. Electrochemical cells create very extreme environments in terms of pH, anodic compartments reach pHs of approximately 2 and cathodic compartments have pHs of approximately 12. There are two main approaches to electrochemical GAC regeneration, they are cathodic regeneration and anodic regeneration. In principle, the regeneration occurs by either direct oxidation on the surface of the adsorbent, by enhanced desorption, or by enhanced desorption into the liquid phase and oxidation in the liquid phase.

Most electrochemical regeneration studies have focused on the regeneration of GAC loaded with a model solute, the most common is phenol. Phenol is a by-product of large-scale industrialized manufacturing and without treatment can end up in a body of water. Phenol is an important target contaminant since it is widely available and very soluble in water (Australian Government Department of Environment and Energy 2019). pH impacts phenol (C_6H_5OH) adsorption in a number of different ways. First, phenol dissociate into phenate ($C_6H_5O^-$) at high pH. This is described by

$$C_6H_5OH \Leftrightarrow H^+ + C_6H_5O^- \quad K = 1.2 \text{ X } 10^{-10} \tag{2.10}$$

$$\text{and } pKa = 9.9 = \frac{[H^+]\cdot[C_6H_5O^-]}{[C_6H_5OH]} \tag{2.11}$$

Second, is that the adsorption capacity of phenol (and for many other compounds) is at a maximum at pHs below the pKa, but decreases significantly at extremely low pHs and as the pH increases above the pKa (Cooney 1999).

Narbaitz and Cen (1994) were one of the first researchers to experiment with the use of GAC regeneration electrochemically, they evaluated it by batch loading a commercial GAC with phenol, electrochemically regenerating it, and finally reloading it in the same manner. They designed a reactor with the batch reactor with three horizontally oriented 7.6 cm diameter platinum sheet electrodes held 2 cm apart by a perforated plexiglass column sections placed in an electrolyte bath. The phenol batch-loaded GAC was placed as a monolayer on the middle electrode and the testing was conducted using very low current densities, as low as 0.2 mA/cm^2. They experimented with different types of electrolytes. The electrolytes used were salt solutions including NaCl, $NaHCO_3$, Na_2SO_4, and CH_3COONa. The best results were obtained with 1% NaCl solutions as the electrolyte, the other salts resulted in ions that presumably ionic free radical scavengers and reduce the free radical concentration and thus decrease the phenol oxidation (Narbaitz and Cen 1994).

The use of 1% NaCl electrolyte yielded a cathodic regeneration efficiency of 88% and decreased by 2% for each subsequent regeneration cycle. Their initial regeneration efficiency was lower than that expected for thermal regeneration, however there was no apparent GAC mass loss after regeneration. Thermal regeneration processes can cause a 10-12% GAC mass loss and the cost of replacing that GAC with virgin material can represent 20-40 % of the cost of GAC regeneration (AWWA and ASCE 2013; San Miguel et al. 2001). Therefore, there may be an economic advantage in regenerating the GAC electrochemically to avoid the cost of replacing the GAC with virgin material. There is also the consideration of the regeneration time of GAC. Cen & Narbaitz (1994) tested various regeneration times from 1 to 10 hours. They subsequently found that the optimal regeneration time for GAC was 5 hours. This is considered a vast improvement from thermal regeneration that could be up to 24 hours at the same scale. Narbaitz and Cen (1994) studied both cathodic and anodic regeneration. The superiority of cathodic regeneration appeared to be associated with the enhanced phenol desorption at the cathode due to the very pH conditions it generates.

In an attempt to improve performance, Karimi-Jashni & Narbaitz (2005b) used different electrochemical reactor configurations and they found the pH in the vicinity of the phenolics-loaded GAC to be critical. Adding electrolyte mixing reduced the pH near the GAC (located at the cathode) and decreased the cathodic regeneration efficiency. They also showed a decrease in regeneration efficiency when GAC was regenerated anodically in the electrochemical cell (Figure 2.8). The regeneration efficiencies were 30% higher when being regenerated cathodically. The overall best regeneration efficiency of the regenerated carbon was 80% which is considered quite low as compared to thermal regeneration which generally is above 95% (Karimi-Jashni and Narbaitz 2005b; Narbaitz and McEwen 2012). It should be noted that Karimi-Jashni and Narbaitz used Equation 2.9 to calculate the regeneration efficiency as opposed to Equation 2.7, that yields more optimistic values, used by Narbaitz and Cen (1994) and many others. The cathodic regeneration yielded the best RE because of the pH at the cathode, where the loaded GAC was located, was higher than the pKa of the adsorbed phenol which facilitated desorption (Karimi-Jashni and Narbaitz 2005b; Wang and Balasubramanian 2009). To investigate if the process could potentially be used to regenerate a column of GAC in place, Karimi-Jashni and Narbaitz (2005b) regenerated multiple layers of GAC particles placed on the cathode of their electrochemical reactor. The tests showed a decrease in the regeneration efficiency with increasing bed depth, this was presumably due to fact that only the GAC layer resting on the cathode was exposed to the highest pH and GAC particle layers above it were exposed to lower pHs decreasing the desorption driving force.

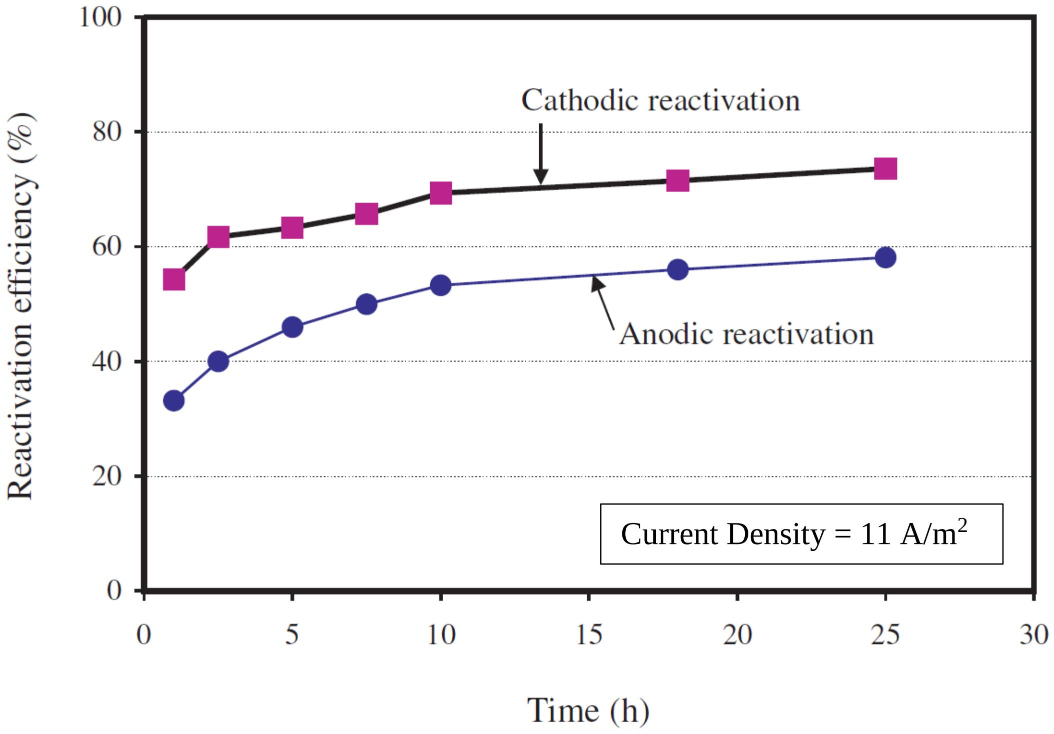

Figure 2.8: Cathodic regeneration versus anodic regeneration for type F-400 of GAC loaded with phenol (Karimi-Jashni and Narbaitz 2005b)

Wang & Balasubramanian (2009) obtained regeneration efficiencies of nearly 100 % for phenol-loaded GAC using anodic regeneration but they still observed a decrease in RE with each regeneration cycle as shown in Figure 2.9. This decrease was not noted in the Karimi Jashni & Narbaitz (2005b) study because they did not evaluate subsequent regeneration cycles beyond the first regeneration. This long-term regeneration efficiency decrease would lead to problems with the decrease in performance and the need for additional virgin GAC to match performance of that of thermal regenerated GAC. Therefore, more research must be performed on electrochemical regeneration systems to improve their long-term performance.

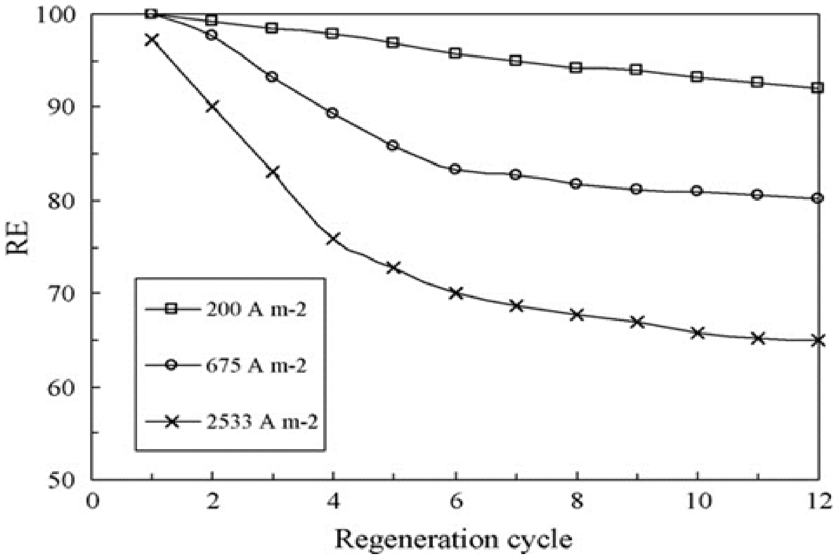

Figure 2.9: Electrochemical regeneration of phenol with GAC at 20, 67.5, and 253.3 mA/cm^2 (Wang and Balasubramanian 2009)

Other researchers such as Berenguer et al. (2010) studied the cathodic and anodic regeneration of phenol but obtained lower regeneration efficiencies (i.e., 70 %) than the Wang & Balasubramanian (2009) study, which yielded REs of nearly 100%. This could be due to a less than optimal reactor configuration as the filter press reactor's anode configuration was enabling the re-adsorption of oxidation by-products of phenol leading to poor desorption of phenolics. This result appears to contradict several studies showing that cathodic regeneration (Figure 2.8) yields somewhat higher RE than anodic regeneration (Karimi-Jashni and Narbaitz 2005b; Narbaitz and Cen 1994; Zhang et al. 2002). Therefore, there might be an appropriate reactor configuration and/or operating conditions that could yield high REs for anodic regeneration. Cathodic regeneration studies were also conducted by García-Otón et al. (2005), they used GAC loaded with toluene. At a current density of 1300 mA/cm^2, versus 1.1 mA/cm^2 used by Karimi-Jashni & Narbaitz (2005b), and a regeneration time of 3 hrs, the cathodic regeneration method yielded REs above 99% (García-Otón et al. 2005). This may be due to the change in the surface charge of the GAC at higher pH levels from positive to negative making the surface repulsive to other negatively sorbed adsorbates.

As previously discussed, GAC adsorbers at water treatment plants may remove trace contaminants but they are primarily loaded with NOM that is present in all natural waters. Therefore, regeneration research needs to investigate the regeneration of GAC loaded at actual treatment plants or is loaded with NOM. There only has been limited research in this area. Narbaitz & Karimi-Jashni (2009) showed that cathodic regeneration could achieve regeneration efficiencies of 70 to 80% (based on the iodine numbers) for GAC from a pilot plant column at the Britannia WTP. They speculated that these relatively high efficiencies were due to use of the iodine number as the GAC capacity. Narbaitz & McEwen (2012) evaluated bench-scale regeneration of NOM-loaded GAC in the lab and loaded GAC obtained from two full-scale WTPs. They quantified the regeneration efficiency based the TOC loadings achieved after batch reloading of the regenerated samples. They had three interesting findings. First, they found that using the iodine number yield much larger RE than when based on NOM (measured as TOC) reloading, thus the use of the iodine number is not recommended. Second, the electrochemically regeneration efficiencies for field-loaded GAC (in continuous flow GAC column adsorbers) were significantly lower (RE < 20%) than the lab batch-loaded GAC, this is presumably due to the GACs continuous exposure to additional NOM. Thus, batch loading with NOM does not appear to be as realistic but it is certainly easier to perform experimentally. Third, the thermal regeneration efficiencies at these WTPs were significantly higher (RE = 85 – 100%) than those achieved electrochemically (RE < 20%) (Figure 2.10). They speculated that cathodic regeneration was not very effective for NOM-loaded GAC because NOM adsorbs irreversibly which limits the extent of high pH driven desorption and regeneration. Thus, electrochemical regeneration of GAC that has been loaded at water treatment plants does not seem practical. However, for application were NOM is not the main adsorbate it may be feasible. Recently, an effective sorption-electrochemical regeneration system has been developed using a promising alternative sorbent, NYEX®, this research will be discussed in the next section.

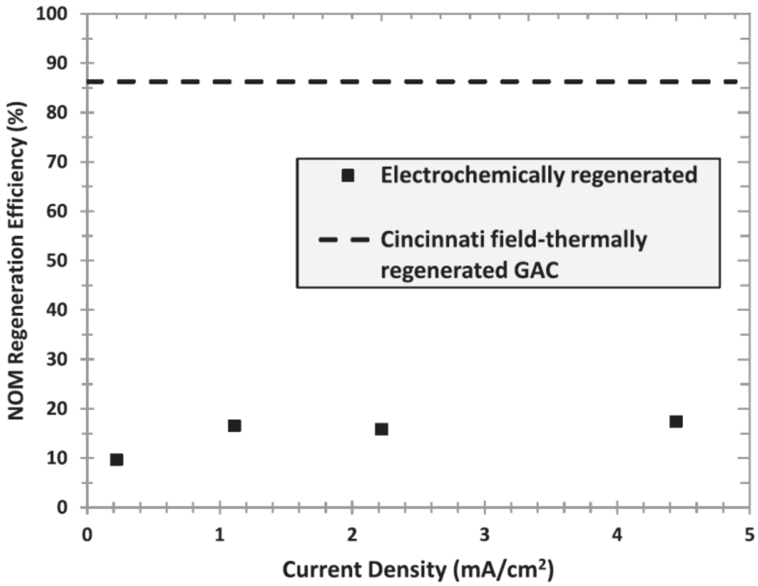

Figure 2.10: NOM regeneration efficiency for GAC loaded at the Cincinnati WTP (Narbaitz and McEwen 2012)

2.7 NYEX® and its electrochemical regeneration.

NYEX® is a graphitic intercalation compound (GIC) developed by ARVIA technologies and Dr. Roberts' group at the University of Manchester (Brown et al. 2004a). ARVIA developed the early prototype of this material called NYEX® 100. It was fabricated with a sulfuric acid treatment though the specific details of the manufacturing process are a trade secret of the company (Asghar et al. 2013). The process enhances the surface of the NYEX® by making it more positively charged and thus enhancing its adsorption for negatively charged compounds. This can be demonstrated by comparing the adsorption of phenol onto graphite (de Oliveira Pimenta and Kilduff 2006) with the adsorption of phenol onto NYEX® 1000 (Asghar et al. 2015), the chemically altered graphite (NYEX® 1000) adsorbed 1.07 times more phenol with a than unaltered graphite assuming that the type of adsorption is irreversible (Asghar et al. 2014; de Oliveira Pimenta and Kilduff 2006). This could be due to the type of raw material of the graphite being of higher quality and the source material for the NYEX® was made from a lesser quality material. (Asghar 2011). NYEX® 1000 has a much smaller total surface area than GAC (~ 1 m^2/g versus ~1000 m^2/g GAC) and thus it has smaller contaminant adsorption capacities than GAC, however it is potentially a good adsorbent due to its highly conductive nature which makes it attractive for electrochemical regeneration. NYEX® has a much smaller surface area than GAC because it does not have a significant pore structure. Thus, NYEX® adsorption is a much faster process than GAC adsorption because the adsorption takes place primarily on the surface of the NYEX® particles and it is not impacted as much by the slow diffusion of the adsorbates into the internal pore structure.

As shown in Figure 2.11, the first anodic electrochemical regeneration of NYEX® 100 improved its atrazine sorption capacity and this high capacity was maintained through subsequent regeneration cycles. Thus, the anodically REs were consistently above 100%. Similar results were observed for NYEX® 1000 (another GIC) loaded with acid violet 17 dye (Mohammed 2011), and phenol (Asghar et al. 2014; Brown and Roberts 2007) (Table 2.1). It should be noted that in the NYEX® electrochemical reactors that a 1 cm deep layer of NYEX® is placed between the anode and the membrane, which is superior to the monolayers of GAC regenerated by the Narbaitz's group.

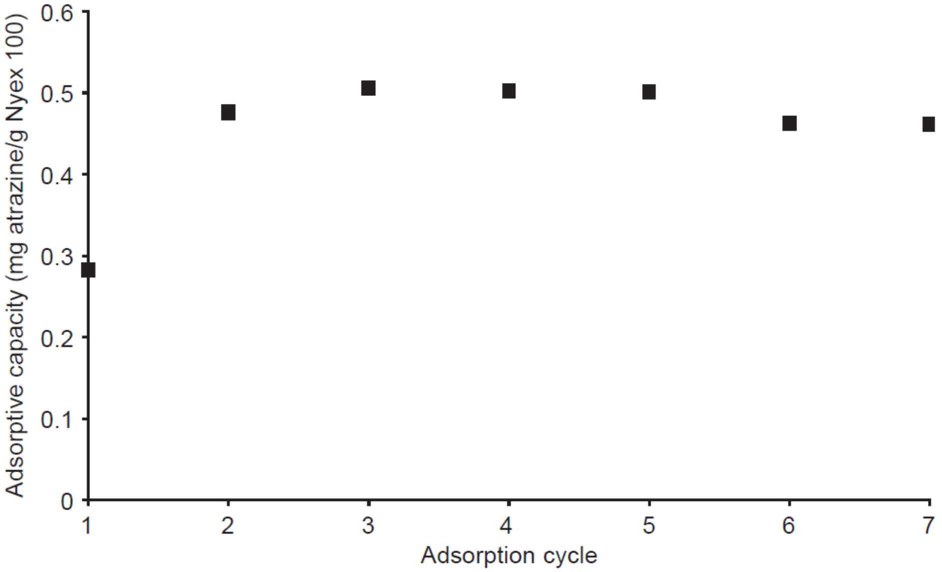

Figure 2.11: NYEX® 100 atrazine adsorption capacity (C_i = 6 mg/L) after numerous cycles of anodic regeneration at 10 mA/cm^2 (Brown et al. 2004a)

Table 2.1: Summary of NYEX® single synthetic organic compound adsorption and electrochemical regeneration from the literature

Adsorbent	Adsorbate	Regeneration Time (min.)	Current Density (mA/cm^2)	Regeneration Efficiency (%)	Reference
NYEX® 100	Atrazine	10	20	>100	(Brown et al. 2004a)
NYEX® 1000	Acid Violet 17	60	5	98	(Liu et al. 2016)
NYEX® 1000	Phenol	45	10	>100	(Asghar et al. 2014)
NYEX® 1000	Ethanol Thiol	20	12	138	(Asghar et al. 2019)
NYEX® 1000	Methyl Propane Thiol	20	12	135	(Asghar et al. 2019)

The complete electrochemical regeneration of NYEX® loaded with several different single contaminant solutions (Table 2.1) is quite an improvement when compared to literature results for cathodic regeneration of phenol-loaded-GAC because of several reasons. First, Narbaitz and Karimi-Jashni (2005) found for phenol loaded GAC it achieved a maximum cathodic regeneration efficiency of 80% versus 100% for NYEX®. This likely shows that the structure of the GAC is being degraded over many adsorption cycles. Second, to achieve this Narbaitz and Karimi-Jashni (2005) needed a regeneration time of 10 hours versus the 20 minutes required for the NYEX® regeneration (Asghar et al. 2014). Third, for the GAC studies the regeneration efficiency gradually decreased in subsequent regeneration cycles, while the 100% regeneration efficiency achieved by the NYEX$^{®}$ systems was sustained. On the other hand, as GAC has a much larger surface area and much larger contaminant adsorption capacity, the GAC regenerations involved significantly larger masses of contaminant than the NYEX$^{®}$ experiments. Thus, GAC's lower electrochemical regeneration performance efficiencies may be at least in part due to the larger contaminant loads.

Brown et al. (2004a) explored the potential mechanisms behind the high NYEX$^{®}$ anodic regeneration efficiencies. They initially thought that the hydrogen ions produced from the electrochemical regeneration were binding to the surface of the adsorbent creating new functional group that were improving the readsorption. However, this was apparently not the case since loading (and reloading) the solute at different pHs had no effect on the mass of contaminant removed from solution. Although, the regeneration of the NYEX$^{®}$ in this low pH environment caused changes to its structure creating edges on the outer surface and generating more outer surface area. This causes an increase in adsorbable surface area of the adsorbent and thus adsorbing more compounds on the second regenerating cycle (Brown et al. 2004a). This phenomenon would be very useful in the long-term adsorption of target contaminants.

In contrast to the research using synthetic organic compounds as solutes, Asghar et al. (2013) investigated the regeneration of NYEX® loaded with humic acid solutions. Although these was a commercial (i.e. Aldrich) soil-extracted humic acid and are not quite the same as aquatic-based humic substances found in surface waters, these solutions have been often used a model NOM (McCreary and Snoeyink 1980). Asghar et al. (2013) revealed that the anodic regeneration of the humic acid-loaded NYEX® 1000 had a RE efficiency of 100% when the reactor was operated a current density of 10 mA/cm^2 for 30 minutes. Given that humic acid are known to be quite recalcitrant and even in advanced oxidation processes, such as ozone oxidation, only fully mineralize 10 to 20% of the humic acid (Betancur-Corredor et al. 2016), the 100% regeneration of NYEX® was rather surprising. This complete regeneration is not likely related to the mineralization of the humic acid, but rather due to the enhanced desorption of the humic acid due to the humic acid adsorbing on the surface of the NYEX® particles and the high conductivity of the NYEX®.

One of the hypothesized mechanisms for the decreased GAC adsorption of target compounds in the presence of NOM is that the some of the sorbed NOM blocks access to internal pores. Accordingly, lacking a significant pore structure NYEX® may not be as impacted as GAC by competitive adsorption involving NOM. As far as the candidate is aware, the adsorption of target compounds on NYEX® in the presence of humics has not been studied. Therefore, the adsorption of target compounds on NYEX® in the presence of humic acids should be studied to determine if the lack of a significant internal pore structure reduces the detrimental impact of competitive adsorption with humic acids.

2.8 Conclusions

NYEX® has been shown to have the potential to adsorb many compounds and it can be completely regenerated by anodic electrochemical treatment. NYEX®'s high conductivity makes it a more suitable adsorbent for electrochemical regeneration. As NYEX® lacks a large internal pore structure it has a much smaller total surface area than GAC, so its adsorption capacity per gram of adsorbent is significantly lower than that of GAC. Accordingly, sorption onto NYEX® takes place on its external surface, so this should enhance the desorption of the solute during regeneration and facilitate direct oxidation in the surface of the adsorbent. In addition, the lack of internal pore structure may be beneficial to NYEX®'s capacity to remove target compounds as pore blockage by competing NOM molecules should not be a factor. This should be evaluated.

Roberts and coworkers have shown that NYEX® loaded with many different contaminants can be effectively regenerated in their anodic regeneration systems. However, there does not seem to be publications from other groups corroborating these results. It seems that confirming their results, particularly the rather surprisingly high regeneration efficiencies of NYEX® is a worthwhile area of research. In addition, as most of the NYEX® research has involved the treatment of single contaminant solutions, the impact of competing solutes on the regeneration efficiency of a target solute should also be studied.

CHAPTER 3: Experimental Methods

This chapter discusses the materials, analytical methods, experimental procedures and the experimental plan followed in this thesis. These are described below.

3.1 Materials

3.1.1 Adsorbent

NYEX® 1000 was supplied Arvia Technologies, Runcorn, England. The 100µm to 700µm NYEX® 1000 particles have irregular shape, are black and readily adhere to surfaces. Figure 3.1 presents a scanning electron microscope (SEM) image of the NYEX® 1000 particles, it shows the particles have a flat plate-like shape with smooth outer surfaces and no apparent pores. According to its manufacturer is surface area is 1 m^2/g (Asghar et al. 2013).

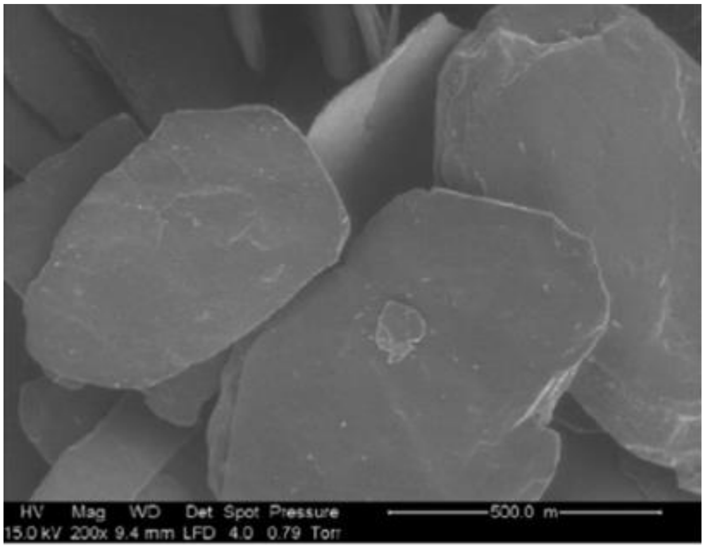

Figure 3.1: NYEX® 1000 under SEM (Liu, et al., 2016)

3.1.2 Adsorbates

3.1.2.1 Humic Acid

Humic acid powder (Sigma-Aldrich, Darmstadt, Germany) was used as a model natural organic matter (NOM). Many researchers have used this product (Asghar et al. 2013; Kilduff et al. 1996; Li et al. 2002; Radian and Mishael 2012). A key advantage of this product is that it is relatively inexpensive at \$38.30 per 100 grams and its concentrated form allows one to prepare humic acid solutions of different concentrations, a critical factor in conducting isotherms with NYEX®. This particular humic acid is extracted from soils and these compounds are the result of many processes of biological breakdown until they have become their most recalcitrant molecular form. The Aldrich humic acid varies in molecular size and has a molecular weight distribution ranging from 3000 to 40 000 g/mol (Chin and Gschwend 1991). Based upon molecular weight averaging, the average molecular becomes 4868 g/mol and thus allowing a more practical approach in quantifying this substance (Chin and Gschwend 1991; Reid et al. 1990; Roger et al. 2010). In addition, this was the same model NOM compound used by Asghar et al. (2013), so it's ideal to conduct confirmatory NYEX® isotherms and NYEX® electrochemical regeneration tests.

3.1.2.2 Atrazine

Atrazine ($C_8H_{14}ClN_5$) was chosen as the model toxic compound for this study primarily because Brown et al. (2004) studied its sorption on NYEX® and the electrochemical regeneration of atrazine-loaded NYEX®, accordingly this work will help confirm their results. Atrazine is an herbicide of the triazine class, its structure is shown in Figure 3.2. It is used for weed control in Canada and the US (Fay et al. 1999). Research has shown that atrazine can create hormone imbalances in both animals and humans (IARC 1991;

Kniewald et al. 1995). There is a possible link between atrazine and ovarian cancer. Research done by Donna et al. (1989) found that the risk for epithelial ovarian cancer is two to threefold as compared to unexposed woman (Donna et al. 1989). Sixty cases between January 1974 and June 1980 were matched with 127 controls with other non-ovarian malignancies in a region in northern Italy were the use of atrazine is extensive. 69% of all the controls showed signs of hormonally disruptive caused malignancies that could have been herbicide related (Crosignani et al. 1984; Donna et al. 1989). Upon ingestion of atrazine, there is 93-100% absorption into the body of rats that have a similar biological makeup as humans (Bakke et al. 1972; Timchalk et al. 1990). Once in the body, it can cause serious damage by deregulating the pituitary-gonadal system of hormone regulation. Atrazine is therefore classified as a Group III (possibly carcinogenic to humans) by Health Canada. Atrazine's breakdown in neutral pH waters is negligible with a half life of two years or more. Atrazine's potential for soil contamination is high and can persist through a full season in temperate climates (Cohen et al. 2009). Thus, the Agricultural Canada priority scheme ranked it highest among 83 pesticides for potential of groundwater contamination (McCrae 1991). In 2001, The United States Geological Survey ranked atrazine as the most commonly found pesticide across the US (Duris et al. 2004; Gilliom et al. 2006). The Europe Union Member States have banned the chemical in 2004 from the list of authorized plant protection products due to its potential to contaminate groundwater for long periods of time (Health Canada 2015). The Canadian guideline for the maximum acceptable concentration of atrazine in drinking water is 5 µg/L (Health Canada 1993). Environmental levels of atrazine in water generally range from non-detectable to 10 µg/L

(Duris et al. 2004; Gilliom et al. 2006). This study used analytical standard grade atrazine (Atrazine- PESTANAL®, Sigma-Aldrich Corporation, St. Louis, MI).

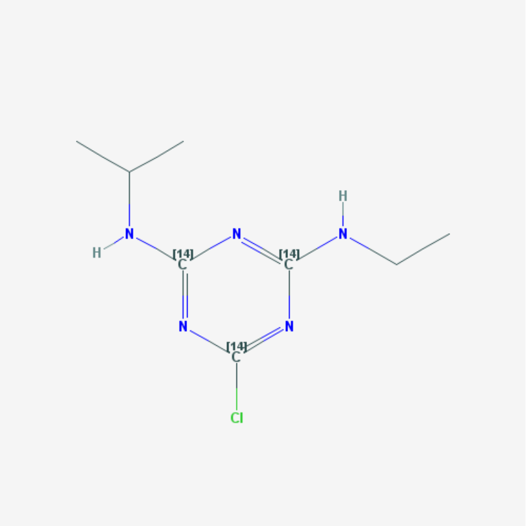

Figure 3.2: Atrazine chemical structure (NCBI 2004)

3.1.1.1 Ultra-pure water

Ultrapure water was used to prepare the humic and atrazine solutions and standards, isotherm and loading blanks, the filter rinsing steps, etc. The ultrapure water was produced using a Milli-Q system (Millipore Corporation, Billerica, MA).

3.2 Analytical Methods

The concentrations of humic acid were quantified in terms of dissolved organic carbon (DOC) while the concentrations of atrazine were measured using High-Performance Liquid Chromatography (HPLC) analysis. The analytical methods followed are described below.

3.2.1 Dissolved Organic Carbon Analysis

The dissolved organic carbon (DOC) concentrations were measured following Standard Methods' method 5310C (APHA/AWWA/WEF 2017) using a UV-persulfate analyzer

(Phoenix 8000, Tekmar-Dohrmann, Cincinnati, OH). The detection limit of this device was below 0.1 mg/L and its upper range of analysis was 20 mg/L. Therefore, concentrated samples had to be diluted before being analysed. The DOC analyzer was standardized using 1, 2, 4, and 8 mg/L potassium hydrogen phthalate (KHP) standards created from a 1 g/L KHP stock solution. The calibration was performed every month or when the verification standards (used at the beginning of each analytical run) deviated by more than 10% from the latest calibration curve. Atrazine is an organochlorinated compound so atrazine solutions will yield a DOC concentration. However, based on its atomic composition the carbon mass to atrazine mass ratio is 0.445, thus the DOC analyzer is not particularly suitable to measure µg/L concentrations of atrazine. In addition, to quantify the atrazine concentration of humic acid-atrazine solutions a chromatographic technic is necessary to isolate the atrazine from the humic acids.

3.2.2 High Performance Liquid Chromatography

Atrazine concentrations were measured HPLC using a modified method adopted from the U.S. Geological Surveys (USGS) (Steinheimer et al. 1990) and Agilent Technologies (Fu 2008). The HPLC analyzer (1100 series, Agilent Technologies, Waldbronn, Germany) used a C18 Reverse Phase column 4.6 mm x 150 mm (C18 Hypersil GOLD column, ThermoFisher Scientific, Waltham, MA, USA), and a UV detector. The analyzer had an autosampler and the HPLC system was operated using the analyzer’s Chemstation software interface. The optimal wavelength to study atrazine is 230 nm with a reference wavelength of 360 nm with an isocratic mobile phase composition of 55% methanol and 45% deionised water. The injection volume used was 100 µL and the mobile flow rate was 1 mL/min. The detection limit of this method is approximately 2 ppb. This a suitable detection limit since the lowest concentration being evaluated was approximately 5 µg/L of atrazine. The quantification of the atrazine concentrations in the HPLC was based on the analysis of water-based atrazine standards. Initially, an alternative atrazine analytical method was evaluated, it involved a pre-concentration step using solid phase extraction (SPE) with methanol elution and an injection volume of 10 µL. The detection limit of this method was 0.4 µg/L (Steinheimer et al. 1990). However, some chromatogram stability problems were encountered in the analysis of atrazine standards. Dr. Pham suggested to try a direct injection method, it worked well so it was adopted. It had the additional benefit that the pre-concentration step was not necessary, but the detection limit was a bit higher (2 µg/L) . The sensitivity of the direct injection HPLC analysis was improved by increasing the injection volume to 100 µL. During the analysis of pure atrazine, the method worked well. With the introduction of humic acids in order to model the competitive adsorption behaviour, there were disruptions in the chromatograms. In order to rectify the problem, potential solutions were examined.

These standards were prepared using a 100 mg/L atrazine stock solution in methanol that was stored in a freezer at -20 ^{o}C. The stock solution was allowed to warm up to room temperature (25 ^{o}C), then the atrazine standards were prepared by adding accurate volumes of the stock solution with a micro pipettor (Single-channel mechanical pipette, VWR Chemicals BDH®, Radnor, PA) into different size volumetric flasks ranging from 100 mL to 1000 mL. The HPLC calibration standards ranged from 5 µg/L to 2 mg/L. The standards were transferred from the flasks using a luer lock syringe with a 0.45 µm cellulose acetate syringe filter, and then inserted into an HPLC autosampler vial. The vials are sealed with septum caps and placed in the HPLC's autosampler to initiate the analysis.

The sequence table for the HPLC analysis of atrazine in water used injections of water blanks in between the injections of samples. The use of three injections of distilled water (blanks) in between each sample was to provide a cleaning step for the column and injector mechanism of the HPLC and to avoid cross contamination of the samples. The use of four atrazine injections per sample was to ensure that there were at least three acceptable chromatograms. An example of the analysis sequence is shown in Table 3.1.

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Table 3.1: Atrazine sequence table in Chemstation

Sample	Number of Injections
Milli-Q water blank	3
Atrazine Sample 1	4
Milli-Q water blank	3
Atrazine Sample 2	4
Milli-Q water blank	3

The atrazine analysis yields a peak that was measured in milli absorbance units (mAu) and the peak area was calculated by the analyzer's software, Chemstation. The calculated peak area was plotted versus the concentration and a calibration curve was developed. Although there was a linear response over the entire range tested, the resulting equation did not accurately represent the lowest concentration standards, thus the calibration curve was divided into two ranges (Figure 3.3). A high range from 200 µg/L to 2000 µg/L, and a low range from 5 µg/L to 200 µg/L where 200 µg/L was the pivot point for both curves. Linear equations were calculated for both ranges using Microsoft Excel®. The instrument had an analytical standard each sample run (every 6-10 samples) to ensure quality control and was recalibrated after replacing the reversed phase column that was reaching the end of its column lifetime.

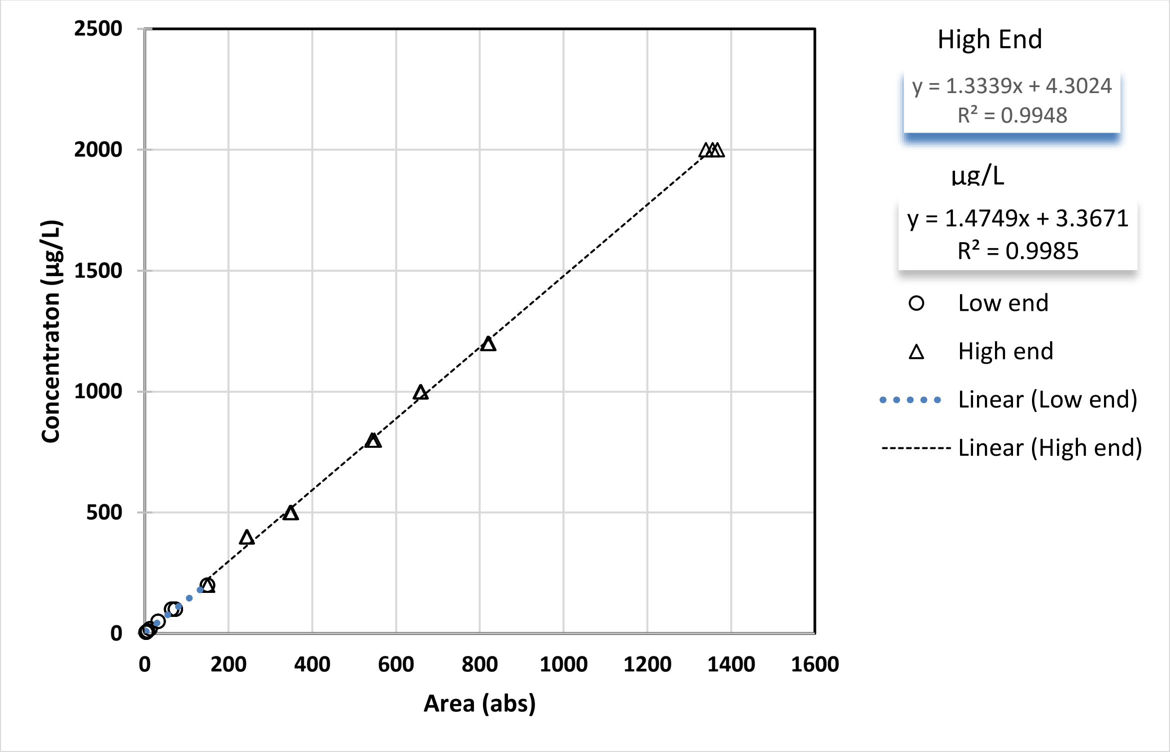

Figure 3.3: Atrazine in H_2O calibration curve measured at 230 nm

The analysis of atrazine in atrazine-humic acid solutions was problematic because the humic acid yielded a large and rather broad peak in the chromatogram at the time when the atrazine peak appears. An example chromatogram of an injection of atrazine and humic acid is shown in Figure 3.4. This phenomenon was likely caused by small linear organic fractions of the humic acid. This can be confirmed since the signal from the linear organics are strong at 230 nm. Furthermore, the phenomenon cannot be accurately predicted. For example, in one analytical run consisting of multiple samples (each injected three or four times), either one injection or possibly all four injections could not be used because the phenomenon would appear. Multiple potential solutions were explored (see Appendix A) and the following approach was selected.

To help keep the column clear of any excess humic acid that could be saturating the column, the blanks injected in between samples were increased from three to four, the four were two pure methanol injections followed by two (milli-Q water) blank injections. This did not increase the reagent consumption and provided more reliable results. The only disadvantage in using this approach is that there may be a risk that the methanol will not suffice in clearing up the buildup of humic acid entirely and it will manifest in the first injection point. By having the HPLC analyse four different injections of each sample, the first can be omitted whilst the other three can be used in the data analysis.

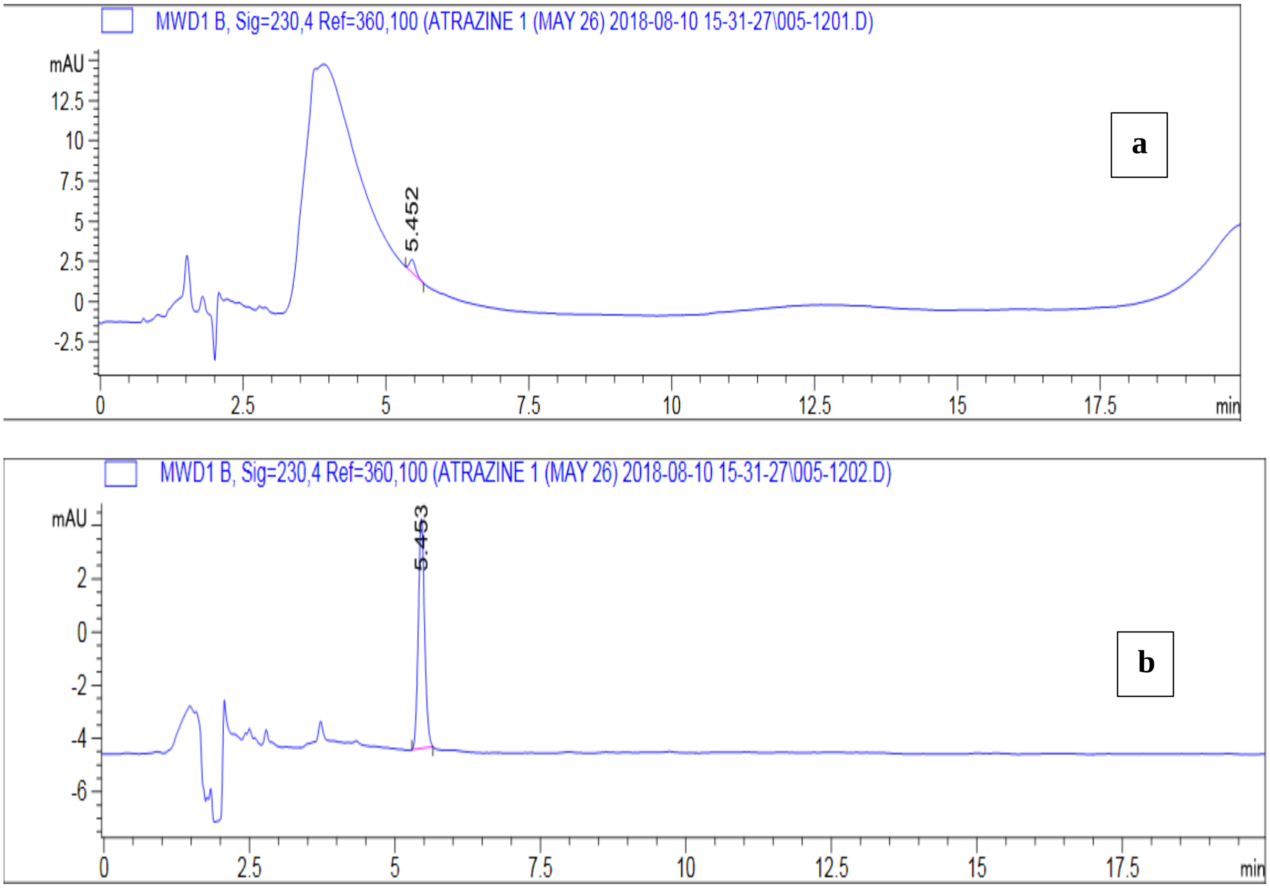

Figure 3.4: Example atrazine chromatograms: a) with the humic acid distortion; and b) without the humic acid distortion

The above method was successful as no further distortions were observed. This is possibly due to the amount of time required to thoroughly run the column and dislodge any organics that may be trapped inside.

3.3 Experimental Methods

The experiments conducted in this research consisted of bottle-point isotherms and electrochemical regeneration tests. The later consisted of batch loading tests, the actual electrochemical regeneration followed by batch reloading tests to assess the regeneration efficiency. These are described in the subsequent subsections.

3.3.1 Isotherm Experiments

Equilibrium studies were performed to determine the adsorption characteristics and behavior of the adsorbent when equilibrium is reached, in essence their maximum adsorption capacity. These experiments were performed using the bottle-point method, i.e., each bottle is a batch contactor that generates a data point in the equilibrium (i.e. isotherm) graph. Initially, they were performed using the same solution and different adsorbent doses in each bottle, which is the more common approach in applied environmental research as one generally cannot change the concentration of the contaminated water (Sontheimer et al. 1988). Due to the unusual results produced by using this approach using NYEX® 1000, later isotherms (indeed the majority) used the alternative bottle point-approach using different concentration solutions in each bottle and the same NYEX® 1000 dose. The adsorbent in question has a relatively low equilibrium time as compared with activated carbon (Asghar et al. 2013, 2014, 2015; Mohammed 2011; Ning 2015). The equilibrium time of NYEX® 1000 is reached after approximately 1 hour of mixing (Asghar et al. 2013).

Prior to conducting the bottle point experiments, the test solutions had to be prepared. First, a 100 mg/L atrazine stock solution was prepared by weighing 10 mg of atrazine powder in the analytical balance, it was then dissolved in methanol (Methanol ≥99.8% HiperSolv CHROMANORM® gradient grade for HPLC, VWR Chemicals BDH®, Radnor, PA) and mixed in a 100 mL volumetric flask until all the powder was dissolved. The stock solution was then stored in a freezer at -20 ^{o}C until it was needed (Rodríguez-González et al. 2013). When the stock solution was retrieved from the freezer, it was given 1 hr to reach room temperature. This allowed the dilution to account for the change of density of methanol at different temperatures. Once at room temperature, dilutions were made in order to achieve the desired initial concentrations for the isotherm experiments. These solutions were prepared by transferring the desired volume of atrazine stock solution (using a micro-pipettor) into 1 L volumetric flasks, filing them with Milli-Q water and mixing them.

For the bottle-point isotherms conducted utilizing a constant adsorbent dose approach the procedure was as follows. The solutions for the test were first prepared, in the case of the atrazine isotherm in a similar fashion as the atrazine standards. The adsorbent loadings were conducted in amber glass 250 mL bottles with Teflon®-lined screw caps, they were labelled and Teflon® tape was wrapped around their threads (in the neck of the bottles) to create a seal with the cap. Then the bottles were weighed with a laboratory scale (PC4400, Mettler-Toledo Inc., Columbus, OH). This value was used later on in order to determine the final volume of liquid in the sample. The mass of NYEX® 1000 was measured with an analytical scale (Model#R200D, Sartorius, Goettingen, Germany), the target adsorbent mass was 2.5 g of NYEX® 1000. The NYEX® 1000 was then loaded into the bottle then the rest of the bottle was filled with the solution up to the neck of the bottle, and then sealed with the Teflon®-lined cap. The final weight of the loaded bottle was measured using the laboratory scale. The NYEX® 1000 dosage was kept constant for each isotherm point while the initial concentration of the mixture varied. For the atrazine isotherm experiment the initial solution concentrations ranged from add the atrazine concentrations used. To attain equilibrium the contents of the bottle(s) were mixed by rotating the bottles for 1 and a half hours in an end-over-end tumbler, it rotated at approximately 12 revolutions per minute. Once the equilibration time was completed, the bottle(s) were removed from the tumbler and first inspected for any leaks. The solute in the bottles were then vacuum filtered through a cellulose acetate membrane with a nominal pore size of 0.45 µm (Whatman®, Sigma-Aldrich, Darmstadt, Germany). The filtration process consisted of a number of steps. First, the filter was first wetted with Mili-Q water and placed on the filter head, the 250 mL filtering cup was put in place. To thoroughly rinse the system and the membrane, 250 ml of Mili-Q water was first filtered through the membrane/filtration apparatus. Then 50 mL of the sample was filtered to waste to saturate the filter holder and membrane with the solute so that the subsequent filtrate is truly representative of the test solution. Afterwards, the rest of the sample was filtered. Finally, the filtrate samples were analyzed to determine the solute concentration, i.e., the solute equilibrium liquid phase concentration (C_e) of each bottle. In addition to the bottles with NYEX® 1000, the experiments included control bottles and blank bottles. The control samples followed the same processing as the test samples except that NYEX® 1000 was not added to these bottles. The control bottles were used to account for losses of solute due to reactions, volatilization and sorption onto the bottles. There were two blank bottles that were similarly processed, one bottle was filled with Milli-Q water and the second with Milli-Q water and the same dose of NYEX® 1000 as in the other bottles. The blanks were intended to quantify if there was leaching from the bottles and/or the filtration equipment.

Then using a mass balance from the beginning of the loading until the end one can calculate the solute equilibrium solid phase concentration (q_e) achieve in each bottle. The mass balance equation is:

$$q_e = \frac{V \cdot (C_{control} - C_e)}{M} \tag{3.1}$$

Where q_e is the solute equilibrium solid phase concentration (mg solute/g NYEX®); V is the liquid volume (L); $C_{control}$ is the solute concentration in the control bottle (mg solute/L); and C_e is the solute equilibrium liquid phase concentration (mg solute/L).

For the bottle-point isotherms conducted utilizing the same solution approach the procedure was the same except that the mass of NYEX® 1000 was varied. Further details on humic acid isotherms and the atrazine isotherms are presented in the next subsections.

3.3.1.1 Equilibrium studies with humic acid

The humic acid isotherms were conducted following essentially the same bottle-point isotherm procedure used for the atrazine solution that was discussed in the previous sub-section, the differences were as follows. The initial step was to create the humic acid solutions. Humic acid (Humic acid sodium salt, Sigma-Aldrich, Darmstadt, Germany) was mixed with Milli-Q ultrapure water for approximately 10 minutes (Millipore Corporation, Billerica, MA) to obtain the desired initial liquid phase concentration for the specific isotherm point. For the humic acid isotherm the initial solution concentrations ranged from 10 mg DOC/L to 25 mg DOC/L. Asghar et al. (2013) found humic acid solution reached equilibrium with NYEX® 1000 in approximately one hour (Asghar et al. 2013). Therefore, a safety factor of 30 minutes was added to this value in order to ensure equilibrium will be reached regardless of the conditions during the experiments. Once the contacting period and filtration steps were completed, the filtered samples the humic acid concentrations were quantified in terms of DOC using the organic carbon analyzer.

3.3.1.2 Equilibrium procedure the atrazine plus humic acid isotherm.

The procedure for the competitive atrazine-humic acid isotherms were performed in a similar fashion except for the following exceptions. The competitive adsorption mixture was prepared in 2L volumetric flasks by adding different volumes of 100 mg/L atrazine stock solution, 24 mg of humic salts and Milli-Q water. In the competitive adsorption experiment each bottle had a different initial concentration of atrazine, the same initial humic acid concentration and a constant mass of NYEX® 1000. After the equilibration period, the liquid samples for analysis were extracted from the bottles using a 6 mL syringe (Norm-Ject® Sterile Luer-Lock Syringe, VWR International LLC., Radnor, PA) and a 0.45 µm syringe filter (0.45 µm cellulose acetate syringe filter, VWR International LLC., Radnor, PA). The syringe was rinsed two times with sample and then the syringe filter was attached. The syringe was then refilled and all the liquid in the syringe was filtered from the syringe through the syringe filter to waste to allow for the filter to become saturated and not impact the solute concentration. More sample was then loaded into the syringe and only 4 mL was filtered to waste, the rest was loaded into an autosampler vial (11mm clear glass crimp top vials, ThermoFisher Scientific, Waltham, MA, USA) to be analyzed by the HPLC analyzer.

3.3.1.3 Isotherm Error Analysis

In order to determine if the isotherm data points are reasonable or are possibly outlier one needs to determine the confidence limits of the data. If repeat tests are conducted the confidence limits can be estimated based strictly on the data. If there are no replicates then the error can be estimated based on error associated with the variables involved in the calculation of the parameter in question. The error bars are calculated with the variance formula and the variance of all the variables that involved in the calculation of the isotherm loading (q). The variance (Var) of the isotherm point's solid phase concentration is calculated by:

$$Var(q) = \left(\frac{V}{M}\right)^2 * \sigma^2_{C_{Control}} + \left(\frac{-V}{M}\right)^2 * \sigma^2_{C_e} + \left(\frac{C_o - C_e}{M}\right)^2 * \sigma^2_V + \left(\frac{(C_o - C_e) * V}{M^2}\right) * \sigma^2_M \tag{3.2}$$

Where $\sigma_{C_{Control}}$ is the standard deviation of the solute concentration of the control samples; σ_{C_e} is the standard deviation of the equilibrium liquid solute concentration; σ_V is the standard deviation of the liquid volumes; and σ_M is the standard deviation of the adsorbent mass.

Equation 3.2 is an estimate that assumes that error of all the variables involved is additive, in reality the variance calculated from experimental replicates tend to be lower because the error in some variables may compensate for that of other variables. The standard deviation (σ), which equals the square root of the variance, is the experimental error that can be expected for the measurement of the given variable. Table 3.2 shows the estimated percent error associated with each variable. The estimated percent error of the variables in the isotherm equation are multiplied by the value variable to yield the standard deviation of that variable.

Table 3.2: Estimated percent error of the variables used to calculate the contaminant loadings

Parameters	Percent Error
C_o	2%
C_e	2%
M	0.02%
V	0.02%

Once the Variance has been calculated, the estimated 95% interval can be calculated using Equation 3.3, this formula can be applied for both the positive and negative range of possible errors. This gives the maximum variation of a data point that can be expected if all the parameters contributed to the error in an additive fashion.

$$q \pm 95\%\ confidence\ interval = q \pm 1.96 * \sqrt{Var(q)} \qquad (3.3)$$

3.3.2 Regeneration Studies

Regeneration studies are necessary to determine how effective the adsorbent (NYEX® 1000) can be electrochemically regenerated. The following subsections will discuss the electrochemical reactor and the procedure followed to determine the regeneration efficiency.

3.3.2.1 Electrochemical reactor.

The electrochemical reactor used in this study was based on that developed by Brown et al (2004), it is shown in Figure 3.5. It is a small batch reactor (5 x 7 cm base) used for the regeneration of the NYEX® 1000 that is loaded in separate batch tests, the loading procedure was very similar to that used in the equilibrium experiments. The reactor uses a perforated plate stainless-steel cathode and a graphitic anode with a metal oxide coating. The reactor included a 350 ion exchange membrane (Daramic 350 membrane, Daramic, Charlotte, NC) which is located immediately beside the cathode and separates the anodic compartment from the cathodic compartment. The reactor uses a potentiostat (Model 410, Electrosynthesis Company Inc., East Amherst, N.Y.) converted into a galvanostat using a 5Ω resistor where the output in volts is converted into outputs of current. The NYEX® 1000 to be regenerated is placed in the anodic compartment which has a thickness of 1 cm. The active area of contact of the NYEX® 1000 with the anode and the ion exchange membrane is approximately 5cm by 1.5cm. This is the area used to calculate the current density. The circuit also includes a multi-meter to determine the amount of current being inputted into the reactor. With the active area of the anode being known (i.e., 5cm by 1.5cm), based on this area one calculates the current density in mA/cm^2. During experimentation, the impact of several regeneration parameters was assessed. These parameters were: 1) Regeneration time 2); Current density; and 3) The number of regeneration cycles.

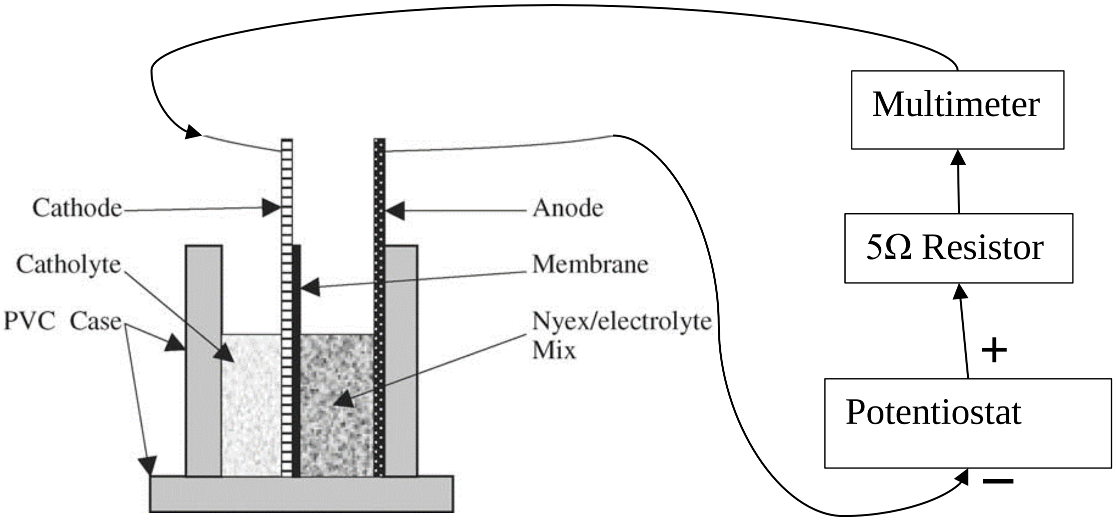

Figure 3.5: Circuit diagram (Brown et al. 2004a)

3.3.2.2 Regeneration Efficiency Assessment Method

The regeneration assessment procedure follows three steps: 1) batch loading of the adsorbent; 2) electrochemical regeneration of the adsorbent; and c) reloading of the adsorbent. These will be discussed in detail below; in addition, the equation used to calculate the regeneration efficiency is presented.

3.3.2.3 Batch loading of the adsorbent.

Firstly, the adsorbate solution was prepared. The 100 mg atrazine/L stock (in methanol) solution must be removed from the freezer and warmed up to room temperature. The 200 µg atrazine /L solutions were prepared by diluting 2 ml of the 100 mg/L stock solution with Milli-Q water in a 1L volumetric flask. This allows sufficient dilution of the methanol as for it to have a negligible impact on the adsorption of atrazine. The levels of atrazine used in this study were higher than those normally encountered in water samples (0 – 10 µg/L), the reasons for the higher levels were: a) because adsorption reduces the contaminant concentrations one has to start with higher concentrations; b) the study used for comparisons (Brown et al. 2004a) used atrazine concentrations in the 0.1 to 10 mg/L range and adsorbed onto NYEX® 100; and c) the detection limits of the analytical method selected. In the case of humic solutions and the competitive adsorption tests using humic acid, the humic salts were added to Milli-Q water and create 12mg DOC/L solutions.

Secondly, the 250 mL amber glass bottle (with Teflon cap) used for the loading step was prepared, it is weighed unfilled using the laboratory scale. Third, the NYEX® 1000 was weighed using an analytical balance, the NYEX® 1000 dose was 12 g/L. Fourth, the NYEX® 1000 was loaded into the amber glass bottle. Fifth, the bottle was filled with the solute leaving a small headspace to facilitate mixing. Sixth, the bottle was caped and reweighed. The mass of solution in the bottle is calculated based on the difference in mass between the full and empty bottles. Seventh, the bottle was placed in an end-over-end tumbler rotating at approximately 12 rpm, to provide the necessary mixing. Eight, after 1.5 hours mixing (i.e., the equilibrium time) the bottles were removed and inspected for any leaks. Ninth, the bottles were opened and samples were extracted using a syringe with a 0.45 μm cellulose Luer lock filter and transferred into a separate container for the chemical analysis (e.g., HPLC autosampler vial for the atrazine analysis). This analysis yielded the equilibrium liquid phase concentration. Tenth, the remaining contents of the amber bottle were vacuum filtered through 0.45 μm cellulose acetate membrane filter (Whatman®, Sigma-Aldrich, Darmstadt, Germany) to recover the NYEX® for the regeneration step.

In order to account for solute losses, as part of the loading process, a control was also performed, that is conducting the loading process in a bottle with the solute but without the

NYEX®. This solute concentration along with the equilibrium liquid phase concentration were substituted into Equation 3.4 to calculate the equilibrium solute loading on the NYEX®.

$$q_1 = \frac{V \cdot (C_{control} - C_{e1})}{M} \tag{3.4}$$

Where q_1 is the solute equilibrium solid phase concentration after the first loading step in mg solute/g NYEX®; V is the liquid volume in L; $C_{control}$ is the solute concentration in the control bottle in mg adsorbate/L; and C_{e1} is the solute equilibrium liquid phase concentration in mg solute/L.

3.3.2.3.1 Regeneration

The mass of NYEX® 1000 collected in the filtration step was loaded into the anodic compartment of the reactor. A 2% NaCl electrolyte is loaded into cathode compartment and also a small amount is used to moisten the NYEX® in the anodic compartment. This enables greater conductivity between the adsorbent particles (Asghar et al. 2013; Brown et al. 2004a). The volume/dimensions of the NYEX® 1000 in the reactor were required in order to calculate the current required so as to apply the desired current density, the dimensions were measured with a ruler. Once the desired current is calculated, the power supply is activated and the voltage is increased or decreased based on the reading in amps of the multimeter. When the current density is achieved, the reactor would be operated for the selected amount of time. The electrochemical regeneration parameters that were varied in this research were the current density and the regeneration time.

3.3.2.3.2 Reloading

Once the regeneration was finished, the power supply was shutoff. Then, the NYEX® was removed from reactor and rinsed into a beaker using a wash bottle filled with a prepared atrazine mixture. Once all the NYEX® 1000 is in the beaker, all of it is transferred into another clean amber glass bottle to start the reloading process following essentially the same steps as the loading process. The bottles are sealed and then weighed on the laboratory scale. A control sample with the mixture was prepared as well. Then, the filled loading bottles were placed in the end-over-end tumbler and rotated for 1.5 hours (the equilibration time). After this, the bottles were removed from the tumbler and inspected for any leaks. A sample were then extracted from each bottle with a Luer lock syringe and syringe filter (0.45 µm cellulose acetate syringe filter, VWR International LLC., Radnor, PA) and analyzed. The resulting concentration is referred to as the reloading equilibrium liquid phase concentration (C_{e2}).

Then using a mass balance, the solute equilibrium solid phase concentration at the end of the reloading cycle q_2 was calculated, that is

$$q_2 = \frac{V \cdot (C_{control} - C_{e2})}{M} \tag{3.5}$$

The above loading cycle was then used to calculate the regeneration efficiency, RE, in this study it was defined as:

$$RE(\%) = 100 \cdot \frac{q_2}{q_1} = 100 \cdot \frac{\left(\frac{V \cdot (C_{control} - C_{e2})}{M}\right)}{\left(\frac{V \cdot (C_{control} - C_{e1})}{M}\right)} \tag{3.6}$$

Narbaitz and Cen (1997) discussed there are alternative definitions that may provide more equitable assessments of the regeneration efficiency and generate somewhat lower regeneration efficiency values than equation 3.6. In this thesis, equation 3.6 was selected as it is the most frequently used equation in the literature and thus provides a fairer comparison with the work of others.

The adsorbent can be collected using vacuum filtration and then dried in an oven at 105 ^{o}C overnight to remove any moisture on the adsorbent and then measured dry using the analytical scale to calculate the final mass of adsorbent.

3.4 Experimental Plan

The objectives of this thesis are to assess the impact of humic acids on the adsorption onto NYEX® 1000 and to assess their impact on the electrochemical regeneration of NYEX® 1000. The first set of experiments will assess the NYEX® 1000 adsorption capacity for humic acids and atrazine. The second set of experiments will consist of NYEX® adsorption isotherms using bi-solute (Humic acid and atrazine) solutions. Together these two set of experiments will help quantify the impact of humic acids on the adsorption of a target toxic compound and determine if the humic acids have as large a detrimental impact on the adsorption of toxic compounds as that observed on activated carbon. The third group of experiments consists of the electrochemical regeneration tests with NYEX® 1000 loaded with atrazine and atrazine plus humic acids. The objectives of these tests are to evaluate the impact on NYEX® 1000 regeneration of the competitive adsorption with humic acids as well as the impact of the electrochemical process variables, including current density and time. Finally, multiple loading and regeneration cycles were conducted to assess the long-term feasibility of the process.

CHAPTER 4: Competitive Adsorption of Atrazine and its Electrochemical Regeneration

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4.1 Abstract

NYEX® is a graphitic intercalated compound (GIC) adsorbent that has been shown to remove a number of contaminants and which can be completely regenerated electrochemically without a loss of adsorbent mass. The objectives of this paper are to determine, if like with activated carbon, the adsorption of trace target contaminants is impacted by the presence of humic acid, and to quantify the impact of competitive adsorption on the electrochemical regeneration. Batch loading tests and batch regeneration tests were performed. The bottle-point isotherms suggest that the constant-adsorbent dose different adsorbate concentration approach should be followed. The competitive adsorption experiments showed that the adsorption of atrazine on NYEX® 1000 was significantly impacted by the presence of humic acids, however surprisingly the adsorption of the humic acids was impacted much more by the competition. Given that NYEX® 1000 lacks a significant internal pore structure, pore blocking was unlikely to be a factor in this competitive adsorption. Electrochemical regeneration yielded regeneration efficiencies of up to 170% indicating the NYEX® 1000 was improved by the process. Multiple regeneration cycles of the atrazine-humic acid loaded NYEX® 1000 showed that the presence of the humic acids did not reduce the long-term atrazine removals.

Keywords: NYEX® 1000, atrazine, humic acid, adsorption, electrochemical regeneration

4.2 Introduction

Activated carbon (AC) is the most extensively used adsorbent in water treatment, industrial wastewater treatment and groundwater remediation for the removal of toxic organic compounds from water. Granular AC (GAC) columns can remove up to 100% of most organic compounds and it has a relatively low cost (Sontheimer et al. 1988). The contaminants attach themselves to sorption sites via a number of different mechanisms, the contaminant removal is enhanced by the vast internal pore network within the AC particles which give them a very large internal surface area (~ 1000 m^2/g) (Crittenden et al. 2012; Sontheimer et al. 1988).

Activated carbon adsorption has a number of limitations. First, due to the nonspecific adsorption, GAC simultaneously removes many contaminants which compete for the available adsorption sites (Ding 2010; Pelekani and Snoeyink 2000; Singh and Yenkie 2004). This competitive adsorption can significantly reduce the removal capacity of the target contaminants (Chowdhury et al. 2013). The extent of the reduction will depend primarily on the characteristics of the solutes, their size, chemical structure and their relative concentration within the water matrix (Summers et al. 2012). In water treatment and groundwater remediation applications, the highest concentration organic compounds in the water are the naturally occurring organic matter (NOM), including humic and fulvic acids, and they can significantly decrease the adsorption capacity of target toxic compounds (Kilduff et al. 1996; McCreary and Snoeyink 1980). It has been theorized the NOM competes for adsorption sites on the AC and it also blocks access to some internal pores. Second, AC's capacity to remove contaminants is limited by the finite number of adsorption sites within the AC. As the adsorption sites on the AC become saturated, the contaminant removal of GAC adsorbers decrease and at some point, the GAC needs to be replaced with virgin or regenerated GAC. Due to the cost of virgin GAC most medium to large facilities have their GAC regenerated on-site, at regional regeneration sites, or by AC manufacturers (Chowdhury et al. 2013; Moore et al. 2003; Narbaitz and McEwen 2012). To avoid contamination problems water treatment plants (WTPs) are only allowed to use virgin GAC or regenerated GAC originating from their plant (Chowdhury et al. 2013). Currently, GAC regeneration is almost exclusively performed by thermal regeneration processes, however this results in the loss of 10-12% of the GAC (AWWA and ASCE 2013; San Miguel et al. 2001).

Due to thermal regeneration method’s significant GAC mass loss, there has been a great deal of research on alternative GAC regeneration methods, these include biological, chemical, electrochemical, microwave, approaches (Chan et al. 2018; Lu et al. 2011; Narbaitz and Karimi-Jashni 2009; Yagmur et al. 2017). Our group has studied cathodic electrochemical GAC regeneration and found it to be quite effective for GAC loaded with phenol and p-nitrophenol (Karimi-Jashni and Narbaitz 2005a; b; Narbaitz and Cen 1994; Narbaitz and Karimi-Jashni 2009, 2012), and they hypothesized that the main cathodic regeneration mechanism was high pH enhanced desorption at the cathode. However, cathodic regeneration was not effective in regenerating GAC originating from two full-scale WTPs at which the principal adsorbate was NOM (Narbaitz and McEwen 2012), the lack of effectiveness was attributed to the principally irreversible chemisorption of NOM on the GAC.

Dr. Roberts and his colleagues have developed an alternative adsorption-electrochemical regeneration system using a graphite intercalation compounds (GIC) called NYEX®(Asghar et al. 2013; Brown et al. 2004b; a; Hussain et al. 2014; Liu et al. 2016; Mohammed 2011). Although NYEX® has few internal pores and a low surface area (~ 1-2 m^2/g), it is highly conductive (Mohammed 2011). This system has shown NYEX® to be effective for removing many different contaminants and it can be electrochemically regenerated. In addition, the kinetics of adsorption on NYEX® are much faster than those for GAC, likely due to NYEX®'s lack of a significant pore structure. The contaminants studied included atrazine (Brown et al. 2004a), phenol (Asghar et al. 2014; Brown and Roberts 2007) and humic acid (Asghar et al. 2013). Given that NYEX® 1000 lacks the large internal pore structure of GAC, it is hypothesized that the removal of trace toxic contaminants by NYEX® would be less impacted than GAC by competitive adsorption with NOM. Thus, the objectives of this thesis are: a) to investigate the adsorption behaviour of humic acid (as a model NOM compound) and atrazine, as a model trace organic contaminant, on NYEX® 1000; b) to evaluate on the competitive adsorption of atrazine with a humic acids; and c) to investigate the impact of the humic acid competitive adsorption on the NYEX®-atrazine electrochemical regeneration efficiency. Atrazine was selected as the model trace toxic contaminant in this study because it is one of the most commonly used herbicides in North American agriculture. Atrazine was the most commonly detected pollutant in surface waters by the USGS in 2001 and in some cases it exceeded the concentration required (0.2 μg/L) to feminize frog populations (Duris et al. 2004; Gilliom et al. 2006). Atrazine has been classified as a Group III (possibly carcinogenic to humans) by Health Canada (Health Canada 1993) and it is banned in the

European Member States in 2004 due to its potential for groundwater contamination (Health Canada 2015).

4.3 Experimental Methods

4.3.1 Materials

The NYEX® 1000 was supplied by Arvia Technologies in the form of a dry powder. NYEX® 1000 has a very low surface BET surface area (~ 1 m^2/g) as compared to commercial AC which generally has surface areas in the 800-1500 m^2/g range (Cannon 1993; Hamdaoui and Naffrechoux 2007; Randtke and Snoeyink 1983; Yeganeh et al. 2006). The average particle size is 484 µm and can range from 100-700 µm (Asghar et al. 2014). The material was very light and had a material density of 0.89 g/cm^3 (Asghar et al. 2013). Due to this material's high conductivity, it would accumulate any charge that is present in its environment and would thus statically adhere onto surfaces during laboratory experiments (Asghar et al. 2013). This phenomenon was observed to be more predominant with the smaller particles which require less charge in order to become electrostatic-adhesive as they weigh less. Prior to the testing pre-washing of the NYEX® was attempted, however because of the electro-adhesive characteristics (particularly of the smaller particles) it led to particle losses. Accordingly, it was decided to perform the experiments using the as-received NYEX®. Similarly, recovering all the NYEX® from one experiment to use in the next experiment was challenging, as the NYEX® particles will adhere to the containers and equipment used. Also, since the smallest NYEX® particles are the most adhesive they may not be recovered and as they also have the largest surface area per unit mass, Ning (2015) speculated that this may impact the adsorption capacity NYEX®.

Atrazine (PESTANAL®, VWR, St. Louis, MI) used in these experiments had a purity of 99.9%. For easier dilution all the aqueous atrazine standards and tests solutions were prepared using a methanol-based 100 mg atrazine/L stock solution. Humic acid solutions were used to model/simulate the NOM found in natural waters. The humic acid solutions were prepared using a soil-derived humic acid sodium salt purchased from Sigma-Aldrich (St. Louis, MI). The dissolved organic carbon concentration to humic acid mass concentration of the humic acid solutions was 0.67. The humic acid product has a wide range of molecular weights, the average molecular is 4868 g/mol (Chin and Gschwend 1991; Reid et al. 1990; Roger et al. 2010).

4.3.2 Adsorption isotherm studies

Bottle-point isotherm tests were conducted to determine the isotherm characteristics for both humic acids and atrazine as single solutes and of bi-solute mixtures of atrazine and humic acid. Initially, the bottle-point tests were performed using the same solution and different adsorbent doses in each bottle, which is the more common approach in applied environmental research as one generally cannot change the concentration of the contaminated water (Sontheimer et al. 1988). Due to the unusual results produced by using this approach with NYEX®, later isotherms (indeed the majority) were performed by the bottle point-approach using different concentration solutions in each bottle and the same NYEX® dose. The tests were conducted using 250 ml glass bottles with Teflon® lined screw caps. Each isotherm included a distilled water blank bottle and a distilled water plus NYEX® blank bottle that were mixed along side the samples, these tests were performed to quantify if there was leaching from the NYEX® and from the bottles. 250 mL control bottles were filled with the adsorbate solution without any adsorbent in order to observe any change in the adsorbate concentration during the loading, they were processed along side the bottles containing NYEX®. The humic acid adsorption kinetics onto NYEX® are very fast, Asghar et al. (2013) found that equilibrium was achieved in 50 minutes. This is much faster than the adsorption of humic acids by GAC which could take one week or 168 hours to complete (McCreary and Snoeyink 1980). Given that humic acids, which have a complex molecular structure and a large molecular weight, achieves adsorption equilibrium on NYEX® within 50 minutes, then atrazine, which has a simpler molecular structure and smaller size, should be adsorbed within 50 minutes or faster. Therefore, as a precaution we adopted a mixing time of 1h30 minutes. These bottles were sealed and placed in an end-over-end tumbler rotating at 12 rpm to provide the necessary mixing for 1h 30 minutes to reach equilibrium. The equilibration time was selected based on the results of Asghar et al. (2013). Afterwards, the contents of the individual bottles were filtered using a vacuum filtration system with a 0.45 um cellulose acetate membrane filters (Whatmann®, Sigma-Aldrich, Darmstadt, Germany). The filtrate was then analyzed for its atrazine and/or humic acid concentrations, the latter was quantified in terms of the dissolved organic carbon (DOC) concentration. For the atrazine isotherms the initial atrazine solutions used in the isotherms ranged from 20 µg/L to 1000 µg/L, for the humic acid isotherm the initial DOC concentrations ranged from 8 mg DOC/L to 16 mg DOC/L. The levels of atrazine used in this study were higher than those normally encountered in water samples (0 – 10 µg/L), the reasons for the higher levels were: a) because adsorption reduces the contaminant concentrations one has to start with higher concentrations; b) the study used for comparisons (Brown et al. 2004a) used atrazine concentrations in the 0.1 to

10 mg/L range and adsorbed onto NYEX® 100; and c) the detection limits of the analytical method selected.

Then using a mass balance from the beginning of the loading step until the end of it one can calculate the solute equilibrium solid phase concentration (q_e) achieve in each bottle. The mass balance equation reduces to

$$q_e = \frac{V \cdot (C_{control} - C_e)}{M} \tag{4.1}$$

Where q_e is the solute equilibrium solid phase concentration (mg solute/g NYEX®); V is the liquid volume (L); $C_{control}$ is the solute concentration in the control bottle (mg solute/L); and C_e is the solute equilibrium liquid phase concentration (mg solute/L). The isotherm data will be modelled with the Langmuir and Freundlich models by using the linearized versions of these models (Sontheimer et al. 1988) and regressed using Microsoft Excel®'s linear regression tool.

4.3.3 Electrochemical Regeneration

A small (5 x 7 cm base) polyvinylchloride (PVC) electrochemical batch reactor (Figure 4.1) was constructed based on the specifications of Brown et al. (2004a). The reactor consisted of parallel divided cells separated by a microporous Daramic 350 membrane (Daramic, Charlotte, NC). The perforated stainless-steel cathode within the anodic compartment was placed immediately besides the membrane. While the graphitic anode with a mixed metal oxide coating (supplied by Alfa Aesar, Tewksbury, MA) was located in the far side of the anodic compartment (i.e., 10 mm from the membrane). For the regeneration, the loaded NYEX® was place in the anodic compartment of the electrochemical reactor and lightly wetted with a 2% w/w NaCl solution. As the NYEX®

was not always uniformly loaded the active area of the anode varied, typically it was 7.5 cm^2. The reactor uses a potentiostat (Model 410, Electrosynthesis Company Inc., East Amherst, N.Y.) converted into a galvanostat using a 5Ω resistor where the output in volts is converted into outputs of current.

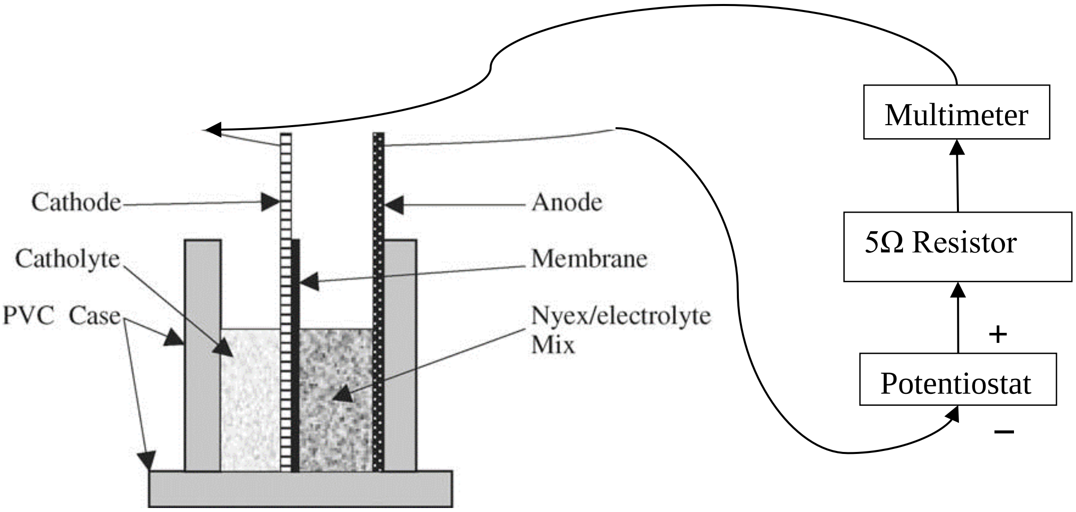

Figure 4.1: Schematic of the electrochemical reactor and circuit diagram (Brown et al. 2004a)

The effectiveness of electrochemical regeneration was assessed based on the following three sets of experiments: 1) batch loading of the adsorbent; 2) electrochemical regeneration of the adsorbent; and c) reloading of the adsorbent. These steps are required to calculate the regeneration efficiency. The procedure to assess the regeneration efficiency of NYEX® loaded with atrazine and that for humic acids plus atrazine solutions was the same, only the initial solute concentrations and the analytical methods used to quantify their concentrations differed. The batch loading was performed in the same fashion as the bottle-point isotherms, 3 g of NYEX® was mixed with 250 mL of µg/L atrazine solution for 1 h 30 min. After equilibrium is reached, a sample was first extracted for the atrazine analysis using a luer lock syringe (Norm-Ject® Sterile Luer-Lock Syringe, VWR International LLC., Radnor, PA)) with a syringe filter (0.45 µm cellulose acetate syringe filter, VWR International LLC., Radnor, PA). Then the NYEX® was recovered through vacuum filtration through a 47 mm diam. 0.45 µm cellulose acetate membrane filter (Whatman®, Sigma-Aldrich, Darmstadt, Germany). Next, the electrochemical regeneration was performed. The recovered loaded NYEX® (approximately 50% dry solids) adsorbent was placed into the anodic compartment of the electrochemical reactor. Then, the adsorbent was lightly wetted with a 2% NaCl solution to enhance conductivity within the reactor (Brown et al. 2004b; a; Karimi-Jashni and Narbaitz 2005a). The cathode compartment was loaded with the same NaCl solution until it was level with the NYEX® bed in the anodic compartment. A DC current was applied based on the active area of the anode, it varied from 5-40 mA/cm^2 with regeneration times ranging from 5 to 50 min. The bed mass was not mixed except by the bubbles that were the by-product of the electrolysis. After completing the electrochemical regeneration, the regenerated NYEX® was transferred from the anodic compartment to a 250 ml glass bottle used for the reloading. Due small size of the anodic compartment and the electrostatic characteristics of the NYEX® this was a problematic step, a wash bottle filled with the reloading solution was used to facilitate the transfer of the NYEX®. To reduce these problems for future research it is recommended that adsorption and electrochemical regeneration be performed in the same reactor, Roberts and colleagues developed such a reactor for the Arvia® Process (Mohammed 2011).

Finally, the reloading step was performed using the same procedure as the loading step, i.e., contacting the regenerated NYEX® with 250 mL of 200 µg/L atrazine solution for 1 h

30 min. At the end of the loading, the solutions were filtered to obtain samples for the atrazine analysis and to recover the NYEX®. The NYEX® was placed in an aluminum sampling dish and dried in 105°C oven to evaporate any excess moisture that would interfere with the final dry weighted value.

The electrochemical regeneration efficiency was calculated using

$$RE(\%) = 100 \cdot \frac{q_2}{q_1} = 100 \cdot \frac{\left(\frac{V \cdot (C_{control} - C_{e2})}{M}\right)}{\left(\frac{V \cdot (C_{control} - C_{e1})}{M}\right)} \tag{4.2}$$

Where q_2 is the solute equilibrium solid phase concentration after the second loading step in mg solute/g NYEX®; q_1 is the solute equilibrium solid phase concentration after the first loading step in mg solute/g NYEX®; V is the liquid volume in L; $C_{control}$ is the solute concentration in the control bottle in mg solute/L; C_{e1} is the solute equilibrium liquid phase concentration after the second loading step in mg solute/L; and C_{e1} is the solute equilibrium liquid phase concentration after the initial loading step in mg solute/L. Narbaitz and Cen (1997) discussed there are alternative definitions that may provide more equitable assessments of the regeneration efficiency and generate somewhat lower regeneration efficiency values than the above. In this study, the above equation was utilized as it is the most frequently used equation in the literature and thus provides a fairer comparison with the work of others.

For the electrochemical regeneration over multiple cycles, several steps of electrochemical regeneration and re-adsorption were repeated, after the final cycle the final adsorbent mass was determined.

4.3.4 Atrazine Analysis

The atrazine analysis was performed using a modification of the HPLC-based direct water injection methods developed by Agilent Technologies and the USGS (Fu 2008; Steinheimer et al. 1990). These concentrations were determined using an Agilent 1100 series HPLC with a reversed phase C18 HyperSil GOLD column. The mobile flow rate was 1 mL/min of a 55:45 $CH_3OH:H_2O$ mixture with an intermediate injection blanks of methanol and water between each sample. The detection limit of atrazine for this method was 2 µg/L. Since environmental levels of atrazine in water generally range from non-detectable to 10 µg/L (Duris et al. 2004; Gilliom et al. 2006), initially, the atrazine analytical method involved a pre-concentration step using solid phase extraction (SPE) with methanol elution which has a detection limit of this method was 0.4 µg/L (Steinheimer et al. 1990). However, upon further examination of the stability of the chromatogram with pure water solutions, it was determined that direct injection from the sample worked well and the pre-concentration step was not necessary. The sensitivity of the HPLC analysis was improved by increasing the injection volume to 100 µL. During the analysis of pure atrazine, the method was working well. With the introduction of humic acids in order to model the competitive adsorption behaviour, there were disruptions in the chromatograms. In order to rectify the problem, potential solutions were examined, additional methanol blanks in between sample injections eliminated the problems. Calibration curves were prepared for atrazine in the 5 to 2000 µg/L range and it was confirmed using several atrazine standards that also contained humic acid. The atrazine standards were prepared using a 100 mg/L atrazine in methanol stock solution and diluted using a mechanical pipette.

4.3.5 DOC Analysis

DOC analysis was performed to quantify the concentrations of humic acid. DOC was analyzed using a UV-persulfate oxidation-based analyzer (Phoenix 8000, Tekmar-Dohrmann, Cincinnati, OH) with a detection limit of 0.1 mg/L using Standard Methods number 5310C, (APHA/AWWA/WEF 2017). Calibration was performed several potassium phthalate standards in the 1 to 8 mg/L range. Higher concentration samples were diluted. Prior to analysis all DOC samples were filtered through a 0.45 µm Whatman® membrane filter.

4.1 Results and Discussion

4.1.1 Adsorption Studies of Humic Acid

Initially, the batch-point isotherms were performed using a constant concentration of humic acid solution whilst changing the adsorbent mass of the NYEX®. As shown by the square symbols in Figure 4.2, the constant initial solute concentration isotherm shows an unexpected pattern. As all the equilibrium liquid phase concentrations were above 0.8 - 1 mg DOC/L, approximately 1 mg DOC/L of the humic acid was not adsorbable, which is rather high but a fairly common phenomena in the adsorption of NOM solutions. Initially, as expected, the adsorption capacity or loadings (i.e., equilibrium solid phase concentrations) increases as the equilibrium liquid phase concentrations (C_{eq}) increases. But as C_{eq} increases beyond 4 mg DOC/L, the loadings level off and then decrease. This was puzzling as this pattern is typical of competitive adsorption, however this was for the adsorption of a single solute. Ning (2015) observed a similar pattern, i.e., drop in capacity for higher C_{eq} values, while conducting constant initial solute concentration bottle-point isotherms for the adsorption of acid violet 17 onto NYEX® 1000. Through several experiments he established the drop occurred irrespective of the initial solute concentration. Ning (2015) speculated about potential reasons for the drop in capacity but he did not identify the cause of the phenomena. Adsorption on NYEX® occurs primarily on the particle surface (Asghar et al. 2014) so the NYEX® adsorption capacity is expected to be greater for the smaller NYEX® particles. It should be noted that the NYEX® particles are not very uniform in size. The lower loadings achieved at the higher equilibrium liquid phase concentration, which correspond to the lower adsorbent doses, may be lower because inadvertently large NYEX® particles were used. However, this seems unlikely because one would expect that particle sizes used would be random which would not yield such consistent pattern of decreasing loadings. An alternative potential reason for the decreasing loadings is competitive adsorption with some unknown compound leaching from the NYEX®. Brown et al. (2004a) observed a NYEX® leaching when they were conducting atrazine experiments and the leachate was causing issues with developing calibration curves. DOC analysis of the distilled water blanks of the current experiment identified there was some leaching that ranged from 0.1-0.3 mg DOC/L.

Certainly, for the bottle points with the lowest adsorbent dosage there would be a greater leaching driving force (i.e., the larger volume of solution per unit mass), so there could be greater interference with the adsorption of the humic acid. Thus, it seems compound(s) leaching from the NYEX® are the most likely explanation for the observed results, and further research should be considered in identifying in quantifying the leaching of organics from NYEX®. Because of the unusual results, the use of an alternative bottle-point isotherm procedure was studied, i.e., the constant adsorbent dose isotherms approach.

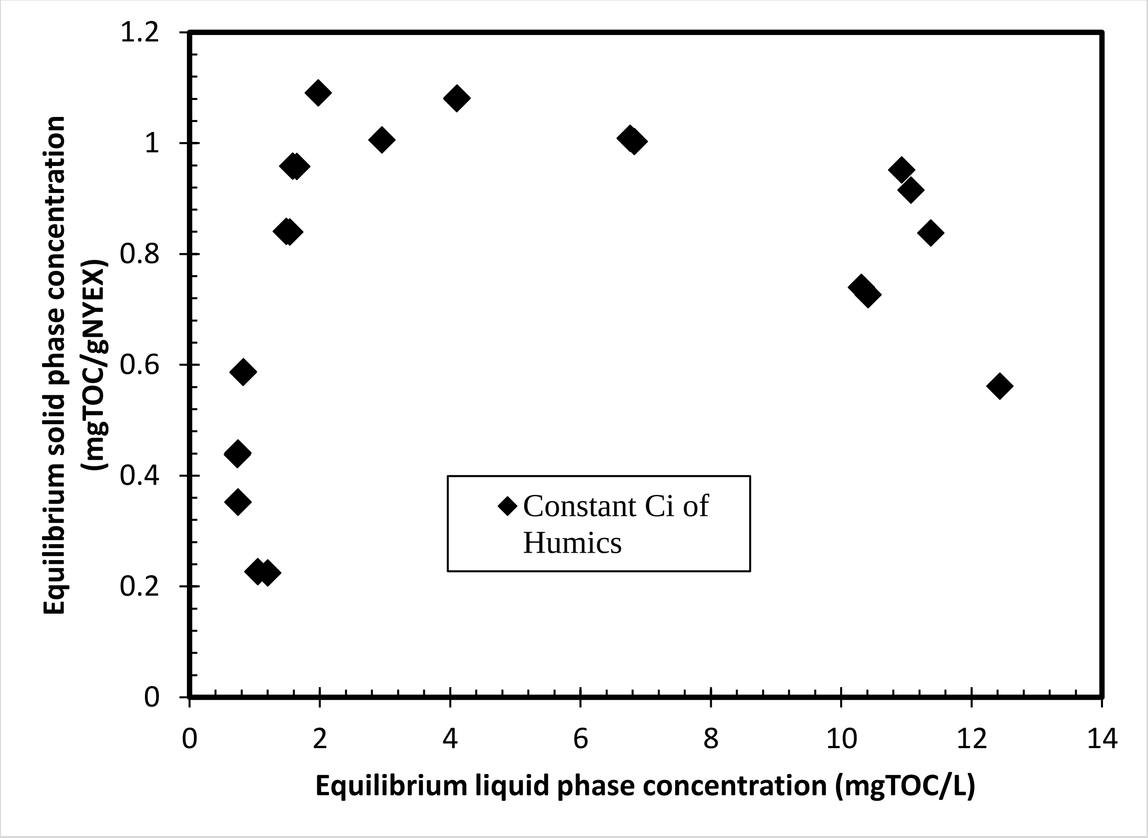

Figure 4.2: NYEX® 1000 adsorption of humic acid using different adsorbent doses and the same concentration solution.

Figure 4.3 shows the humic acid – NYEX® 1000 isotherm generated using a constant adsorbent dose varying the concentration of adsorbate (shown as triangles) and for comparison it also includes the constant solute concentration isotherm (shown as squares). The change in the experimental procedure has a significant impact on the isotherm shape. The constant adsorbent dose isotherm shows a clear increasing equilibrium loading with increasing equilibrium liquid phase concentration pattern. Accordingly, the constant adsorbent dose bottle-point isotherm method was used for all of the remaining isotherm experiments. The data shows some scatter which is likely due to the lack of uniformity in the NYEX®, this level of scatter has been observed by other researchers studying NYEX®

adsorption and regeneration (Asghar et al. 2013). Due to the scatter in the constant dose isotherm data it is not immediately evident if the can best described by a Langmuir or Freundlich model.

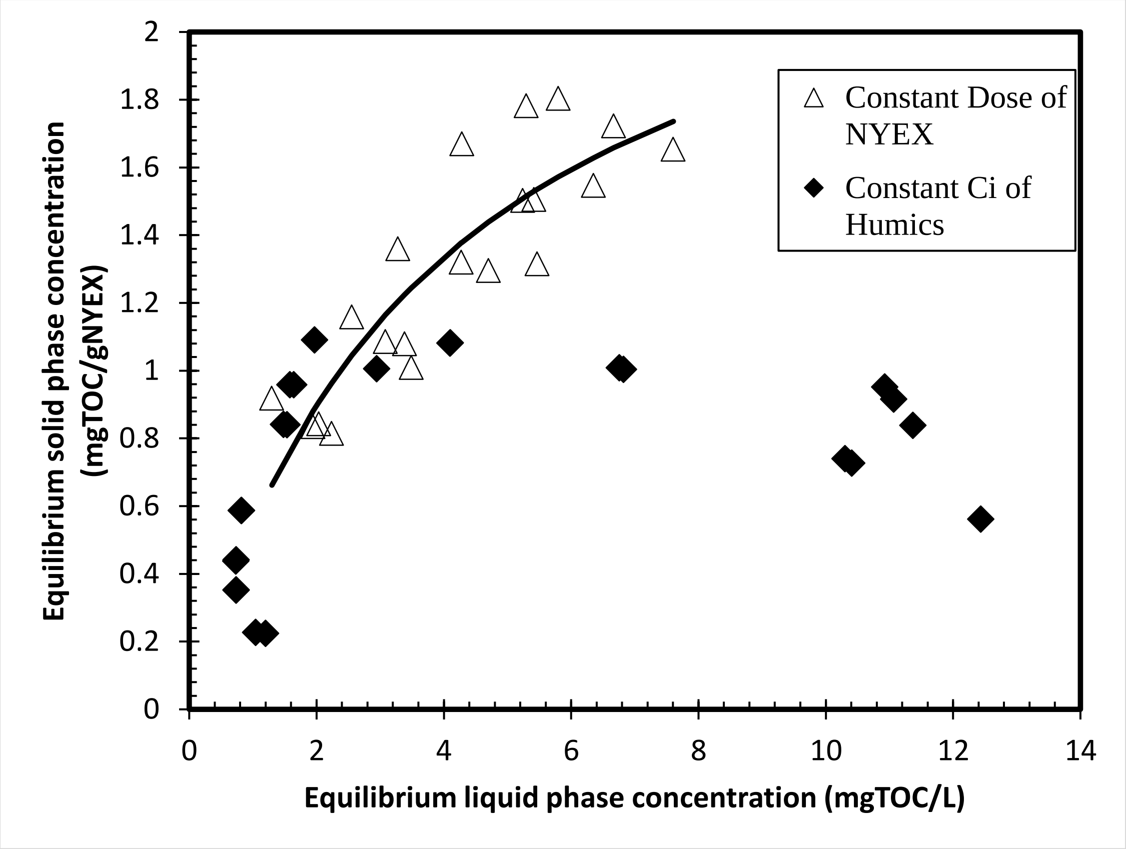

Figure 4.3: Alternative NYEX® 1000 adsorption of humic acid isotherms: a) using a constant dose of NYEX® and b) using a constant C_i of humic acid

Table 4.1 shows the results of linear regression of these two models. Based on the R^2 coefficient the Freundlich model fits the data considerably better than the Langmuir model, the relatively low R^2 values are attributed to the scatter of the data. The average absolute errors also indicate that the Freundlich model describes this data better. It should be noted that Asghar et al. (2013) used humic acid concentrations directly instead of DOC in the current study, so conversion was required to compare the data. In addition, our regression analysis of the data in their graphs yielded different regressed coefficient values than those reported in their tables. Using the DOC concentrations of our standard solutions we obtained a DOC/humic acid ratio of 0.67, which was used to convert the two data sets on the same basis. The best fit Freundlich exponent (1/n) in the current study was 0.49 and its 95% confidence limits was 0.354 to 0.623, these values overlap with the 0.495 $\underline{+}$ 0.0794 value obtained in the reanalyzed Asghar et al. (2013) data for the same adsorbate-adsorbent combination. So, they are statistically the same. The values of K_{FREUND} (at 0.658 ± 0.136 mgDOC/g NYEX$^{®}$*(L/mg)$^{1/n}$) is somewhat larger the 0.54 mg DOC/g NYEX$^{®}$*(L/mg)$^{1/n}$ converted/regressed value from based on the Asghar et al. (2013) data. Although the 95% confidence limits of K_{FREUND} overlap, the loadings in the current study are higher than those reported by Asghar et al. (2013). Given that the humic acid sorption capacity of the NYEX$^{®}$ 1000 used in this study are somewhat higher than those tested by Asghar et al. (2013), the two batches of NYEX$^{®}$ 1000 are possibly somewhat different.

Table 4.1: Humic acid isotherm model coefficients and quality of fit.

		Best fit & 95% confidence limits	Absolute Percent Error	R^2
Freundlich Model	K_{FREUND} [(µg DOC / g AC)/(µg DOC/L)$^{1/n}$]	0.658 ± 0.136	10.5	0.769
	1/n	0.490 ± 0.133		
Langmuir Model	Q_m	1.80 ± 0.698	13.7	0.4097
	K_{LANG}	0.708 ± 0.550		

4.1.2 Adsorption Studies of Atrazine

The atrazine isotherm developed in Figure 4.4 shows a clear favourable adsorption trend and the data shows less variability than that for the humic acid data. As expected, the atrazine adsorption capacities on NYEX® 1000 is significantly smaller than those for activated carbon. For example, at an equilibrium liquid phase concentration of 40 µg/L the adsorption capacity for NYEX® 1000 is 3 µg atrazine/g, while from atrazine-PAC isotherms in the literature the adsorption ranged from 3200 to 16200 µg atrazine/g (Ding 2010; Knappe et al. 1998; Li et al. 2003**.** The difference is even larger when comparing this material with atrazine-GAC isotherms in the literature that can range from 56900 to 113600 µg atrazine/g (Schreiber et al. 2007; Sontheimer et al. 1988; Speth and Miltner 1990). Since the surface area of PAC and GAC is derived almost entirely from the internal pore structure, it is accepted that the adsorption capacity of a GAC and the same GAC ground to a powder is essentially the same. Accordingly, the 35.5-fold range of ATZ loadings calculated from the isotherms or from graphs reported in the literature, is puzzling and it seems to indicate some type of errors by some researchers. The figure also includes the best fit Freundlich and Langmuir simulations as well as the data's error bars estimated using an estimated error analysis. The Freundlich and Langmuir regression analysis results are presented in Table 4.2.

Table 4.2: Atrazine isotherm model coefficients and quality of fit.

		Best fit & 95% confidence limits	Average Absolute Error	R^2
Freundlich Model	K_{FREUND} [(μg ATZ / g AC)/(μg ATZ/L)$^{1/n}$]	0.147 ± 0.044	14.7	0.972
	1/n	0.827 ± 0.0526		
Langmuir Model	Q_m	49.2 ± 6.58	7.57	0.909
	K_{LANG}	$1.74*10^{-3}$ ± $9.8*10^{-5}$		

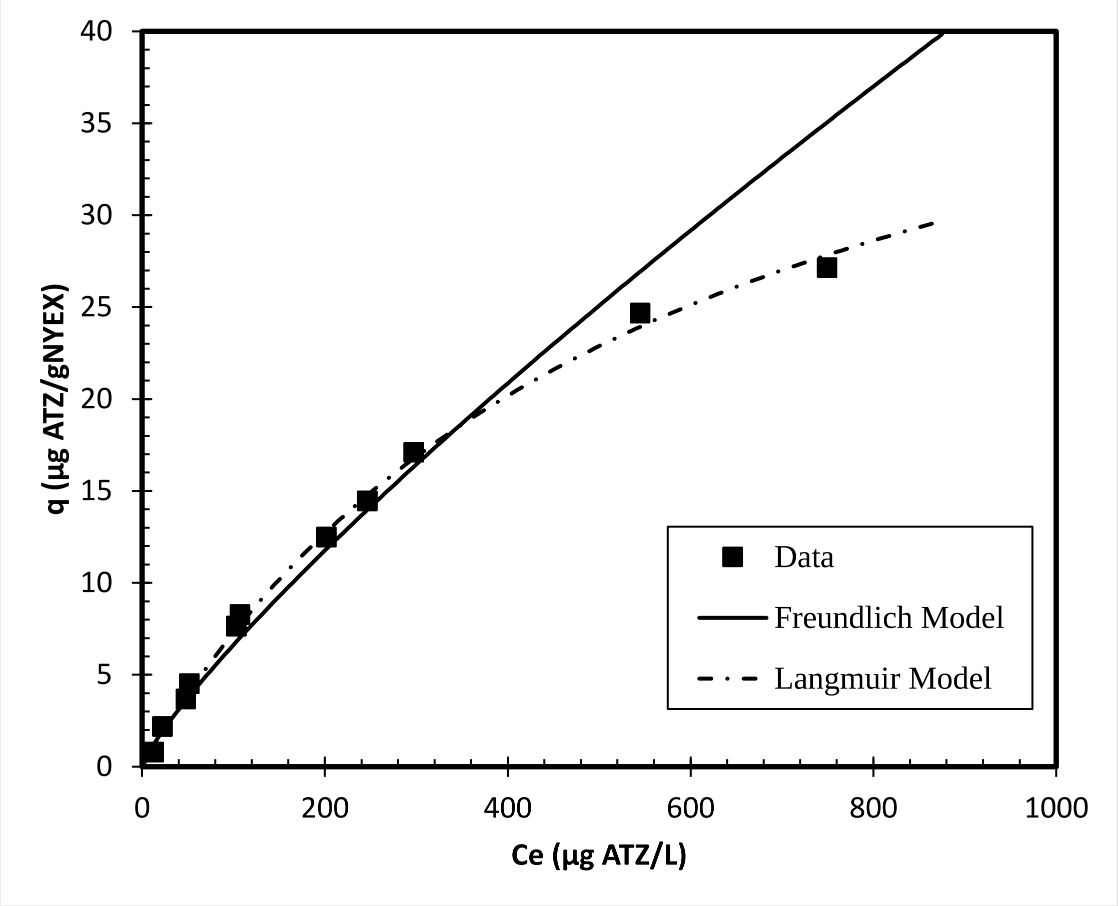

Figure 4.4: NYEX® 1000 single-solute atrazine adsorption isotherm

While the R^2 values for the linear regression results presented in Table 4.2 seem to indicate that the atrazine isotherm data is better described by the Freundlich model, however visual observation of the simulations (Figure 4.4) and the average absolute error indicated otherwise. The reason for this apparent contradiction seems to arise from log transformations of the Freundlich model that is necessary to conduct a linear regression of the data. Unfortunately, the atrazine adsorption data available in the literature is for NYEX® 100 not for the NYEX® 1000 used in this study. The NYEX® 1000-atrazine isotherm's Freundlich constants (K_{FREUND} = 0.147 (µg atrazine/g NYEX®)/((mg atrazine/L)$^{0.827}$) and 1/n = 0.827) were significantly different from those found by Brown et al. (2004) (K_{FREUND} = 0.279 (µg atrazine/g NYEX®)/((mg atrazine/L)$^{0.55}$) and 1/n = 0.550) for their atrazine-NYEX® 100 isotherm. The NYEX® 100 tested by Brown et al. (2004) had a significantly higher atrazine sorption capacity, for example at an equilibrium atrazine liquid phase concentration of 700 µg/L they found that NYEX® 100 has an atrazine capacity of approximately 229 µg/g NYEX® 100 while in the current study the capacity is approximately 27 µg/g NYEX® 1000.

Figure 4.5 shows that the presence of humic acid reduces the atrazine adsorption capacity, for example at an equilibrium atrazine liquid phase concentration of 700 µg atrazine/L the atrazine capacity decreases by approximately 41%. On average the competition with the humic acids decreased atrazine sorption capacity by 37%. This could be due to the strong bonds of the humics blocking the atrazine from being adsorbed on the adsorption site of the NYEX®.

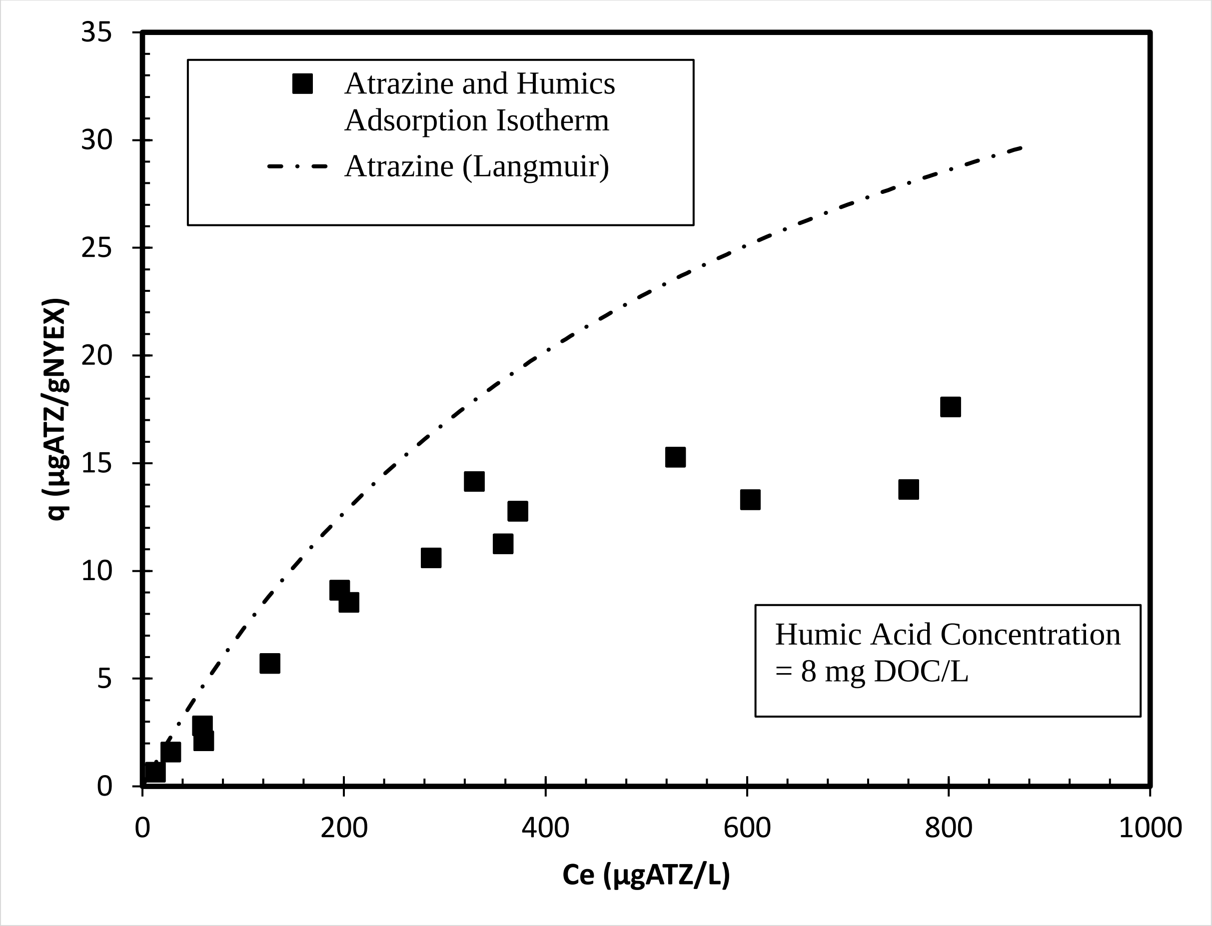

Figure 4.5: NYEX® adsorption isotherm for atrazine in the presence of humic acid

Unfortunately, the DOC concentrations for the above competitive adsorption experiments were not performed. However, the impact of the competitive adsorption on the humic acid adsorption can be assessed using the bi-solute loading results which are part of regeneration experiments presented in the later parts of this manuscript. For the loading tests with the closest initial humic acid concentration (i.e., 9.37 mg DOC/L) the equilibrium humic acids loading was only 0.046 mg DOC/g NYEX® compared with 2.83 mg DOC/g NYEX® predicted by the humic acid Freundlich isotherm. This represents a 98% decrease in the humic acid capacity, which is a surprising finding for two reasons. First, in target-organics/NOM AC competitive adsorption tests the literature concentrates on the target compound sorption only contains a limited number of reports on the adsorption of the NOM in their experiments. Narbaitz and Benedek (2004) showed that competitive adsorption with 1,1,2 trichloroethane did not significantly decrease the adsorption of a river water NOM. Second, in the current NYEX® 1000 study the adsorption of atrazine decreased the humic acid adsorption capacity by 98% while the humic acid only decreased the atrazine adsorption capacity by an average 37%. So, the atrazine is the dominant solute. This is contrary to that observed in target-organics/NOM competitive adsorption tests with AC. Two common factors cited for the dominance of NOM in competitive adsorption on AC are higher adsorbability of the NOM and much larger concentrations in the solutions tested. Based on an Aldrich humic acids molecular weight of 4868 g/mol (Roger et al. 2010), the molar humic acids concentration in the adsorbate solutions was estimated to be 1.64 x 10^{-3} mmol/L. When the single solute isotherm data for humic acids and atrazine isotherms developed above were compared on a molar basis, the humic acids had significantly higher adsorption capacities, thus this was not factor in atrazine's dominance in the competitive adsorption tests. The initial atrazine concentrations of the various points in Figure 4.5 were different in all cases. If the initial atrazine concentration and the initial humic acids concentration are compared on a DOC basis, the humics are present in much higher concentrations. This is the reasoning provided by other researchers for low impact on the NOM adsorption capacities of competition with trace level contaminants (Ding 2010; Li et al. 2003) However, on a molar basis the initial atrazine concentration was significantly higher than the humic acid initial concentration, so this possibly explains that atrazine was the dominant solute in the above tests. It should be noted that most AC target-organics/NOM competitive adsorption tests in the literature use the NOM present natural waters which have average molecular weights around or below 1000 g/mol (Ding 2010; Li et al. 2003; Smith 1991), and thus their initial NOM concentrations on a molar basis is significantly higher than that of the target trace contaminant. In addition, given that the adsorption sites on NYEX® 1000 are on the surface the dominance of atrazine may be related to faster diffusion as it has a much higher liquid phase molecular diffusivity (6.5 x 10^{-10} m^2/s) than the humic substances (1.88 x 10^{-10} m^2/s) by a factor of 3.5 (Park et al. 2003; Sontheimer et al. 1988). Given the unusual results obtained for the competitive adsorption on NYEX®, these results should be verified and repeated for other target compounds and/or atrazine and other humic substances. The next section will discuss the electrochemical regeneration of the NYEX® 1000 testing various parameters.

4.1.3 Electrochemical Regeneration

4.1.3.1 Impact of Regeneration Time

The first set of regeneration tests investigated the impact of regeneration time at a constant current density for NYEX® that was loaded with an atrazine-humic acid mixture. For these regeneration tests a current density of 20 mA/cm^2 was chosen based on Brown *et. al* (2004a) who found it to yield the highest regeneration efficiency for atrazine-loaded NYEX® 100. Figure 4.6 shows that the regeneration efficiency increased linearly for regeneration times of 5 to 30 minutes and decreased somewhat for the one longer regeneration time evaluated. Full regeneration was achieved with regeneration time of 20 minutes, and 10 additional minutes increased the efficiency to approximately 160%. This high value was presumably achieved because the electrochemical regeneration modified the surface of the NYEX® 1000. No comparable atrazine-NYEX® 1000 data is available in the literature. For the regeneration of atrazine-loaded NYEX® 100 Brown et al. (2004a) found that for a regeneration time of 10 minutes and a current density of 20 mA/cm^2 (the same as the current study) achieved over 100% RE. It is hypothesized, that the higher regeneration time (30 min. vs. 10 min.) was necessary to regenerate the NYEX® 1000 due to the presence of humic acid. There is the possibility that the enhanced adsorption occurred during the second loading cycle because during the first regeneration some compounds leached from the NYEX®.

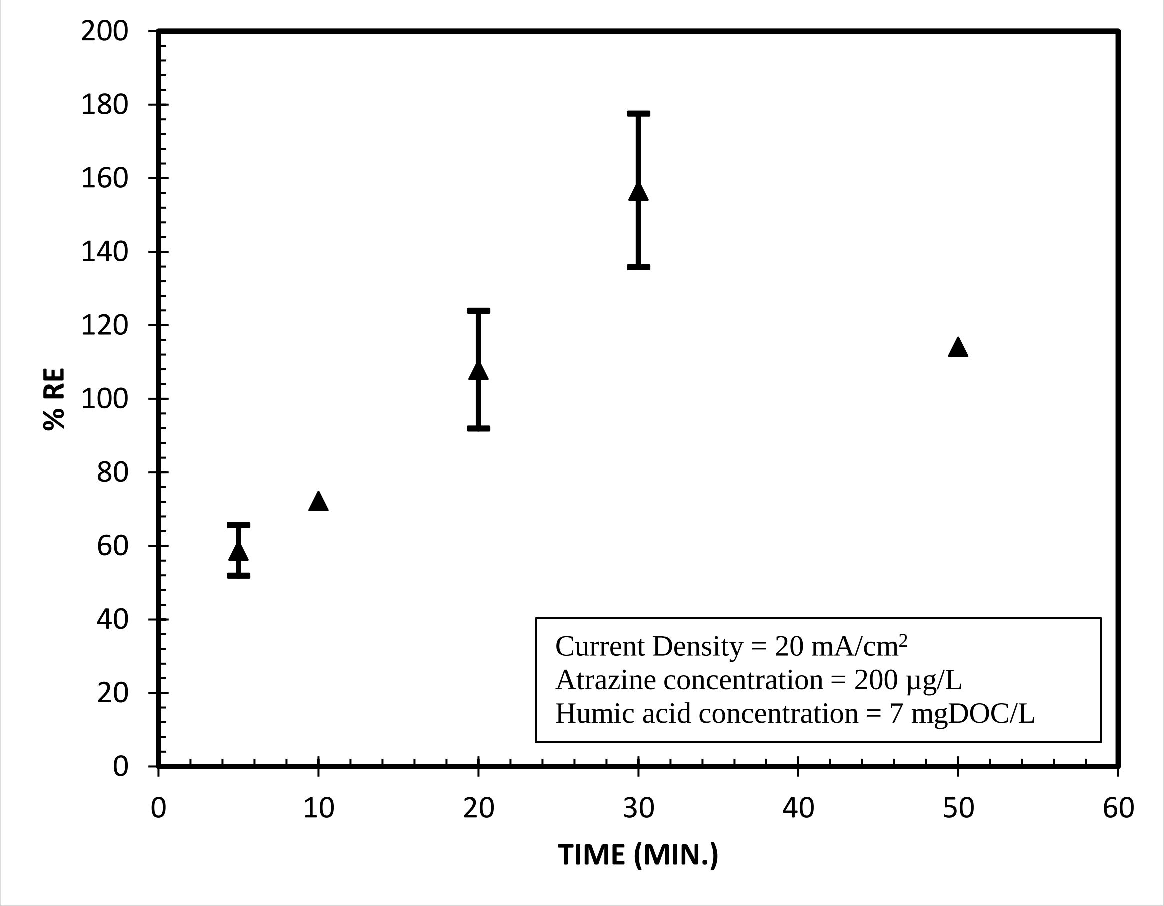

Figure 4.6: Atrazine regeneration efficiency as a function of regeneration time

4.1.3.2 Impact of current density on regeneration efficiency

Given that competitive adsorption with humic acid reduce the atrazine adsorption capacity, it was speculated that the NYEX® anodic regeneration efficiency will be lower for the NYEX® loaded with atrazine-humic mixture than that loaded with the single-solute atrazine solution. The impact of current density on atrazine regeneration efficiency was evaluated with NYEX® loaded with just atrazine and also with NYEX® loaded with atrazine and humic acid (Figure 4.7).

For the atrazine loaded NYEX® (the squares in Figure 4.7) the regeneration efficiency increased with increasing current density up to 20 mA/cm^2, reaching a RE of approximately 140%. The regeneration efficiency remained constant at higher current densities. These results are consistent with the findings of Brown et al. (2004) for the regeneration of NYEX® 100 loaded with atrazine. They found that the optimal current density was 20 mA/cm^2 and for higher values the RE decreased. They attributed this behaviour to side reactions that would consume more electricity.

Tests were conducted to establish the impact of current density for the regeneration efficiency of NYEX® loaded with an atrazine-humics solution showed a somewhat different pattern (the triangles in Figure 4.7), the regeneration efficiency continued to increase approximately linearly up to a current density of 30 mA/cm^2. Accordingly, the above mentioned side reactions do not seem to affect the NYEX® when humic acids are present (Brown 1995). It is possible that the strong polarity of the humic acids is disrupting the atrazine side reactions that occur at the increased current densities. Brown (1995) hypothesized that this was the case in his atrazine experiments. This would mean that the humic acids are actually benefitting the regeneration rather than being a hindrance.

Surprisingly, upon regeneration there was a slightly higher equilibrium atrazine loading achieved by the NYEX® loaded with atrazine plus humic acid than by the NYEX® loaded with just atrazine (15 µg atrazine/g NYEX® 1000 versus 13.1 µg atrazine/g NYEX® 1000). This suggest the electrochemical regeneration of NYEX® minimally loaded with humic acid helps improve the adsorbent to the point that compensates for the competitive adsorption impact of the humics in subsequent loading cycles. This will be discussed in the next section.

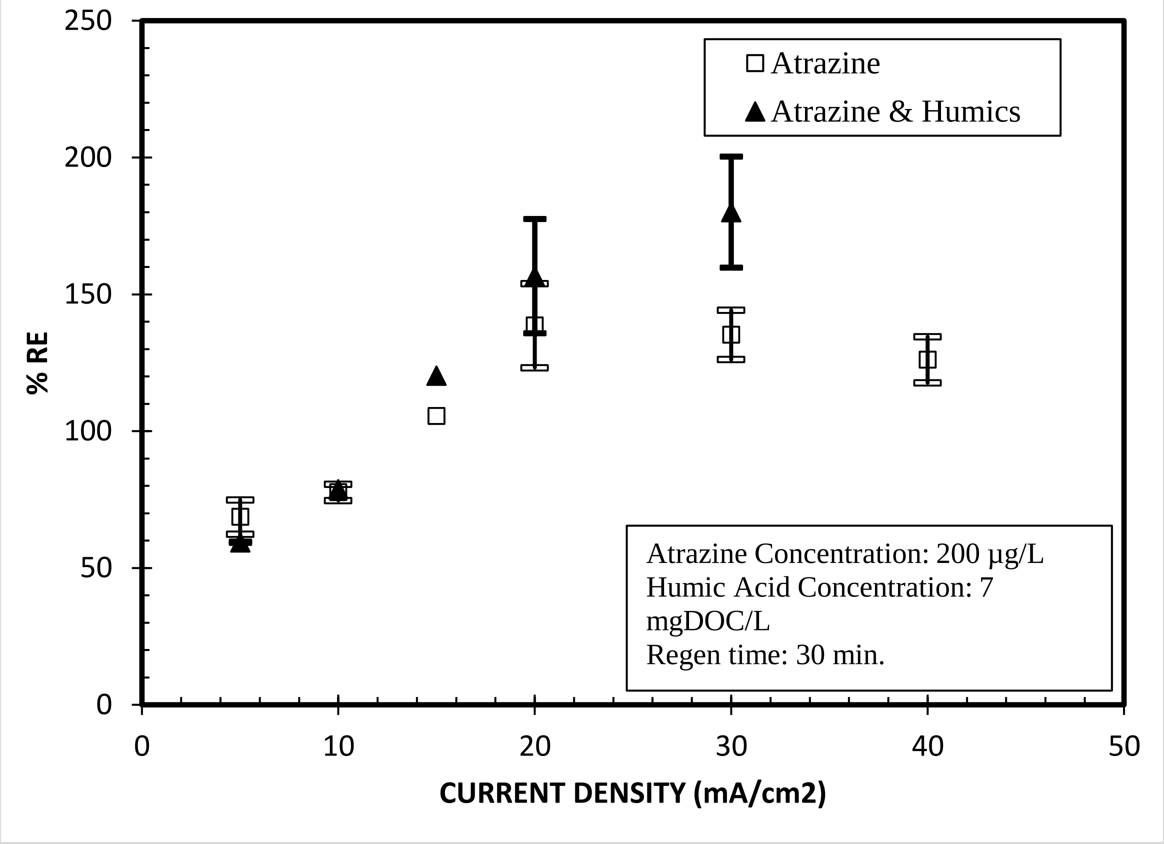

Figure 4.7: Atrazine RE efficiency versus current density for NYEX® 1000 loaded with atrazine and humic acid and NYEX® 1000 leaded with atrazine

This pattern in Figure 4.7 is consistent with results found by Asghar (2011) for the adsorption of acid violet 17 onto NYEX® 1000 and its regeneration. For current densities above 15 mA/cm^2, the %RE flattened and did not increase above 85% (Asghar 2011).

4.1.3.3 Multiple Regeneration Cycles

Multiple cycle tests were performed in order to determine the consistency of the electrochemical regenerations and to evaluate the long-term performance of the process. Regeneration tests were conducted at the previously identified optimal conditions, a current density of 20 mA/cm^2 and a regeneration time of 30 minutes. These tests were performed both with NYEX® loaded with atrazine and with NYEX® loaded with atrazine plus humic acid. The initial solute concentrations were the same as in the previous tests. The regeneration of NYEX® loaded with just atrazine, as shown as squares in Figure 4.8 was 120% in the first regeneration cycle and increased to 140% in the second and subsequent cycles. The fact that the first regeneration cycle resulted in a regeneration over 100% suggests the electrochemical process altered the surface of NYEX® surface. This possibly resulted in the bonding of hydrogen ions to the NYEX® and improved it as an adsorbent of negatively charged species. Atrazine behaves as a weak base in aqueous solutions and has a pKa of 1.60 (NCBI 2004), thus at a neutral pH atrazine should be in its ionized form and likely more attracted to the H+ ions on the NYEX® (Weber 1970, 1993; Weber et al. 1969). Since humic acids are known to contain both positive and negative charges the positive charges, this may result in the repulsion of the humic acids, thus lowering its adsorption capacity on electrochemically regenerated NYEX®. In addition, the higher loading may possibly be achieved by the availability of sorption sites that become available due to the leaching of some organics originally on the NYEX®. Brown et al. (2004a) experienced issues with the leaching of unknown compounds from the NYEX® that were making their atrazine analysis difficult and the control samples in the current study also detected some organic compound leaching for the NYEX® 1000. The consistent performance over the next cycles showed consistent long-term performance. Brown et al. (2004a) also showed that NYEX® 100 research which shows consistent atrazine regeneration efficiencies above 100%.

The regeneration of NYEX® loaded with atrazine plus humic acid, identified as the triangles in Figure 4.8, showed a similar RE pattern but with somewhat higher RE values. In this case, the long-term RE was approximately 170%. To confirm these higher values were not an artifice of the RE formula, the data of these experiments was replotted in terms of the equilibrium atrazine loading achieved in the multi regeneration cycle experiments (Figure 4.9). This graph shows for the second and subsequent cycles achieved the same atrazine loadings for both the atrazine-only solutions and the atrazine-humic acid solutions. This implies that in these loading cycles the humic acids were no longer competing with atrazine for the NYEX® sorption sites. And indeed, the adsorption of humic acids in the second and subsequent cycles was negligible. It is hypothesized that the electrochemical regeneration leaves a residual charge on the NYEX® and it minimizes the adsorption of humic acids through charge repulsion. Future studies should attempt to confirm this hypothesis. Regardless of the mechanism, it is evident that the RE graph (Figure 4.8) gives a false impression in that the performance for the atrazine-humic acid mixture is superior to that for the atrazine alone solutions. On the other hand, Figure 4.9 demonstrates that the presence of humic-acids does not have a long-term detriment to the removal of atrazine by NYEX® 1000 adsorption/oxidation systems. Presumably, the presence of the humic acid during the first electrochemical regeneration cycle led to a slight change of the NYEX® during this regeneration, and this change resulted in the higher atrazine sorption capacity in later loading cycles. It is noteworthy that the electrochemical regeneration compensated for the decrease in atrazine sorption capacity due to the competitive adsorption with humic acid.

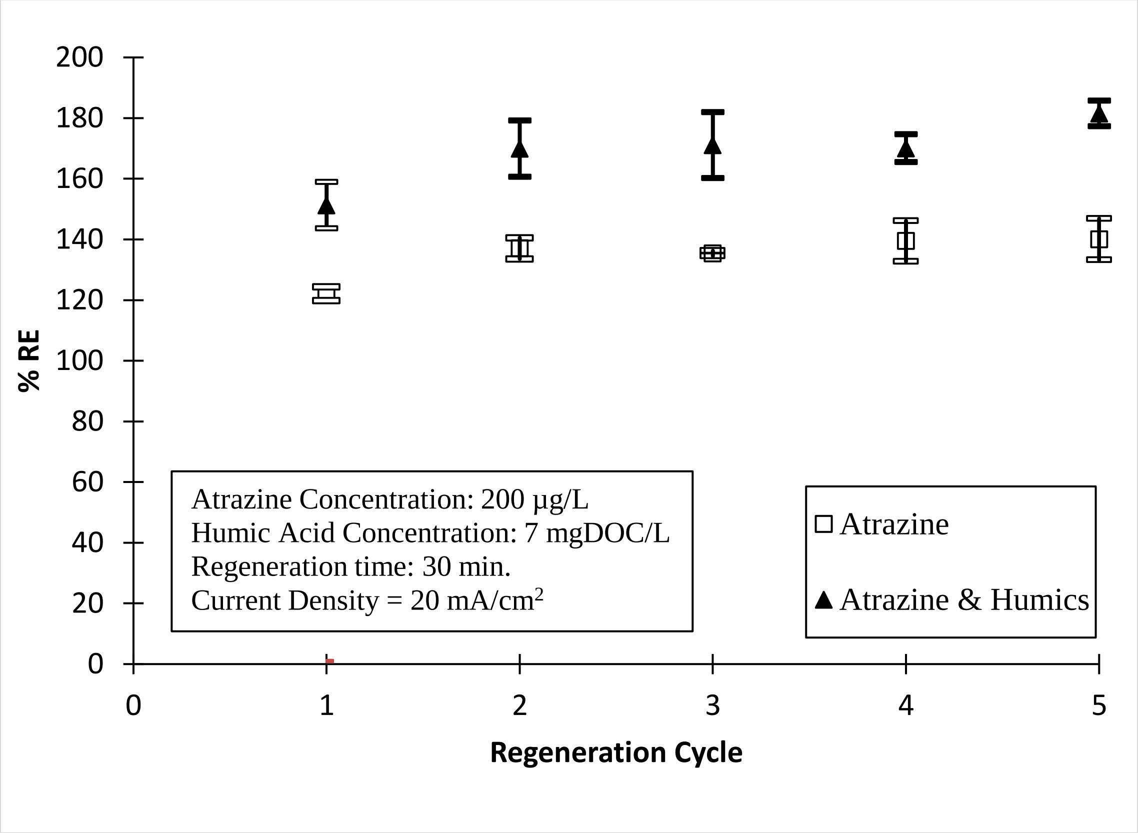

Figure 4.8: Impact of multiple regeneration cycles on the regeneration efficiency of NYEX® loaded with atrazine and NYEX® loaded with atrazine and humic acid

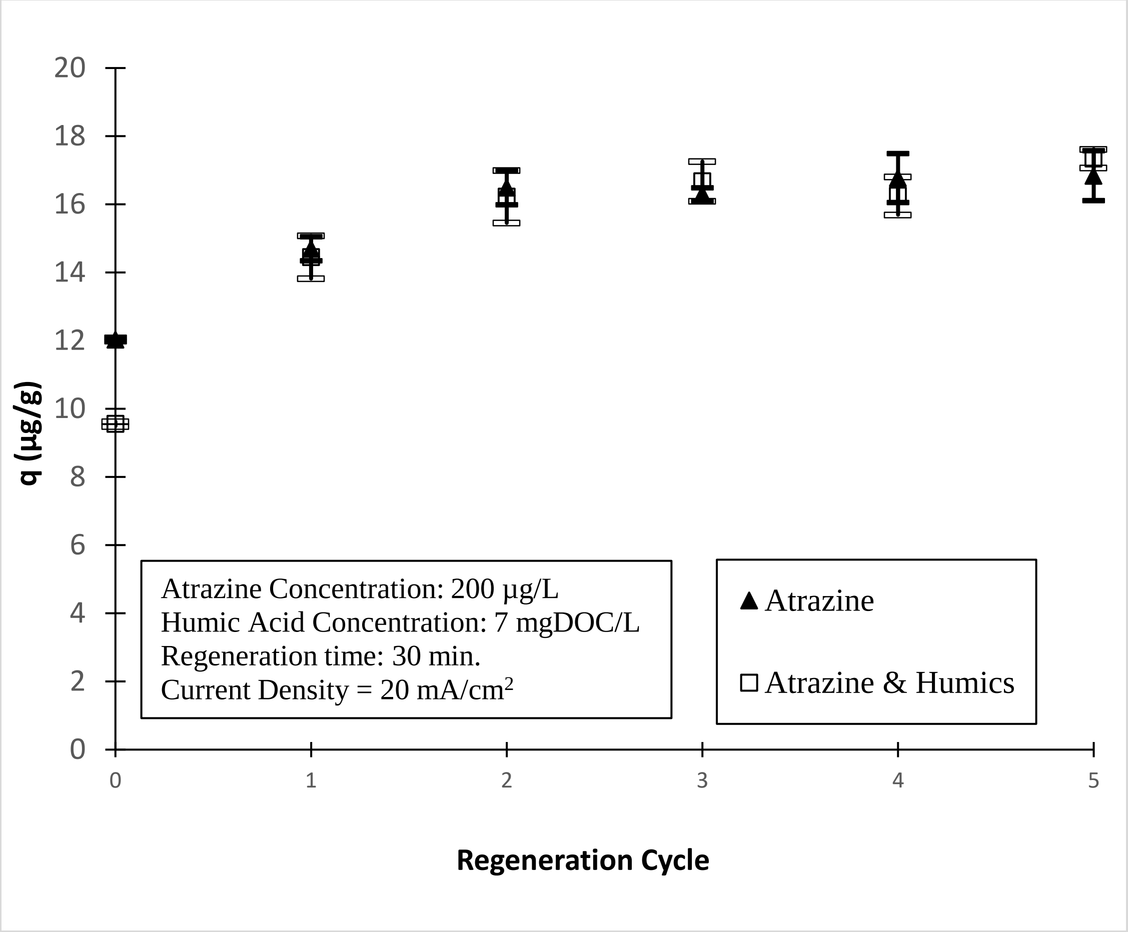

Figure 4.9: Multiple cycles of NYEX® regeneration using q_{ee} with atrazine and atrazine & humic acid

4.4 Conclusions

The humic acid bottle-point isotherm conducted using the same solute and different NYEX® 1000 doses yielded unexpected lower loadings for the smallest NYEX® dosages, this is consistent with the findings of Ning (2015). The lower loadings could be caused by competitive adsorption with organic compounds leached from the NYEX® 1000, this requires further investigation (Ning 2015). Unfortunately, due to the electrostatic adhesive characteristics of NYEX® it is very difficult to pre-wash NYEX® without the loss of the smallest particles, which are those providing the higher surface area per unit mass. The bottle-point method with a constant adsorbent dose yielded reasonable results and it is recommended for experiments with NYEX®. The humic acid isotherm yielded similar results to the data reported by Asghar et al. (2013). The humic acid single solute isotherm was not as uniform as the atrazine isotherm showing great variability in the adsorption behaviour of the humic acids. The atrazine-humic acid-NYEX® 1000 isotherms demonstrated that, like with activated carbon, there is significant competitive adsorption on NYEX® between the target trace toxic compound (atrazine) and humic acid. Since NYEX® 1000 has virtually no internal pore structure, the competitive adsorption is not related to pore blocking by the humic acids, which was one of the hypothesized mechanisms for competitive adsorption onto activated carbon (Summers et al. 2012). Surprisingly, the competition decreased the humic acids sorption capacity significantly more (e.g. 98% decrease) than the atrazine capacity (average 37% decrease). It is speculated that this was caused by: a) the initial atrazine concentrations (on a molar basis) were significantly higher than those of the humic acids; and b) the diffusion of atrazine is significantly faster.

The electrochemical regeneration of atrazine loaded NYEX® and NYEX® loaded with an atrazine –humic acid solution was very effective. For several combinations of regeneration time and current densities it achieved regeneration efficiencies of over 100%, presumably the electrochemical processing altered the NYEX® improving its adsorption capacity. However, the multi-cycle loading/electrochemical regeneration tests showed that NYEX® loaded with atrazine-only solutions and the atrazine-humic acid solutions yielded the same long-term atrazine loadings. Thus, the humic acid competition did not hinder NYEX®

1000's long-term removal of atrazine. These findings should be confirmed with other trace organic contaminants and other sources of NOM.

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CHAPTER 5: Conclusion and Recommendations

5.1 Conclusions

The main objective of this thesis was to study the competitive adsorption of atrazine and humic acid onto NYEX® 1000 and NYEX®'s electrochemical regeneration behaviour. The conclusions of this thesis are as follows.

1. Based on the results of the humic acid – NYEX® isotherms, the constant solution-varying adsorbent dose bottle-point procedure is not recommended for NYEX® isotherms. Leaching of compounds from the NYEX® is plausible explanation for the decrease in capacity at the higher equilibrium liquid phase concentration/lower adsorbent dose data points. The constant dose method was chosen since the results were not as affected by the leaching effect of the NYEX® 1000.
2. The coefficients of the Freundlich isotherm regressed from the NYEX® 1000-humic acid isotherm data yielded were statistically the same as those derived from those obtained from the data published by Asghar et al. (2013). The single-solute atrazine onto NYEX® 1000 yielded significantly lower atrazine capacities than those reported by Brown et al. (2004a) when adsorbing atrazine onto NYEX® 100, however, NYEX® 1000 and NYEX® 100 are different materials.
3. The presence of humic acid depressed the NYEX®-atrazine adsorption capacity by an average 37%, similar to what one would expect for the adsorption onto AC. Since NYEX® lacks the large internal pore structure of GAC, pore blockage does not seem to be a significant factor in the competitive adsorption decrease in atrazine sorption capacity. Surprisingly, the adsorption capacity of humic acid

decreased by 98% when competing with atrazine. It is speculated that this was due at least in part to the higher atrazine molar concentrations in the solution and higher molecular diffusivity of atrazine. Therefore, atrazine was the dominant adsorbate.

4. Electrochemical regeneration of atrazine-loaded NYEX® 1000 and atrazine-humic acid loaded NYEX® 1000 was very successful in that under many conditions atrazine regeneration efficiencies over 100% were achieved. The electrochemical processing appears to modify the NYEX® 1000 leading to higher atrazine sorption capacities. For the conditions tested, increasing electrochemical regeneration current density increased the atrazine regeneration efficiency atrazine-humic acid loaded NYEX® 1000. However, it was slightly different for atrazine-only loaded NYEX® 1000 in that the regeneration efficiency decreased slightly for current densities above 20 mA/cm^2. Brown (1995) suggested that in the regeneration of the atrazine-only loaded NYEX® at higher currents there were current-consuming side reactions, it is speculated that humic acids disrupted these reactions.
5. Multiple loading/regeneration NYEX® test cycles showed that the presence of humic acid appeared to improve the NYEX®'1000s atrazine sorption capacity so that it compensates for decrease in atrazine sorption capacity caused by competitive adsorption. It is speculated that a residual positive charge left on the NYEX® 1000 turned its surface acidic, that could explain the attraction of a weak base such as atrazine.

5.2 Recommendations

1. The variable dose experiments with NYEX® 1000 requires more thorough examination, particularly trying to identify compounds leaching from the adsorbent.
2. To reduce the electrostatic adhesion problems in the transfer of the NYEX® particles, it is recommended that future NYEX® adsorption/electrochemical regeneration be performed in the same reactor, such as that developed by Roberts and colleagues. This will also help reduce the time required to conduct the experiments. Liu et al. (2016) used one such reactor.
3. To Pre-treat the NYEX® through electrochemical regeneration to enhance the surface of the NYEX® in order to study the impact of electrochemical processing on the adsorption of humic acid.
4. The NYEX® competitive adsorption findings of this study should be confirmed using other trace organic contaminants and other sources of NOM.
5. When increasing current density for regeneration sorbed atrazine onto NYEX® 1000, there is a decrease in regeneration efficiencies. This is not the case in the sorption of atrazine & humics onto NYEX® 1000 where there was only an increase in regeneration efficiency as current density increases. It was speculated this was caused by side reactions involved that are causing the decrease in regeneration efficiency and why these side reactions do not affect the multi-component regeneration. Therefore, further research is needed in order to identify the specific side reactions.

6. The multiple cycles of regeneration showed very little change in the regeneration efficiencies using the same NYEX® 1000 batch of both the single solute and multi-solute regenerations after 5 regeneration cycles. Therefore, it is worth investigating if the NYEX® 1000 can sustain these results on a long-term basis. This would particularly worthwhile if there is deterioration of the adsorbent after a large number of regeneration cycles.

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Appendix A

Comments on the Atrazine Analytical Method Development

This Appendix is to highlight additional subject matter required during the method development phase for the analysis of atrazine and atrazine & humic acid.

Firstly, the retention time could be increased by raising the percent amount of methanol in the mobile phase to 90%. The likely result of this approach is that the distortion would still occur and the atrazine can be recovered at a later retention time. The main issue with this method is that the consumption of methanol would potentially be greater. For instance, the amount of methanol will be increased by 35% to 90%. With an average operating time of 20 hours and a mobile flow rate of 1 mL/min, the overall consumption of methanol would be 1,080 mL of methanol. Comparing this scenario using 55% methanol the consumption would be 660 mL. That is an overall increase of 420 ml for every 20 hours of operation. This method would constitute a greater increase in the consumption of reagent which would be more efficient in the consumption of reagents during the HPLC analysis.