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Pyrolysis of Wastewater Treatment Sludges for the Production of Oil and Adsorbents

By

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A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements of the degree of

Master of Applied Science

In Environmental Engineering

Department of Civil and Environmental Engineering
Carleton University
Ottawa, Ontario, Canada

The Master of Applied Science in Environmental Engineering is a joint program with the University of Ottawa, administered by the Ottawa-Carleton Institute for Environmental Engineering

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Acknowledgements

The author would like to express sincere appreciation to Professor W. J. Parker, who provided helpful guidance during the research and preparation of this thesis. Appreciation is here expressed: for technical support by C. Stanley and T. Pierre; for many valuable experimental advices by S. Hamid and writing advices for this thesis by S. Ranya and S. Laura. Also, thanks are expressed to environmental laboratory technician T. Marie for helpful support for this project. Finally, I would like to thank my family, particularly my wife Junghyun Choi and my parents for their patience and the many personal sacrifices they made.

Abstract

Sewage sludge treatment is one of the most difficult problems in the field of wastewater treatment because of increasing expenses and environmental sensitivity. Pyrolysis to produce bio-oil and adsorbents from sewage sludge is a promising way, to not only improve economical value but also, reduce pollutants associated with sludge. The aim of this study was to evaluate the production of oil and adsorbents from raw, wasted activated and digested sludges. The pyrolysis was performed in a laboratory scale horizontal batch reactor. The operating temperature ranged from 250 to 500°C while a gas phase residence time of 20 minutes was maintained with 50 mL/min of nitrogen gas as a purge flow.

The maximum oil yield was achieved with primary sludge at 500°C. Temperature and volatile solids were the most important factors affecting the yield of oil and phenol adsorption capacity of the char, however sludge type also affected the both results. Pretreatment of sludge by either acid or base did not improve the quantity of the products, though it did affect the volatile solids fraction of the samples. The phenol adsorption capacity of the char was affected by pretreatment. The use of a catalyst (zeolite) reduced char recovery.

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List of Acronyms and Nomenclature

BET	Brunauer, Emmett, Teller equation
BOD ₅	five-day biological oxygen demand
C.I.	confidence intervals
COD	chemical oxygen demand
ds	dried sewage sludge
FS	fixed solids
M	mole
MAF	mass as feeding
NCG	non-condensable gases
OD	outside diameter
rpm	revolution per minute
SCW	supercritical water
SRT	solid residence time
SS	stainless steel
STD	standard deviation
TCD	total conductive detector
TWAS	thickened waste activated sludge
UV	ultraviolet
VS	volatile solids
WAS	waste activated sludge

ΔH_{vap}	latent heat for vaporization of water, 2090 kJ/kg
ΔT	temperature difference between initial and 105°C, °C
ΔT_{target}	difference between target and 105°C, °C
b	Langmuir adsorption constant
C_0	concentration of phenol before contacting with adsorbent, mg/L
C_{char}	carbon fraction in mass of char, %
C_{ds}	carbon fraction in dried sludge, %
C_E	cost of electricity, CDN 4.3 ¢/kW·hr
C_e	concentration of liquid phase, mg/L
C_{loss}	mass fraction of carbon lost during pyrolysis, %
C_{oil}	carbon fraction in oil, %
C_R	cost of required energy, ¢
Cp_{water}	specific heat capacity of water, 4.18 kJ/kg·°C
Cp_{ds}	specific heat capacity of dried sludge, 1.95 kJ/kg·°C
E_{char}	calorific value of char, kJ/g-char
$E_{consumed}$	energy consumption for pyrolysis and drying, kJ
E_{ds}	calorific value of dried sludge, kJ/g-ds
E_{oil}	calorific value of oil, kJ/g-oil
K_f	Freundlich constant,
M_{ads}	mass of char contacted with phenol solution, g
M_{char}	mass of char in dried sludge, g
M_{ds}	mass of dried sludge, g
M_{oil}	mass of oil yield of dried sludge, g

M_{rw}	mass of reaction water in oil, g
M_{oil+rw}	mass of oil with reaction water, g
M_{ws}	unit mass of wet sludge after dewatering, kg
$\overline{M}_{vs}$	mass of volatile solids after pretreatment, g
$\overline{M}_{oil}$	mass of oil basis of treated dried sludge, g
n	Freundlich exponent
Q_{target}	energy required to heat sludge to reach target temperature, kJ
Q_{total}	total energy consumption for sludge pyrolysis, kJ
q_e	adsorption capacity of adsorbent after equilibrium, mg-phenol/g-adsorbent
q_{e-TS}	adsorption capacity of adsorbent basis of total solids, mg-phenol/g-adsorbent
q_{e-VS}	adsorption capacity of adsorbent basis of volatile solids, mg-phenol/g-adsorbent
q_{max}	maximum adsorption capacity of Langmuir isotherm, mg-phenol/g-adsorbent
$q_{max,char}$	q_{max} of adsorbent, g-phenol/g-adsorbent
$q_{max,ac}$	q_{max} of commercial activated carbon, g-phenol/g-activated carbon
r^2	correlation coefficient
V	volume of phenol solution used, L
V_{char}	economic value of char, ¢/kg
V_{ac}	economic value of commercial activated carbon, ¢/kg
W	water content, %

CHAPTER 1

INTRODUCTION

The management of municipal wastewater treatment sludges is a difficult and expensive problem to solve for wastewater engineers. Generally, half to one kilogram of sludge are produced per kilogram of five-day biological oxygen demand (BOD_5) treated [Eckenfelder, 2000]. The sludge resulting from domestic wastewater treatment processes usually consists of a complex semisolid-liquid heterogeneous mixture of organic and inorganic materials. The solids contain typically 60 to 80 percent organic matter. The organic materials in primary sludge are comprised of 20 to 30 percent crude protein, 6 to 35 percent fats and 8 to 15 percent carbohydrates [Metcalf and Eddy, 2002]. Although sewage sludge contains various valuable materials, it is often wasted as an undesirable and invaluable substance.

Processing and disposal is one of the most complex problems associated with the byproducts of wastewater treatment. The processing consists of stabilizing, conditioning and dewatering to achieve reduction in the odour and quantity of organics solids, as well as eliminating disease-causing organisms and removing the water content of the end product for easy handling [Metcalf and Eddy, 2002].

The disposal of sewage sludge, whether treated or untreated, is an increasing problem in recent year for municipalities. Over 7 mega tons of dried sewage sludge were produced in 1990 in the U.S [McGhee, 1991]. Canadian municipalities have spent \$12-15 billion annually for sewage sludge treatment [Buberoglu and Duguay, 2004].

The common disposal processes for sewage sludge include landfilling, land application and incineration. However, conventional disposal processes have certain limitations. Disposal in landfills is still the most frequently chosen alternative for sludge in Europe and the U.S [Hall and Dalimier, 1994; McGhee, 1991]. However landfilling is not always desirable because of the limitation in available landfill volume. Land application or the use of sewage sludge as a fertilizer can result in the accumulation of harmful components, such as toxic metals, in the soil [Vasseur et al., 1999]. Incineration is an effective way for reducing sludge volume and results in improved thermal efficiency and stabilizing of the organic materials of sludge [Werther and Ogada, 1999]. However, the air emissions produced from incineration are undesirable and are restricted by regulation.

In recent years, several alternative disposal processes have been introduced for the beneficial use of sewage sludge. These include wet air oxidation, pyrolysis, supercritical water oxidation and microwave incineration [WERF, 1998]. Of these processes, pyrolysis of sewage

sludge for production of bio-oil generally has more benefits than the others in which no valuable product is reclaimed.

Pyrolysis is the thermal decomposition of organic substances in oxygen-free circumstances at temperatures ranging between 250 to 900°C. The process involves a complex series of chemical reactions to decompose organic materials. The synthesized oil, char and gas products of pyrolysis can be used as fuel [Bridle 1982, Caballero et al., 1997]. Therefore, pyrolysis of sewage sludge has generated significant interest for the beneficial use of sewage sludge in the past two decades. Particular interests in this process are high oil recovery and lower emissions of NO_x and SO_x. It also avoids the formation of toxic organic compounds such as dioxins, with low operating costs as compared to incineration [Caballero et al, 1997].

In addition, several recent investigations have been carried out to use the chars from pyrolysis of sewage sludge as adsorbents [Lu et al., 1995; Lu and Lau, 1996]. The effect of several pyrolysis conditions on char adsorbance capacity have been studied to overcome the limitation of practical usage [Tay et al. 2001; Chen et al., 2002]

The most significant merit of this technology is that the resulting products have reduced undesirable properties. Recent studies have focused on how to raise the economic value of products from sewage

sludge pyrolysis; specifically on practical use of chars and gases. The objectives of this research are:

- 1) to characterize the pyrolysis of different types of sewage sludges in laboratory-scale apparatus.
- 2) to evaluate the use of additives to improve oil and char recovery.
- 3) to investigate the capacity of chars from pyrolysis as adsorbents.
- 4) to identify the optimum conditions for recovery of the oil and solids and to analyze the economic values of the products.

CHAPTER 2

Literature Review

2.1 Formation and Production of Sewage Sludge

Sewage sludge is generated in significant quantities when mechanical and biological processes treat municipal and industrial wastewaters. The sludges consist of complex heterogenous mixtures of organic and inorganic materials.

Mechanical processes in primary clarification remove the incoming untreated coarse and heavy solids. Generally, primary sludge is produced from these mechanical processes that remove 50 to 70 percent of suspended solids and 25 to 40 percent of BOD₅ [Metcalf and Eddy, 2002].

The overflow from the primary clarifier is often biologically treated with coagulation to stabilize the organic matter using a variety of micro-organisms in an aeration basin. In the secondary treatment, sludge is generated and is typically referred to as waste activated sludge (WAS).

The primary sludge and WAS are typically processed to reduce odour, quantities of organic solids and pathogens with stabilization, conditioning and dewatering processes. Digestion is the most common method of sludge stabilization and conditioning. It involves partial

conversion of the organic matter into gas and a stabilized residue with the help of anaerobic or aerobic bacteria. Therefore, digested sludge is a stabilized and it is sometimes dewatered prior to offsite transport.

2.2 Disposal Options for Sewage Sludge

The complex problems in sewage sludge treatment have several causes. First, most pollutants removed by decontamination processes will reappear in sewage sludge. These substances can become offensive when decomposed. Second, numerous micro-organisms present in the sludge matrix impose risks to public health and safety [Metcalf and Eddy, 2002]. Third, toxic compounds, such as heavy metals like mercury, can endanger humans and ecosystems [Werther and Ogada, 1999].

2.2.1 Traditional Disposal Methods

The land application of sewage sludge in several countries has been underway since the late 1970's as an alternative disposal route for sewage sludge. Several Canadian provinces, such as Ontario, Quebec, Manitoba and Saskatchewan, have used sludge as a soil amendment for over a decade [Vasseur et al, 1999]. The nitrogen and phosphorus contents in sewage sludge ranging between 1.5 and 5 percent and 0.8 and 11 percent respectively, make it useful as fertilizer and soil conditioner [Metcalf & Eddy, 2002]. This disposal option has been found to cause accumulation of toxic elements into sludge-amended soil in the recent past. Countries using sewage sludge as agricultural fertilizers have limits

on the land application of sludge. For example, the U.S. Environmental Protection Agency (U.S. EPA) controls the reuse and disposal of the sludge with 40 CFR Part 503 [U.S. EPA, 1993]. Similarly, European Union (EU) applies the sludge disposal limitations found in 86/278/EEC [Hall and Dalimier, 1994].

Landfilling is one of the main sludge discharge processes. However, the future of sludge disposal through landfilling is doubtful. Disposal in a sanitary landfill requires a significant amount of space. Also, a large volume of soil is required to cover the waste in order to prevent leaching of harmful compounds such as heavy metals, and phenols. Landfill sites are difficult to locate and are strictly regulated due to the odour emission and the potential of ground water contamination. For these reasons, sewage sludge should ideally be odour-controlled, dewatered and stabilized prior to landfilling [Metcalf and Eddy, 2002].

2.2.2 Incineration

Incineration is a desirable alternative for reusing sludge when compared to other disposal methods. This method is most effective for volume reduction and energy recovery from sewage sludge. Mechanically dewatered sludge can be decreased in volume by 90 percent, and toxic organic compounds can be thermally decomposed by incineration [Werther and Ogada, 1999]. It is also possible to recover 23 to 28 MJ/kg of volatile solids from dried primary and digested sludge by incineration

[Herbert et al., 1978]. However, incineration can result in toxic emissions such as dioxins. The treatment of these toxic gases incurs high cost. Furthermore, the air emissions from incineration are more restricted by regulations. In the U.S, new incineration facilities have not been built because of public resistance [Water environment federation, 1996].

2.3 Alternative Disposal Routes for Sewage Sludge

The issues associated with conventional means of sewage sludge disposal have prompted the development of alternative disposal routes. These include wet air oxidation, supercritical water oxidation, pyrolysis and microwave pyrolysis. The Water Environmental Research Foundation (WERF, 1998) classified the concentrated thermal technologies as established, innovative, and embryonic, as shown in Table 2.1. These methods are modified thermal processes that solve the problems of incineration and reap benefits from sewage sludge. The operating temperature and pressure ranges for incineration, wet air oxidation and hydrothermal oxidation are illustrated in Figure 2.1.

Table 2.1: WERF Classification of Thermal Technologies

Established	Innovative	Embryonic
Multiple Hearth Furnace	Wet Air Oxidation	Gasification of Char
Fluidized Bed Furnace	Melting Furnace	Catalytic Extraction
Combustion with Solid Waste	Sludge-to-Oil Process	Supercritical Water Oxidation
Wet Oxidation	Oxygen Injection	Microwave Incineration

Figure 2.1: Operating Temperature and Pressure Ranges

(James and Dennis, 2002)

2.3.1 Wet Air Oxidation

Wet air oxidation processes were first demonstrated in the U.S. in 1984 and 1985 [U.S. EPA, 1987]. The operating conditions of wet air oxidation processes for sewage sludge include an operating temperature of 150 to 330°C and pressure of 1 to 22 MPa in the aqueous phase. Either air or oxygen is employed as the oxidant and the reaction is typically accomplished in a deep shaft (1500 m).

The high pressure involved prevents boiling of sewage sludge at these temperatures. Therefore, the organic matter in the sewage sludge can be thermally decomposed by hydrolysis and oxidation. Carbon dioxide, water and nitrogen are generated during the process. This process is employed commercially because of the easily achieved and controlled reaction conditions.

The first commercial sewage sludge wet oxidation plant was built in Netherlands in 1992 [Werther and Ogada, 1999]. This system employs a 1200 m deep cement-encased well with a 960 mm diameter. The capacity of the facility is 62 dry-ton/day operating at 280°C and 10 Mpa, with 70 percent reduction efficiency for chemical oxygen demand (COD). Wet oxidation has merits such as complete destruction of all pathogens and viruses as well as the control of heavy metals and odours.

2.3.2 Supercritical Water Oxidation (Hydrothermal Oxidation)

Supercritical water (SCW) oxidation is a hydrothermal wastewater treatment process that occurs above the critical point of water at 374°C and 21.8 MPa. With reduced density, viscosity and dielectric constant as well as increased diffusivity in the supercritical region, SCW creates an efficient oxidizing environment. Therefore, low-polarity organic compounds mixed completely in supercritical water result in decomposition within a short residence time of 20 to 29 seconds [Yutaka, 2000].

In 2001, a supercritical water oxidation facility for sewage sludge treatment was built in Harlingen, Texas [James and Dennis, 2002]. This process is operated at elevated pressure and temperature to destroy pathogens and achieve full conversion of organic matter to carbon dioxide. The capacity of the Texas supercritical process is 9.8 dry-ton/day of sludge with destruction efficiencies of 99.9 percent and 75.4 percent for COD and total solids respectively.

2.3.3 Pyrolysis

Pyrolysis involves the thermal decomposition of organic compounds under oxygen free conditions at temperatures ranging between 250 and 900°C. Three products are usually produced: oil, char and gas. The relative proportions of these depend on the pyrolysis methods and reaction parameters such as final temperature, heating rate, residence

time and sample size. Heating rate are typically characterized as slow (less 1 °C/sec), medium (5 to 100 °C/sec), fast (500 to 10⁵ °C/sec) and flash (over 10⁵/sec) [Mühlen, 1989]. Pyrolysis technology can convert solid biomass and wastewater sludge, which are difficult and costly to manage, to a liquid product. This endothermic reaction involves a complex series of chemical reactions that decompose and breakdown organic materials. The reported heats of pyrolysis range from 300 to 1600 kJ/kg and are affected by characteristics of biomass (type of wood or sludge), final temperature and sample size [Tang and Neil, 1964; Caballero et al., 1997; Dugaard and Brown, 2002].

Generally, lower temperature conversion processes in the temperature range between 275 and 500°C have been used to produce oil from sewage sludge. The oil obtained has a high viscosity and high heating values of 29 to 38 MJ/kg and can be used as fuel [Campbell and Bridle, 1986; 1989].

2.3.4 Microwave Pyrolysis

Sewage sludge pyrolysis by microwave is one of the most recent technologies in the field of sewage sludge treatment. Martin et al. (2002) illustrated the effect on sewage sludge based on microwave receptor escalating microwave energy. Microwave treatment was used to dry a sewage sludge that had a moisture content of 78 percent. However, in the same system, suitable microwave receptors such as char from pyrolysis of sewage sludge increased the temperature up to 900°C. This study also

emphasized that microwave treatment of sewage sludge can achieve 80 percent volume reduction and considerable time and energy savings compared to conventional heating processes such as drying and pyrolysis.

2.4 Pyrolysis of Sewage Sludge

2.4.1 Review of the History of Pyrolysis Processes

Sludge pyrolysis technology was introduced as a thermo-chemical conversion process in 1940's. Bayer et al. (1981) designed a continuous laboratory-scale plant (5 kg/day) that demonstrated the production of synthetic crude oil under oxygen free conditions. The operating conditions were around 300°C, and at atmospheric pressure with a residence time of three hours. They demonstrated the fundamental mechanics of the conversion reactions involved in sludge pyrolysis with their research. They showed that organic substrates generate liquid hydrocarbons by thermal decomposition with metal catalysts and proved that the proteins and lipids in sewage sludge generate oil and char.

2.4.2 Review of Continuous Bench-Scale Pyrolysis Processes

In the 1980's, Environment Canada embarked on a major technology development and demonstration of oil production processes from sewage sludges. Campbell and Bridle (1986; 1989) reported favourable results with both bench and pilot scale continuous reactors. They studied primary sludge, which were mixed raw and WAS and anaerobically digested sludge. The dried sludge (4 to 7 percent moisture present) had

volatile solids (VS) contents of 55 to 64 weight percent, calorific values of 15 to 18 MJ/kg-TS and carbon contents of 24 to 36 percent.

The operating parameters and a summary of the results of the bench-scale reactor are shown in Table 2.2. At the optimum temperature of 450°C, oil yields, based on dried sludge, from primary and digested sludge ranged from 22 to 46 and from 13 to 29 weight percent respectively. Reaction water yields of 3 to 16 weight percent were observed and this response was independent of the operating parameters. The yields of non-condensable gases (NCG) ranged from 3 to 12 percent and increased with temperature due to vaporized VS. It had a calorific value that ranged from 2 to 9 MJ/kg.

Table 2.2: Bench-Scale Operating Parameters and Results
(Campbell and Bridle, 1989)

Parameter	Primary Sludge	Digested Sludge
Feed Rate, g/h	750	750
Optimum Temperature, °C	450	450
SRT, min	20	20
Oil Yield, wt. %	22 – 46	13 – 29
Oil Viscosity, centistokes	23 – 168	9 – 27
Oil Calorific Value, MJ/kg	33 – 38	32 – 42
Char Yield, wt. %	40 – 66	41 – 73
Char Calorific value, MJ/kg	7 – 23	6 – 17
NCG Yield, %	3 – 12	4 – 12
NCG Calorific value, MJ/kg	2 – 6	4 – 6
Reaction Water Yield, %	3 – 15	7 – 16

NCG: non-condensable gases

Figure 2.2 presents typical data that was generated by Campbell and Bridle (1989) and demonstrates trends in oil yield as a function of temperature and sludge type. The data for oil yield in Figure 2.2 have been plotted on the basis of VS rather than total solids to normalize the effect of different VS content because primary sludge generally included more VS than digested sludge. Figure 2.2 demonstrates that the primary sludge produced higher yields of oil than the digested sludge. This indicates that the VS in primary sludge contain more of the components which are converted to oil than those in digested sludge due to the destroyed VS in the digestion process.

Figure 2.3 presents the yield of char as a function of the pyrolysis temperature. The char yields vary from 40 to 73 percent with operating temperatures. The char yield behaviours differed as compared to the oil yields with decreased char yield with increasing pyrolysis temperature. The results indicated that VS in the dried sludge was vaporized with increasing temperature leaving less material to end up as char.

The elemental characteristics of the oil produced were quite stable over a wide range of operating conditions. The typical ratio of C: H: O: N: S was 76: 11: 6.5: 4: 0.5 percent. In terms of its carbon content (70 to 80 percent), it corresponds to that of heavy crude oil [Werther and Ogada, 1999]. The elemental characteristics of the char were affected by operating temperature. The carbon, hydrogen, and nitrogen contents in the char decreased with increased temperatures.

Figure 2.2: Effect of Temperature on Oil Yield from Bench-Scale Process
(Campbell and Bridle, 1989)

Figure 2.3: Effect of Temperature on Char Yield from Bench-Scale
process (Campbell and Bridle, 1989)

2.4.3 Fluidized Bed Pyrolysis Processes

A fluidized bed reactor for pyrolysis of sewage sludge with a short sludge residence time (SRT) and small particle size was introduced in the mid 1980's. Piskorz et al. (1986) studied dried primary and waste activated sludge mixtures with an average particle size of 250 μm . They defined the oil from this process as a mixture of tar and light oil (liquid organics). The maximum yields of oil were as high as 53 percent of the total mass as feeding (MAF) and were obtained at a temperature of 450°C. The tar yields were up to 52 percent MAF at 400 to 450°C with a 0.55 second residence time.

Piskorz et al. also reported increased tar yield from sludge treated with strong acid. The sludge was treated in heated acid (HCl, pH 0.8) at 90°C for 10 minutes, washed in distilled water, then dried and screened (250 μm). They demonstrated that the acid extraction removed 41 percent of inorganics and 19 percent of organics from the sludge sample. The acid treated sludge increased the yield of tar from 52 percent MAF to 65 percent MAF while the char and gas yields were slightly reduced.

Stammbach et al, (1989) researched pyrolysis of digested sewage sludge in a continuous bench-scale fluidized bed reactor. The operating conditions were 500 to 650°C with a residence time of 1.4 second and feed rate of 1 to 5 kg-ds/hr. The dried sewage sludge (ds) contained 7 to 10 percent water and organic matter content in the sludge was 54 percent.

Stammach et al. found that the production of organic liquids, tar, gas and reaction water was not only dependent on temperature, but also influenced by sludge particle size and the heating rate. The application of zeolite as a fluid cracking catalyst increased the selective production of gas and oil by reducing the yield of tar. They estimated that the economics of this process were not favourable because of high investment as well as operation and maintenance costs.

2.4.4 Review of Commercial Plants

The first full-scale commercial plant (30 dry-ton/day) to convert sewage sludge to oil was built in Perth, Western Australia [Bridle et al., 1997]. The main products from the process were synthetic oil, inert gases and combustion heat. This process produced 200 to 300 liter of synthetic oil/ton-dried sludge. The oil produced by this process was similar in quality to medium fuel oil and could be used for the generation of electricity. The inert ash and combustion heat produced were reused as building materials and heat sources. These results supported that the oil from pyrolyzed sewage sludge has enough economical value to use as fuels.

2.5 Recent Studies of Sewage Sludge Pyrolysis

Recent studies have concentrated on the characterization of pyrolysis products such as oil, char, and non-condensable gas (NCG) under different pyrolysis conditions such as temperature, heating rate and acid pretreatments [Caballero et al., 1997; Inguanzo et al, 2002]. The

preparation of activated carbon from pyrolysis of sewage sludge as an adsorbent for pollutant removal was another subject of recent studies [Lu et al., 1995].

2.5.1 Characterization of Pyrolysis Products

Caballero et al. (1997) characterized the products formed by primary and secondary pyrolysis of three sewage sludges that had different elemental compositions. This investigation was carried out with an apparatus that treated 1 to 2 mg of an untreated sludge sample using a heating rate of 10 to 200 °C/sec (Figure 2.4). The primary pyrolysis achieved sludge decomposition at 700°C. The gases from the primary pyrolyzer were processed in a secondary reactor that operated at temperature between 290 and 650°C.

They verified the possibility of using pyrolysis as an alternative to incineration and controlling the products of pyrolysis such as char that can be deposited in landfills and gases formed by total cracking of the light oils and tars. They found that the maximum yield of gases was obtained at 700°C with a 30 seconds residence time in the primary reactor. The gaseous products were methane, ethylene, ethane, propylene, propane, methanol, acetic acid, acetaldehyde, C₄-hydrocarbons, CO, CO₂, and water.

Inguanzo et al. (2002) found that pyrolysis conditions, such as heating rate and final pyrolysis temperature, influenced the characteristics of the resulting gases, oil, and solid residues. Their experiment was performed with 20 grams of the 1 to 3 mm particle size fraction and with helium flow rate of 100 mL/min to provide an inert environment. The pyrolysis temperatures were 550, 650 and 850°C and the heating rates ranged from 5 to 60 °C/min. This study reported that increased pyrolysis temperatures decreased the char yield and that the oil remained almost constant while the gas yields were increased. Furthermore, the heating rate was important at low pyrolysis temperatures.

2.5.2 Preparation of Activated Carbon from Pyrolyzed Sewage Sludge

Another current topic of study is the use of chars from pyrolysis as adsorbent for adsorption. The benefits of this technology include a reduction in the volume of the sewage sludge and the production of a cheaper adsorbent than commercial activated carbon.

2.5.2.1 Surface Area Development during Pyrolysis

Lu et al. (1995; 1996) reported on surface area and pore structure development of chars during pyrolysis of sewage sludge. This experiment used anaerobically digested sludge after digestion. The pyrolysis temperatures were 400 to 850°C with a nitrogen gas flow rate of 200 cm³/min and a SRT of 0.5 to 3 hours in an isothermal reactor that was heated by a vertical furnace. The specific surface area of the dried

Figure 2.4: Experimental Apparatus of Caballero et al (1997)

sludge, as determined by the nitrogen adsorption method, was $4.74 \text{ m}^2/\text{g}$. The surface area and pore structure characterization was performed with an accelerated surface area and porosimetry system (ASAP 2000, Micromeritics). It is a fully automatic and computerized system which performed the adsorption (N_2 at -196°C) and collected and processed the data simultaneously. Surface area was based on the Brunauer, Emmett, Teller (BET) equation using the nitrogen adsorption method. Micro-pore surface area was evaluated using the Halsey theory of adsorption film by the t-plot method [Sontheimer et al., 1988].

Lu reported that weight loss of the sludge sample was dependent on temperature and independent of SRT. Increased temperature resulted in increased weight loss and a reduction in the yield of char because of increased volatilization. The pore structure of char as adsorbent was created due to removal of volatile matter.

The results of an evaluation of surface area using the BET model (S_{BET}) for different temperatures and batch SRT are shown in Figure 2.5. Temperature was a major factor in developing the surface area. The higher pyrolysis temperature (750 and 850°C) developed BET surface area approximately 30 to $60 \text{ m}^2/\text{g}$ than lower temperature with SRT 0.5 to 5 hours.

Figure 2.5: BET Surface Area vs Time at Various Temperatures (Lu et al., 1995)

Lu and Lau. (1996) found that the surface area of adsorbent produced from pyrolyzed sludge increased with acid treatment. The micro-pore area and BET surface area increased 80 and 150 m²/g-adsorbent respectively, with 3M of H₂SO₄ as compared to the adsorbent treated with 1M H₂SO₄ as 60 and 120 m²/g-adsorbent respectively. In their experiments, the properties of dried sludge were 52 weight percent VS and the pyrolysis operating conditions were 200 cm³/min of nitrogen with 3 hours SRT at 650°C.

2.5.2.2 Optimizing the Preparation of Activated Carbon

The optimization of processes for preparation of adsorbents derived from pyrolyzed sewage sludge has been investigated by Lu et al. (1995; 1996) and Tay et al. (2001). However, the adsorbents generated from sewage sludge had limitations in practical usage because of unsatisfactory adsorptive properties and performances [Lu and Lau, 1996].

To overcome the economical drawbacks, Tay et al. (2001) considered the impact of activating agent, heating temperature, dwell time and heating rate on the preparation of activated carbon from digested sewage sludge. The digested sample, with a total solids content of 20.5 percent, was dried at 103°C for 24 to 36 hour and had a uniform size (0.5 to 2 mm). The dried digested sludge was pretreated in a bath of 5M ZnCl solution for 24 hours. After drying, it was pyrolyzed at a heating rate of 15 °C/min to a final temperature of 500°C that was maintained for 2 hours. The nitrogen gas flow to maintain an oxygen free circumstance was 400 cm³/min. The pyrolyzed product was then post-treated with 3M HCl and rinsed with deionized water.

Tay et al. (2001) found that the activating agent (ZnCl_2) improved the absorption capacity and that the heating temperature also affected adsorption capacity especially for phenol. Undigested sewage sludge possessed higher adsorptive properties than that of anaerobically digested sludge.

Chen et al. (2002) reported adsorption results based on the optimized process of Tay et al. (2001) (Table 2.3). The data were found to be well fit (correlation coefficient, $r^2 > 0.96$) by Langmuir and Freundlich isotherms. For adsorption of phenol, the adsorbent from pyrolyzed sludge had Langmuir maximum adsorption capacity ($q_{\max}$) and Freundlich constants (K_f) of approximately 1/3 and 1/5 of commercial activated carbon (BESTCHEM) respectively. This identified the possibility of practical usage of sludge-derived adsorbents.

Table 2.3: Langmuir and Freundlich Isotherm Constants
for Phenol Adsorption (Chen et al., 2002)

Adsorbate	Activated Carbon	Langmuir		Freundlich	
		$q_{\max}$ (mg/g)	r^2	K_f (mg/g)	r^2
Phenol	Sludge derived	46.95	0.97	2.69	0.96
	BESTCHEM	142.86	0.98	15.65	0.96

$q_{\max}$: maximum adsorption capacity derived from Langmuir isotherm

K_f : Freundlich isotherm constant r^2 : correlation coefficient

2.6 Summary

All the literature suggests that sewage sludge production will increase continuously as the population and consumption grows. Also, conventional disposal processes such as land application, land filling and incineration have decreased. However, thermal sludge disposal processes are growing practices.

In the past two decades, thermal disposal of sewage sludge has been researched in order to develop practical and economically beneficial processes such as pyrolysis, microwave pyrolysis, wet air and supercritical water oxidation. These technologies have just been introduced to the market. More research is required to further develop thermal treatment processes.

The products of sludge pyrolysis are oils (organic liquids and tar), gases, char and reaction water. The char can be prepared as adsorbents. Temperature is the most important factor not only for yields of oil and char but also for the surface development of char for use as an adsorbent.

Chapter 3

Experimental Plan and Methods

Samples of primary, thickened waste activated (TWAS) and digested sludges were collected from the city of Ottawa wastewater treatment plant to analyze the potential economic benefit of the recovery of oil and char from the pyrolysis. The collected sludges were dewatered and dried and then were either mixed with a catalyst or pretreated with acids or a base. The individual sludges were then pyrolyzed and the products of pyrolysis such as oils and chars were analyzed. The chars from pyrolysis were prepared subsequently as an adsorbent for phenol adsorption. Finally, the dried sludges, oils, chars and adsorbents were characterized with respect to volatile fraction, elemental composition and calorific values. An overview diagram for this research is presented in Figure 3.1.

3.1 Experimental Apparatus

A laboratory-scale cylindrical batch pyrolysis reactor was designed. It was made of four parts; gas inlet, reactor, outlet, and temperature controller as shown in Figure 3.2.

The role of the gas feed was to provide a constant supply of nitrogen gas to the reactor. Nitrogen gas was selected to maintain oxygen-free conditions because of its lower cost as compared to helium. The pressure

Figure 3.1: Diagram of Research Overview

1.Nitrogen gas cylinder 2.Flow meter 3.Preheating coil 4.Chamber 5.Reactor 6.Heating tape 7.Thermocouple
8.Temperature controller 9.separator 10.Vial 11.Condensing coil 12.Connector 13. Lid

Figure 3.2: Pyrolysis Apparatus

From the gas cylinder was fixed at 10 psig with the regulator and the gas pressure was controlled by a ball flow meter to maintain 50 mL/min. This gas flow was measured at the end of the condensing coil (vented part) using a bubble flow meter.

The gas that was initially at room temperature was preheated through swagelok stainless steel (SS) tube (0.3 cm of OD and 1.5 m of length) using the latent heat in the chamber. The preheating of the nitrogen gas minimized the temperature drop when the gas stream entered in the reactor. The body of the apparatus consisted of a horizontal stainless steel reactor that was 160 mm long, 40 mm in diameter. The insulated chamber minimized temperature fluctuations. The reactor was mounted on a 5° slope inside the chamber for easy oil flow into the separator. The chamber was employed to minimize the temperature fluctuation of reactor.

The reactor was wrapped with heating tape that was regulated by a temperature controller. A thermocouple was located 1 to 2 cm above the dried sludge to reduce the temperature variability between the detector and sample.

An Omega CN77000 temperature controller with a type K thermocouple (0.16 cm of OD and 30 cm of length) was employed to detect and

regulate the operating temperatures between 250 and 500°C. The thermocouple and reactor was sealed using Swagelok connectors. The temperature was maintained using Amptek heating tape (2.5 cm wide, 60 cm long and 312 Watt) that was wrapped around the reactor. There was a general temperature variation on the order of $\pm 10^{\circ}\text{C}$ associated with the on/off mode controller. Therefore, target temperatures were determined as the average value measured every minute over the solid residence time (SRT). This SRT was measured from the time that the temperature controller indicated the target temperature. The pyrolysis temperature variability observed with a target temperature of 350 °C is presented in Figure 3.3. The heating rate varied from 21 to 27 °C/min over all the operating conditions.

The oil and gases formed as products from sewage sludge pyrolysis and nitrogen gas from the reactor were transferred to a separator through the connecting tube (50 mm in length and 0.64 mm in OD). The separator (0.3 cm OD of SS swagelok Tee tube connector) split the oil and gas flows. A glass vial (2.5 ml of volume) was placed at the bottom of separator, connected vinyl tube and sealed. The condensing tube (0.3 OD of SS swagelok tube and 1.5 m in length) coil located at the top of the separator allowed the condensable gases to drip back down to the oil collector at ambient temperatures.

Figure 3.3: Temperature Variability and Average Temperature at 350°C

3.2. Experimental

A brief summary of the experimental plan is illustrated in Figure 3.4. The experimental procedure for this work includes four stages: sample preparation, catalyst and pretreatment, pyrolysis, and preparation of adsorbent from char.

3.2.1 Sample Preparation

Three types of sewage sludges were collected from the ROPEC wastewater treatment plant in Ottawa, Canada. Primary sludge was collected from the primary settling tank. TWAS was collected after centrifugal thickening of the waste activated sludge. Digested sludge was collected as cake after digestion and mechanical dewatering.

Primary sludge and TWAS were dewatered in the laboratory using a centrifuge programmed 6000 revolution per minute (rpm) for 10 minutes. Each sewage sludge sample was dried for 24 hours at 105°C in an air convection laboratory oven. After removing the supernatant liquid and drying, each sample was stored in an airtight container. The primary sludge was generally reduced to a size from half to one centimeter because the sludge was agglomerated during the treatments. However, TWAS and digested sludge was stored without size reduction.

3.2.2 Catalyst and Pretreatment of Dried Sludge Samples

Catalyst and pretreatment of dried sludge samples were selected to evaluate the possibility of improving oil and char recovery. This research

Figure 3.4: Diagram of Experimental Plan

evaluated the use of zeolite as a catalyst and acids and a base for pretreatment.

3.2.2.1 Sludge Samples with Catalyst

The zeolite (SiO_2) without alumina produced by Acros was blended with 5 grams of dried sludge in a laboratory bowl. Mixing ratios of 0.15, 0.2, 1 and 1.5 g-zeolite/g-ds were evaluated to find the optimum amount of catalyst for the dried sludge. Samples were stored in a labeled airtight container.

3.2.2.2 Acids and Base Pretreatment

The agents employed for pretreatment of dried sludges were 3M HCl, 98 percent and 0.1M acetic acid and 3M NaOH. To determine the effect of acid concentration on VS fraction and mass reduction, different concentrations of the same agent (98 percent and 0.1 M acetic acid, pH 1.0 and pH 3.5 respectively) and similar pH solutions of different agents (3M HCl of pH 0.8 and 98 percent acetic acid of pH 1.0) were used. The strong base (3M NaOH of pH 13.5) was employed to compare the difference between acid and base pretreatment.

Two pairs of precisely weighed dried sludge samples (50 grams each) were put in labeled 500 mL flasks and the agents (100 mL) were added to each flask. The flasks were placed on an orbital shaker for 20 minutes at 150 rpm. After shaking, the sludges were washed several times in

deionized water and dried at 105°C for 24 hours in an air convection oven. The mass of each sludge sample was measured to determine the mass reduction associated with the pretreatment.

3.3 Pyrolysis of Dried Sewage Sludge

In this study, 5 grams of dried sewage sludge was used for each run even though the pretreated sludges had lost mass during treatment. Therefore, the oil and char yields of the pretreated sludge samples required additional consideration in the analysis.

3.3.1 Pyrolysis Conditions

After sample preparation, 5 grams of dried sample was placed in the reactor and it was tightly sealed using lid at both end. The nitrogen gas flow rate to maintain oxygen free conditions was 50 mL/min. The solids residence time (SRT) at the target temperature was fixed at 20 minutes for all runs of the experiment.

3.3.2 Collection of Products

Oil and reaction water derived during the pyrolysis was collected in weighed and labeled 2.5 mL vials that were located on the bottom of the separator and were connected with a flexible vinyl tube. After collecting the oil, the vial was placed in a weighed 25 mL glass test tube. The oil residual (mainly tar) was washed with acetone from the stainless steel tube between the separator and condenser and collected. The acetone

solution was placed in a 50°C water-bath for 24 hours to evaporate the acetone, and the retrieved oil mass was then measured. The residual char in the reactor was collected and weighed after cooling and stored in airtight containers.

The reaction water that was mixed in the collected oil was difficult to separate mechanically in a separatory funnel as the amount of oil was insufficient to apply this method. Therefore, the fraction of reaction water of each sludge sample was calculated in preliminary experiments. The oil was collected from 20 grams of sludge sample to reduce measurement error. The individual sludges without pretreatment were pyrolyzed at operating temperatures of 250 to 500°C. The collected oil was evaporated in a 50°C water bath for 24 hours.

3.4 Adsorbents from Chars by Pyrolysis

TWAS and digested sludge chars that were generated with and without pretreatment solutions were used for preparation as an adsorbent.

3.4.1 Preparation of Adsorbents

The chars from primary sludge were not used because of their soft nature. Most of these chars dissolved during acid treatment. Furthermore, the chars from TWAS and digested sludges that were pyrolyzed at less than 400°C were not selected for the same reason. These chars floated on the water surface during rinsing and as adsorbents in the phenol solutions.

Therefore, the TWAS and digested sludge char samples pyrolyzed at over 400°C were considered as adsorbents.

The use of strong acid (3M HCl) for cleaning the produced chars has been reported in other studies [Tay et al. 2001]. The char from TWAS and digested sludge was mixed with the acid solution. In general, 15 to 20 mL of acid was required to soak 10 grams of char. The acid treated char was crushed and sieved to a uniform size of 0.5 to 2 millimeter to make it similar to commercial activated carbon from Fisher Scientific. Then, the ground sample was rinsed again to remove fine particles that affected subsequent UV readings. After drying, the final product was weighed to determine the mass removal between char to adsorbent.

3.4.2 Measurement of Phenol Adsorption of the Adsorbents

To measure the phenol adsorption capacity of the adsorbents from pyrolysis, five phenol solutions were prepared with concentrations of 0, 50, 100, 250, and 500 mg/L. The blank (0 mg/L) that contained deionized water was used as a baseline for the UV reading. Each adsorbent was precisely weighed at 0.25 g and put in five different flasks (125 mL). The flasks were filled to 50 mL with the prepared phenol solutions. The flasks were then sealed with parafilm to avoid evaporation and placed on an orbital shaker at 150 rpm for 8 hours. The equilibrium time was determined in preliminary tests. Ten samples were analyzed to measure the phenol adsorption of an adsorbent at a specific pyrolysis temperature

or pretreatment. For example, two different adsorbents were prepared from the pyrolysis of TWAS at 400°C to duplicate the experiment. Each adsorbent was then tested at five different concentrations.

To determine the phenol adsorbed on the adsorbent, the concentration of the equilibrium phenol solution was determined using UV adsorption (CARY13, Varian) at 270 nm. The wavelength was selected on the basis of the work of Annadurai et al. (2003). The zero point of UV reading was determined with pure deionized water. The UV value of each sample was measured with consideration for the blank in the group. For example, if a UV reading of a sample of 50 mg/L was 0.1 and the reading of a blank was 0.01, the UV reading was considered as 0.09.

3.5 Analysis Methods

The volatile solid fraction, elemental composition and calorific values of the dried sludge samples and products from pyrolysis were determined.

3.5.1 Volatile Solids Fraction

The volatile solids and fixed solids (ash) fraction of dried feed samples and chars were measured as per Standard Methods (APHA-AWWA-WEF, 1998).

3.5.2 Elemental Analysis

The elemental compositions of all sludge samples, oil and chars were

measured by an external laboratory at the University of Ottawa. The content of carbon, hydrogen, nitrogen and sulfur (C, H, N and S) were measured directly, while oxygen content was measured by difference.

In this procedure, the samples were weighed in tin capsules. The capsules were loaded with standard chemical (sulfanilic acid) into a Vario EL III elemental analyzer (Elementar Americas, Inc). Samples were flash combusted at about 1,800°C and carried by helium through columns of reducing/oxidizing chemicals to produce N₂, CO₂, H₂O and SO₂. The gases were separated with specific adsorption columns so that the thermal conductivity detector (TCD) could detect each gas separately. The routine analytical precision was ± 0.1 percent. The data was corrected using a calibrated standard. Calculations were done based on the weight and area under the curve of the peak detected by the TCD.

3.5.3 Calorific Values

A Parr Oxygen Bomb Calorimeter (1300 series) was employed to measure the calorific values of the three types of dried sludge samples, oils, and chars. Prior to the test the samples were mixed with diesel fuel because they did not completely combust in the reactor. The measured enthalpy of the diesel fuel was 42.5 ± 2 kJ/g. The procedure and calculation followed the standard method provided in the manual from the manufacturer.

Chapter 4

Results and Discussion

This research aimed to identify the optimum conditions for the recovery of oil and chars from sewage sludge pyrolysis and to analyze the potential economic benefit of their recovery. Final temperature was considered as a variable hence other parameters were fixed such as heating rate, sample size and SRT. Three different sewage sludges were considered to examine these objectives. Primary, TWAS and digested sludge were collected and the products were analyzed.

4.1 Preliminary Experiment Results

From the literature review, the water content of the dewatered sludge samples, volatile solids fraction of dried sludge samples and chars, as well as the reaction water in oil, were considered to affect the analysis of pyrolysis products. In other literature, nitrogen flow rate and SRT were reported as variables that may affect the oil yield. The temperature range for this project was between 250 and 500°C and was based on the literature review that revealed most oil from sewage sludge was derived under 500°C [Campbell and Bridle, 1986; 1989].

For this research, primary sludge and TWAS were collected as liquid and then dewatered using laboratory equipment while digested sludge was

collected as cake after mechanical dewatering at the wastewater plant. As such, each sludge contained different water fractions after dewatering. The differences in water content affected the economic value analysis of sludge samples due to the differing energy consumption in the drying process.

Table 4.1 presents preliminary results that were obtained in this study. The laboratory-centrifuged primary sludge and TWAS had water content of 75 and 91 percent respectively. The water content of TWAS was higher than primary sludge after the same dewatering process due to the different characteristics of individual sludge. Mechanically dewatered treated digested sludge contained 70 percent of water. Therefore, the difference of water content depended on the dewatering mechanism, and individual characteristics of sludges.

Table 4.1: Preliminary Experiment Results

Sludge Type Preliminary Result	Primary	TWAS	Digested
Water Content, %	75	91	70
Reaction Water, wt% (g-water/g-ds)	1-5	1-4	1-3
VS Fraction, wt.%			
Dried Sludge	84	69	59
Char			
300°C	66	56	47
400°C	55	41	35
500°C	54	39	27

The VS fraction of dried sludge was found to be one of the most important factors affecting the oil yield in pyrolysis processes [Bridle, 1982]. Therefore, the measured VS fractions were fundamental data to analyze the relationship pyrolysis products and dried sludge. The VS fractions of primary, TWAS and digested sludges were 84, 69 and 59 weight percent respectively based on the total solids (TS). In general, the VS in primary sludge would be reduced with biological treatment and the digestion process [Metcalf & Eddy, 2002]. Therefore, primary sludge had the highest VS content, while digested sludge after stabilizing contained the least. The VS fraction of char from pyrolyzed primary, TWAS and digested sludge varied between 54 and 66, 39 and 56, and 27 and 47 weight percent respectively at temperatures between 300 and 500°C. Individual chars showed the same trend with yields decreasing with increasing temperature. This result indicated a relationship between pyrolysis temperature and the VS in char as mentioned in the literature review. This hypothesis was proven in the following sections.

The reaction water of primary, TWAS and digested sludge, outlined in Table 4.1, ranged from 1 to 5, 1 to 4 and 1 to 3 weight percent basis of the entering mass of dried sludge. The reaction water produced during pyrolysis affected the oil yield, calorific value of the oil, and oxygen content in elemental analysis. Therefore, determination of this value was important to reduce the error in analyzing the pyrolysis products.

Nitrogen flow rates of 25, 50 and 100 mL/min were employed to evaluate the relationship between flow rates and oil yields that was reported by Inguanzo et al. (2002). The oil yield from primary sludge at 500°C at 25, 50 and 100 mL/min did not differ significantly and was found to be 46.5 ± 1.5 weight percent, based on the oil before separating reaction water and TS. Hence in subsequent experiments, the flow rate was fixed at 50 mL/min because the lowest flow rate (25 mL/min) was difficult to sustain at a stable value. The higher flow rate resulted in slightly increased variability in the operating temperatures and was thus not employed.

The oil yields from dried primary sludge as a function of SRT in the pyrolysis chamber are presented in Figure 4.1. The standard deviations (STD) of the data at lower temperatures (250 and 300°C) were higher due to the unsteady production of oil caused by the small oil yields. At lower operation temperatures (250 and 300°C) the most of the oil was derived after 10 to 20 minutes of pyrolysis. However, most oil was derived in the first 10 minutes of pyrolysis at higher temperatures (400 and 500°C). Therefore, based on this information, the SRT was fixed at 20 minutes for all subsequent experiments.

In conclusion, the preliminary experiments determined fundamental data that was employed to determine the operating conditions in the subsequent experiments. Water content was found to depend on the

Figure 4.1: Fractional Oil Yield as a Function of Pyrolysis Time and Temperature

dewatering mechanism, and individual characteristics of sludge. The VS fraction of dried sludge and char depended on the sludge types and pyrolysis temperatures. The reaction water in oil ranged from 1 to 5 weight percent. The nitrogen flow rate did not affect oil yields and was fixed at 50 mL/min. Oil yields were function of SRT as well as pyrolysis temperature and was fixed at 20 minutes for all experiments.

4.2 Outline

Sludge samples and products were evaluated with respect to pyrolysis temperature, calorific value, elemental analysis, carbon mass balance and the effect of additives in order to accomplish the research aims of identifying optimum pyrolysis conditions and potential economic benefit.

All the subsequent data is expressed as the average value from replicate pyrolysis tests and analytical measurements. The mass of dried sludge and total solids were considered as having the same value because all dried sludges contained less than 0.5 percent water after drying; hence it was applied for measuring calorific values and mass fraction of elements.

In general, the 95 percent of confidence intervals (C.I.) of the oil and char yields were estimated to be within ± 2.5 percent of the mean values and for most of data, accurate to within ± 1.5 percent. The 95 percent C.I. of the calorific values were estimated to be within ± 10 percent of the mean values. In the elemental analysis, 95 percent C.I. of oil was

estimated to be within ± 1 percent, while the char and dried sludge values were within ± 5 percent, although most of the given data were accurate to within ± 2 percent. Reproducibility of all pyrolysis and analysis test was good with the replicate run usually within 3 percent error limit.

4.2.1 Effect of Temperature on Oil and Char Yields

The yields of oil (Y_{oil}) and char (Y_{char}) based on TS were calculated using Equations 4.1 and 4.2. The oil yields based on VS were determined by dividing the values from Equation 4.1 by the volatile fraction of the sludge. The effects of temperature on the oil and char yields are illustrated in Figures 4.2 and 4.3, respectively. The detailed data for the plots is included in Appendix A.

$$Y_{oil} = \frac{M_{oil+rw} - M_{rw}}{M_{ds}} \times 100 \quad (4.1)$$

$$Y_{char} = \frac{M_{char}}{M_{ds}} \times 100 \quad (4.2)$$

Where,

M_{ds} : mass of dried sewage sludge, g

M_{oil+rw} : mass of oil with reaction water, g

M_{rw} : mass of reaction water in oil, g

M_{char} : mass of char in dried sludge, g

Figure 4.2: Effect of Temperature on Oil Yield for Three Sludge Types

The data for oil yield in Figure 4.2 have been plotted on the basis of both TS and VS. The oil yields based on the TS of primary, TWAS and digested sludge ranged between 8 and 42, 12 and 33 and 4 and 26 weight percent, respectively. Primary sludge derived 10 to 20 weight percent more oil yield than the other sludge types at pyrolysis temperature from 300 and 500°C. The primary sludge had a higher volatile solids content than the other sludges studied. As the oil would be generated from the volatile solid (Bridle, 1982) it would be expected that higher yields on the basis of TS would be generated. Hence, the plotted data, based on TS, was normalized on a VS basis.

The oil yields of primary, TWAS and digested sludge based on VS ranged between 9 and 50, 18 and 48 and 7 and 44 weight percent respectively over the range of pyrolysis temperatures (Figure 4.2). The yields from digested sludge were slightly lower than the other sludges. Work by Campbell and Bridle (1989), presented in the literature review (Figure 2.2), identified the same trend. They reported that the VS in primary sludge and TWAS contained more of the components which were converted to oil than in digested sludge. This implies that the VS destroyed during sludge digestion process contains high fractions of the oil precursors.

Based on both TS and VS, primary sludge yielded the most oil with TWAS and digested sludge placing second and third respectively for all

temperatures except 250°C. The oil yields of primary and digested sludge continuously increased with increasing temperature over the range evaluated. However, TWAS attained a maximum yield at around 450°C. This result for TWAS indicated an optimum temperature for oil yield. The best operation temperature for the other sludge types appeared to be above 500°C.

In conclusion, it was found that oil yields varied between sludges. However, the effect of temperature on oil yield was similar for all sludge types. The oil yield in all sludge types steeply increased between 250 and 400°C with a shallow increase or a maximum point for temperatures over 400°C. The reduced oil yields from digested sludge suggest that the VS destroyed during the sludge digestion process contained high fractions of oil precursors.

In Figure 4.3, the char yield was plotted on the basis of TS because a portion of fixed solids (FS) will ultimately end up as char. Figure 4.3 shows that the effect of temperature on char yield was very different from that of oil yield as the char yield decreased with increasing temperature as less material was left after pyrolysis of the VS. The char yield from primary, TWAS, and digested sludges ranged between 33 and 85, 43 and 77 and 53 and 87 weight percent respectively. The char of primary sludge steeply decreased as compared to the other sludges over

Figure 4.3: Effect of Temperature on Char Yield for Three Sludge Types

the temperature range from 250 to 350°C due to the sharply increased VS decomposition converted to oil remaining less material to end up as char. Digested sludge produced higher char yields than the other sludges over all temperatures as the digested sludge contained more FS and less VS than the other sludges.

4.2.2 Calorific Values of Sludge, Oils and Chars

Calorific value is one of the most important factors in estimating the economic value of oils. The measured calorific values of dried samples, oils, and chars that were generated at two different temperatures are outlined in Table 4.2. The detailed data and calculation procedures are included in Appendix B.

Table 4.2: Calorific Values

	Primary	TWAS	Digested
Dried Sludge (MJ/kg-TS)	22.9±0.6 (27±0.8)	19.4±0.5 (28±0.8)	17.4±0.7 (30±1.2)
Oil (MJ/kg-oil)			
300°C	35.9±1.8	37.1±1.2	38.5±3.6
500°C	37.6±1.1	37.6±1.1	37.7±1.4
Char (MJ/kg-TS-char)			
300°C	21.0±0.8 (32±1.2)	19.6±1.3 (35 ±2.3)	15.8±0.8 (34±1.7)
500°C	17.0±1.0 (32±1.8)	12.5±0.3 (32±0.8)	9.7±1.1 (36±4.0)

*(): Calorific value based on VS, MJ/kg-VS-char

In Table 4.2, the calorific values based on TS of primary, TWAS and digested sludge were 22.9, 19.4 and 17.4 MJ/kg-TS respectively.

However, on the basis of VS the calorific values were 27, 28 and 30 MJ/kg-VS respectively. These results indicate that the calorific value of dried sludge correlated well with VS and did not present significant difference between sludge types when expressed on the basis of VS content.

The calorific values of the chars based on TS at 300°C were similar to dried sludge and ranged between 15.8 and 21.0 MJ/kg-TS-char, while the results at 500°C reported significantly lower values ranging from 9.7 to 17.0 MJ/kg-TS-char. However, the calorific values of all chars based on VS did not present significant differences ranging from 32 to 36±4.0 MJ/kg-VS-char. These results illustrated that only the VS in char affected the calorific value. Therefore, the higher calorific value of char on the basis of TS with lower temperatures was due to less VS (associated calorific value) remaining as char at higher temperatures. The pyrolysis process did however appear to modify the calorific value of the VS in the char when compared to the original raw sludge. At 500°C the calorific value of the char-VS was approximately 20 percent higher than the raw sludge values. Hence, it would appear that pyrolysis selectively removed organics in lower calorific value.

The calorific values of the produced oil (Table 4.2) did not appear to differ between the pyrolysis temperatures and sludge types with the value ranging from 35.9 to 38.5 MJ/kg-oil.

An energy balance that considered dried sludges and pyrolysis products was calculated using Equation 4.3 and the results are presented in Table 4.3. The calculation was based on the energy per unit mass of dried sludge and the energy that was present in the oil and in the char. The energy loss (E_{loss}) values quantify the energy of the dried sludge that was not transferred to the oil and char and includes energy associated with the gas phase which was not measured.

$$E_{loss} = M_{ds}E_{ds} - (M_{oil}E_{oil} + M_{char}E_{char}) \quad (4.3)$$

where

M_{ds} : mass of dried sewage sludge, g

E_{ds} : calorific value of dried sludge, kJ/g-ds

M_{oil} : mass of oil yielded from M_{ds} , g

E_{oil} : calorific value of oil, kJ/g-oil

M_{char} : mass of char yielded from M_{ds} , g

E_{char} : calorific value of char, kJ/g-char

From Table 4.3, it can be seen that in general, the energy loss during pyrolysis of dried sludges was 3 to 10 percent with the exception of TWAS at 300°C. This negative value (energy generation) was attributed to experimental errors in measuring the oil and char yields as well as calorific values. The most energy loss observed was with digested sludge at 500°C with a value of 2.3 MJ/kg-ds. For all cases, the energy loss increased with increasing pyrolysis temperature. It is believed that the energy was lost with produced gases during pyrolysis. However, energy

of the vented gases (non-condensable gases, NCG) is difficult to measure and they were not considered as major products in this work. Campbell and Bridle (1989) reported the yield and calorific value of NCG of digested sludge was 4 to 12 weight percent and the NCG included 4 to 6 MJ/kg-TS at 450°C in a bench-scale continuous system. They found the NCG yields were primarily a function of operating temperature. Caballero et al. (1997) reported the NCG was composed mainly of methane, ethane, CO and CO₂.

Table 4.3: Energy Balance

Temp. °C	Yield			Calorific Value			Energy loss MJ/kg-ds	Fraction of energy lost
	Oil wt. %	Char wt. %	Total yield wt. %	Dried Sludge MJ/kg-ds	Oil MJ /kg-oil	Char MJ /kg-TS-char		
Primary								
300	26.0±1.3	59.9±1.6	85.9	22.8±0.6	35.9±1.8	21.0±0.8	0.9±0.16	4.1±0.7
500	41.8±1.0	32.6±0.2	74.4	23±0.6	37.6±1.1	16.9±0.6	1.6±0.5	6.9±2.1
TWAS								
300	17.6±0.1	66.5±1.3	84.1	19.4±0.5	37.1±1.2	19.6±1.3	-0.16	-0.8
500	32.4±0.1	42.7±0.3	75.1	19.4±0.5	37.6±1.1	12.5±0.3	1.9±0.7	9.9±3.5
Digested								
300	13.8±0.8	74.9±1.5	89.8	17.4±0.7	38.5±3.6	15.8±0.8	0.5±0.1	2.8±0.8
500	26.1±0.4	52.5±0.7	80.1	17.4±0.7	37.7±1.4	9.7±1.1	2.3±0.17	13.1±1.0

In this work, it is possible to predict the NCG production from the difference between the actual and theoretical total yields. The theoretical total yield as summation of oil and char yield should have been 100 percent while the actual total yield did not reach the theoretical yield as

presented in Table 4.3. This work assumed the difference to be the yield of NCG and ranged from 10 to 25 percent, depending on sludge types and temperatures. The NCG yield was increased with temperature in all sludge types.

4.2.3 Elemental Analysis

Table 4.4 outlines the elemental analysis of the dried sludges and the pyrolysis products. The elemental concentrations of the dried sludges and chars were based on the mass of TS, while the oil values were based on the mass of bio-oil. The mass fraction of the individual elements was determined by combustion of the samples as outlined in section 3.5.2. Dried sludge and char contained ash. This ash concentration, shown in Table 4.4, was not produced by the analyzer but was the measured value of FS from VS/FS analysis. Therefore, the oxygen and ash (fixed solid) concentration were less reliable due to the measurement errors associated with the temperature difference between the analyzer (1800°C) and standard method for VS/FS analysis (550°C). The results of elemental analysis for all the samples and products are presented in Appendix C.

4.2.3.1 Elemental Analysis of Oil

The results of the elemental analysis of the oil samples are presented in Table 4.4. It can be seen that the carbon content of the oils ranged between 63 and 74 percent overall sludge types and operating temperatures. Oxygen, nitrogen, hydrogen, and sulfur concentrations

Table 4.4: Results of Elemental Analysis

Element Sludge type	Mass fraction (%)					
	N	C	H	S	O	Ash
Primary						
Dried Sludge	2.7±0.78	44.1±3.6	6.1±0.48	0.4±0.12	30.4±4.7	16.3±0.004
Oil						
300°C	2.7± 0.2	65±0.1	9.6±0.4	0.5±0.004	22±0.1	
500°C	3.9±0.01	72±0.02	9.6±0.08	0.3±0.04	14.2±0.16	
Char						
300°C	3.4±0.05	42.6±0.3	4.0±0.15	0.7±0.21	15.6±0.01	33.7±0.32
500°C	3.8±0.06	42.6±1.8	2.1±0.12	0.2±0.04	5.7±2.0	45.6±2.08
TWAS						
Dried Sludge	6.8±0.38	36.7±0.26	5.4±0.29	0.5±0.02	19.6±0.6	31±0.53
Oil						
300°C	6.8±0.14	62.8±1.0	9.7±0.1	0.5±0.03	20.2±0.9	
500°C	8.5±0.03	64.6±0.4	9.4±0.05	0.4±0.01	17.1±0.4	
Char						
300°C	6.6±0.78	37.7±4.1	4.2±0.56	0.4±0.06	6.9±5.4	44.2±1.38
500°C	5.3±0.2	27.3±0.93	1.9±0.23	0.6±0.21	4.1±1.15	60.8±0.74
Digested						
Dried Sludge	4.8±0.06	31.1±0.2	4.6±0.24	0.7±0.01	17.9±0.25	40.9±0.08
Oil						
300°C	5.6±0.11	69.4±0.7	9.7±0.07	0.6±0.05	14.7±0.05	
500°C	6.3±0.02	74.4±0.68	9.9±0.07	1.0±0.25	8.4±0.68	
Char						
300°C	4.8±0.01	32.7±0.06	3.8±0.04	0.7±0.06	5.5±0.09	52.5±0.1
500°C	3.4±0.31	21.3±0.11	1.3±0.07	0.5±0.04	0.8±0.3	72.7±1.6

were found to be between 9.5 and 9.9, 8 and 22, 2.7 and 8.5 and less than one percent, respectively. Oxygen composition was determined by difference since the elemental analyzer only measured the concentration of C, H, N and S. Hence there is likely more error associated with the values of this element.

From Table 4.4, it can be seen that for primary sludge, the carbon content of the oils from pyrolysis temperatures of 300 and 500°C increased 65 ± 0.1 percent to 72 ± 0.02 percent respectively, while the value of dried sludge was 44.1 ± 3.6 percent. Therefore, the carbon content of the oil products increased 21 to 28 percent through the pyrolysis process as compared to those of dried sludge.

The content of hydrogen in the oil increased by approximately 3.5 percent, while the oxygen content decreased from 8 to 16 percent when compared to the dried sludge. The other elements (nitrogen and sulfur) showed small differences of less than one percent.

The calorific value of the oil from primary sludge varied from 35.9 to 38.5 MJ/kg-oil for 300 and 500°C and the dried sludge value was 27 MJ/kg-VS. Hence, the calorific value of oil increased by 9 to 11.5 MJ as compared to the sludge. This result supported the common knowledge that the calorific value of the oil was a function of the elemental composition with respect to carbon and hydrogen content.

4.2.3.2 Elemental Analysis of Char

From Table 4.4, it can be seen that the elemental composition of individual chars varied between the different pyrolysis temperatures (300 and 500°C). An increase in the ash content of 12 to 20 percent was observed with increasing temperature for all the chars due to the decreased VS. In addition, decreased carbon, hydrogen and oxygen content were observed with increasing temperature for all sludge types. The carbon content of the chars from TWAS and digested sludge decreased approximately 10 percent with increasing temperature. The hydrogen and oxygen content of all the chars decreased by about 2 to 10 percent with increasing temperature. The only exception to this pattern was the carbon content of primary sludge at 500°C, which had the same content as that observed at 300°C (42.6 percent). The concentrations of N and S did not exhibit temperature dependence. Hence, the elemental composition (C, H and O) in char was function of pyrolysis temperature. The calorific value of chars based on TS decreased 4 to 7 MJ/kg with increasing temperature as decreasing VS.

4.2.4 Carbon Mass Balance

A mass balance on carbon was performed to evaluate the recovery of carbon that was initially present in the dried sewage sludges. This work assumed all carbon recovery was associated with the pyrolysis products (oil and char) and all carbon lost was caused by NCG. Hence the carbon lost (C_{loss}) was calculated using Equation 4.4.

$$C_{loss} = \frac{M_{ds}C_{ds} - (M_{oil}C_{oil} + M_{char}C_{char})}{M_{ds}C_{ds}} \times 100 \quad (4.4)$$

where

C_{loss} : mass fraction of carbon lost during pyrolysis, percent

M_{ds} : mass of dried sewage sludge, g

C_{ds} : carbon fraction in dried sludge, percent

M_{oil} : mass of oil from dried sludge, g

C_{oil} : carbon fraction in oil, percent

M_{char} : mass of char from dried sludge, g

C_{char} : carbon fraction in mass of char, percent

The results of the carbon mass balance for this work are shown in Table 4.5. The outlined values were averaged values for all the individual tests. The carbon lost at temperatures of 300 and 500°C from primary sludge was 4.4 ± 0.6 and 6.6 ± 1.4 , for TWAS was 1.6 ± 1.5 and 11.2 ± 0.4 and for digested sludge was -9.6 ± 0.3 and 1.6 ± 1.4 respectively. Hence, approximately 90 percent of the carbon in the dried sludges was recovered in the oils and chars for all sludge types. However, the digested sludge at 300°C was found to generate carbon using this method. This result was likely due to experimental errors in measuring the yields or carbon quantities.

The increased carbon lost with increasing pyrolysis temperature would be expected due to the increased NCG production which contains carbon

compounds such as methane, ethane, CO and CO₂. However, the information in Table 4.5 provides weak proof to validate the hypothesis due to the high variability between the individual carbon loss results. Only the carbon lost in TWAS presented significant difference with increasing temperature, while the carbon loss results of primary and digested sludge outlined no significant difference due to the high variability between results. However, the results from Table 4.5 suggested that little carbon was lost during the pyrolysis and hence most of the fuel value should be recovered in the oil and char.

Table 4.5: Carbon Balance

Temp. °C	Yield, wt.%		Carbon fraction			Carbon lost %
	Oil g-oil/g-ds	Char g-oil/g-ds	Dried sludge g-C/g-ds	Oil g-C/g-oil	Char g-C/g-char	
Primary						
300	26.0±1.3	59.9±1.6	44.1±3.6	65.2±0.1	42.6±0.3	4.4±0.6
500	41.8±1.0	32.6±0.2	44.1±3.6	72±0.02	42.6±1.8	6.6±1.4
TWAS						
300	17.6±0.1	66.5±1.3	36.7±0.26	62.8±1.0	37.7±4.1	1.6±1.5
500	32.4±0.1	42.7±0.3	36.7±0.26	64.6±0.4	27.3±0.93	11.2±0.4
Digested						
300	13.8±0.8	74.9±1.5	31.1±0.2	69.4±0.7	32.7±0.06	-9.6±0.3
500	26.1±0.4	52.5±0.7	31.1±0.2	74.4±0.68	21.3±0.11	1.6±1.4

4.3 Effect of Catalyst and Pretreatment on Oil and Char Yields

The effects of a catalyst (zeolite) as well as the use of acids and a base as pretreatments for the sludges on oil and char yields were studied. It was hypothesized that chemical treatment would change the composition of the organic fraction of the sludges and hence affect the oil yields. The chemical additives were mixed with the dried sewage sludge prior to pyrolysis.

4.3.1 Effect of Catalyst

The use of zeolite as a catalyst to assist in sludge decomposition was evaluated. Figure 4.4 presents the yields of oil and char based on the dried sludge versus the mass ratio of catalyst to dried primary sludge pyrolyzed at 500°C. From Figure 4.4, it can be seen that the addition of catalyst resulted in lower char yields but did not substantially impact the yield of oil. Stammach et al. (1989) applied a zeolite in a bench-scale continuous fluidized bed reactor with anaerobic digested sludge at temperatures ranging from 500 to 650°C. They reported that pyrolysis of the dried sewage sludge with the catalyst increased the production of gas and oil versus tar due to cracking of tar without significant impact to oil yield. This result is similar to the results shown in the Figure 4.4. The oil yields were not substantially affected by the dose of catalyst, while the char yield decreased with increasing dose of zeolite. This result suggests that the catalyst resulted in increased conversion of VS to gas; therefore, the catalyst did not positively impact oil and char yields.

Figure 4.4: Effect of Catalyst on Yields of Oil and Char

4.3.2 Effects of Pretreatments

Acid and base pretreatment of dried sludge was employed to study the effect on oil yield and adsorption capacity that may result from either an increased or decreased VS fraction in the dried sludges. Acetic acid, hydrochloric acid and sodium hydroxide were used as pretreatment agents to treat the dried sewage sludges. Two different concentrations of acetic acid were employed (98 percent and 0.1M). The pH values of hydrochloric acid and 98 percent and 0.1M acetic acid solutions were 0.8, 1 and 3.5 respectively, before contacting with the sludge. A 3.0M solution of sodium hydroxide was used as a pretreatment solution and had a pH value of approximately 14.

Pretreatment of the dried sludges introduced experimental error in the measurements of mass. Pretreated sludge was difficult to control during rinsing with deionized water because the primary sludge became semi-liquid that required filtering during the rinsing which affected weight loss. TWAS and digested sludge produced some floating solids that were lost. After rinsing, TWAS and digested sludge were dried in a convection oven at 105°C, while primary sludge required additional centrifuging for dewatering. Therefore, the mass reduction data contains some errors and the data for primary sludge is less reliable than the other data.

Table 4.6 presents the mass reductions, VS fraction and oil yields. The presented oil yield, on the basis of TS and VS are based on the mass of dried sludges after treatment (treated) to determine the effect of pretreatment

Table 4.6: Results of Pretreatments

	Mass reduction, wt. %			VS fraction, wt. %	Oil yield wt. %	
	VS	FS	Total		TS basis	VS basis
Primary						
Untreated				84±0.04	42±1.0	50±1.1
3M HCl	40.2±4.8	26.4±5.9	38±4.8	81±1.4	40±0.3	49±0.5
98% A. Acid	24.8±2.7	7.4±3.4	22±2.9	81±2.2	39±0.2	48±0.3
0.1M A. Acid	17.0±1.4	4.4±1.6	15±1.4	80±0.2	38±0.5	48±0.6
3M NaOH	65.0±3.0	11.6±5.7	53±4.7	56±1.9	27±0.2	47±0.8
TWAS						
Untreated				69±0.5	30±0.1	48±0.2
3M HCl	21.9±1.4	27.4±1.5	26±1.6	68±1.1	32±1.2	47±1.4
98% A. Acid	13.9±0.7	9.8±0.7	12±1.0	70±0.4	33±1.2	47±1.4
0.1M A. Acid	13.0±1.4	1.6±0.2	9±1.4	66±1.5	31±0.4	47±0.6
3M NaOH	26.2±1.3	1.6±0.9	17±1.0	63±1.1	29±0.4	46±0.8
Digested						
Untreated				59±0.08	25±0.4	44±0.5
3M HCl	23.7±0.7	30.7±0.7	26±0.7	60±1.3	30±0.7	50±0.9
98% A. Acid	19.5±2.6	1.3±3.2	12±2.7	54±2.0	26±0.6	48±0.7
0.1M A. Acid	12.7±0.3	1.3±0.3	8±0.3	55±0.04	26±0.8	47±0.9
3M NaOH	29.1±0.1	0.8±0.2	16±0.1	50±0.06	24±0.2	48±0.7

on oil yield. The raw data is presented in Appendix D. The oil yield based on the mass of treated VS (Y_{oil-VS}) was calculating using Equation 4.5.

$$Y_{oil-VS} = \frac{\overline{M}_{oil}}{\overline{M}_{VS}} \times 100 \quad (4.5)$$

where

$\overline{M}_{VS}$: mass of volatile solids after pretreatment, g

$\overline{M}_{oil}$: mass of oil basis of treated dried sludge, g

In Table 4.6, the VS and FS reductions by acids and base treatment were calculated based on the mass of VS and FS in the sludges before treatment. The VS reduction of primary, TWAS and digested sludge by acids ranged from 17.0 to 40.2, 13.0 to 21.9 and 12.7 to 23.7 weight percent respectively, and the FS reduction ranged from 4.4 to 26.4, 1.6 to 27.4 and 1.3 to 30.7 weight percent respectively. The total mass reduction by acid ranged from 15 to 38, 9 to 26 and 8 to 26 weight percent respectively. The results indicate that treatment of the sludge with lower pH solutions resulted in increased VS and FS reduction as well as total mass reduction.

The VS reduction of primary, TWAS and digested sludges were 65, 26 and 29 weight percent when treated with the base. Overall the sludge types, this VS reduction presented higher values than those of acids. The FS reduction with base in primary sludge presented negative value

(generated FS) due to the error from measuring of total mass reduction or formation of precipitation at high pH values. With assumption that FS reduction with base in primary sludge was considered as zero, in general, the FS reduction by base presented lower values than the acids. This result indicates that more VS and less FS in dried sludge would be extracted with base.

From Table 4.6, it can be seen that the oil yield normalized on the basis of the treated VS at 500°C of primary sludge and TWAS ranged from 47 to 49 and from 46 to 47 weight percent respectively. This did not present an improvement compared to the untreated sludges that had yields of 50 and 48 weight percent respectively. The digested sludge yields ranged from 47 to 50 weight percent that represented an increase of 3 to 6 weight percent as compared to the untreated value of 44 weight percent. As presented in section 4.2.1, the oil yields on the basis of VS from untreated primary sludge and TWAS were higher (50 and 48 weight percent) than digested sludge (44 weight percent) at 500°C. However, the oil yields on the basis of VS of pretreated, primary, TWAS and digested sludge were not different and ranged from 46 to 50±1.4 weight percent. This result indicates that the VS in dried sludge samples after acid and base treatment contained similar components oil production.

4.4 Use of Sewage Sludge Pyrolysis Char as an Adsorbent

Char from pyrolyzed sewage sludge can be used as a low-cost adsorbent.

This section will outline the portion of the study that dealt with determining the phenol adsorption capacity of chars from TWAS and digested sludge. The char from primary sludge was not tested as an adsorbent due to its softness. The phenol concentrations employed (50, 100, 250 and 500 mg-phenol/L) were determined from work by Chen et al., (2002). The adsorption capacity of the solid phase based on TS of char (q_{e-TS}) was determined using Equation 4.6. The values based on the VS of char (q_{e-VS}) were determined by dividing the TS based value by the volatile fraction. The units of q_{e-TS} and q_{e-VS} were milligram of phenol per gram of adsorbent on the basis of either TS or VS. The UV readings and raw data that were employed to determining q_e are presented in Appendix E.

$$q_{e-TS} = \frac{V(C_0 - C_e)}{M_{ads}} \quad (4.6)$$

Where

C_0 : concentration of phenol before contacting with solid, mg/L

C_e : concentration of phenol after equilibrium, mg/L

V : volume of phenol solution used, L

M_{ads} : mass of char contacted with phenol solution, g

The 95 percent C.I. of the adsorption test and analysis results were estimated to be within ± 12 percent and most of data were accurate to within ± 6 . Reproducibility of all adsorbents and analysis tests was good with the replicate runs usually within ± 1 to 6 percent.

4.4.1 Preliminary Experiment Results

Preliminary experiments investigating the use of char as an adsorbent involved two components. First, the period required for adsorption equilibrium was determined for both adsorbents from TWAS char and digested sludge char. Second, the adsorption capacity of phenol on a commercial activated carbon was also determined in a preliminary experiment to evaluate the value of the adsorbents from the sewage sludge.

Figure 4.5 presents the solid phase concentrations versus time for the equilibrium experiments. From Figure 4.5, it can be seen that phenol adsorption on both adsorbents was achieved after 8 hours. The standard deviations of the data in the first 2 hours presented larger variability than other data. The error likely resulted from the high adsorption rate as adsorption occurred during the measurement of UV readings.

Adsorption capacity of commercial activated carbon (0.5 to 2 mm) from Fisher Scientific is illustrated in Figure 4.6. The economic value of adsorbents from the pyrolyzed sludges was evaluated based on the adsorption capacity of this activated carbon. The measured maximum adsorption capacity was 125 mg-phenol/g-activated carbon with the 500 mg-phenol/L solution. This value was used as a basis to evaluate the value of adsorbents from sewage sludges.

Figure 4.5: Adsorption Equilibrium of Adsorbents from Chars

Figure 4.6: Adsorption Capacity of Commercial Activated Carbon

4.4.2 Characteristics of Char from Pyrolysis

Chars from TWAS and digested sludge that were pyrolyzed at temperatures below 400°C were not appropriate for adsorption as these adsorbents floated on the surface of the solution or dissolved to produce small particles. Therefore, only the chars from samples pyrolyzed at 400 and 500°C were used. The adsorbent produced from these chars did not incur these problems.

4.4.2.1 Effects of Temperature and Sludge Type

Figure 4.7 illustrates that the temperature and sludge type affected the adsorption capacity (q_{e-TS}) of the prepared adsorbents from untreated dried sludge. The q_{e-TS} values from TWAS and digested sludge at 500 mg-phenol/L from the higher pyrolysis temperature (500°C) were 10.9 and 9.2 mg-phenol/g-adsorbent, while those at the lower temperature (400°C) were 7.8 and 5.5 mg-phenol/g-adsorbent respectively. In both sludge types, the adsorption capacity, on the basis of q_{e-TS} , from higher pyrolysis temperature derived approximately 40 to 70 percent higher values as compared to those of lower temperatures. Lu et al. (1995) as summarized in Figure 2.5 found that the BET surface area of adsorbents from higher temperatures (750 and 850°C) as determined by the nitrogen adsorption method generated 3 to 5 times higher values than lower temperature (650°C).

Figure 4.7: Effect of Pyrolysis Temperature and Sludge Type on Phenol Adsorption

Table 4.7 was employed to compare the adsorption capacities of the sludge types in Figure 4.7. The VS fraction of the TWAS ranged from 63 to 70 percent and the adsorption capacities ranged from 9.0 to 12.7 mg-phenol/g-adsorbent (Figure 4.8). The VS fractions of digested sludge ranged from 50 to 60 percent and the adsorption capacities ranged from 8.7 to 9.9 mg-phenol/g-adsorbent (Figure 4.9). The results indicate that the VS content of the pyrolyzed sludge affect the adsorption capacity. Lu et al. (1995) reported “the removal of volatile matter during pyrolysis creates the elementary pore structure for the char as adsorbent”

In other words, TWAS that contained more VS than digested sludge would create more surface area for adsorption. Therefore, adsorption capacity of adsorbent from sludge was affected by the initial VS fraction as well as pyrolysis temperature.

Table 4.7: VS Fractions and Adsorption Capacities at 500°C

	Control	3M HCl	98% A.Acid	0.1M A.Acid	3M NaOH
TWAS					
VS of dried sludge after treatment, wt.%	69	68	70	66	63
q_{e-TS} , mg/g	10.9	12.7	12.6	10.9	9.0
Digested					
VS of dried sludge after treatment, wt.%	59	60	54	55	50
q_{e-TS} , mg/g	9.2	9.9	9.7	9.2	8.7

q_{e-TS} : adsorption capacity basis of total solids

4.4.2.2 Effect of Pretreatment on Adsorption Capacity

Figures 4.8 and 4.9 present the observed adsorption capacities on the basis of TS and VS (q_{e-TS} and q_{e-VS}) respectively for the adsorbents from treated TWAS and digested sludges that were pyrolyzed at 500°C.

Figure 4.8 presents the q_{e-TS} versus phenol concentration for treated TWAS. The maximum q_{e-TS} values demonstrated a significant difference with the pH value of the acids and base. The adsorbents prepared with lower pH acids (3M HCl of pH 0.8 and 98 percent acetic acid of pH 1.0) had the greatest adsorption capacities with a maximum value of about 12.7 mg-phenol/g-adsorbent at 500 mg-phenol/L. The adsorbent prepared with 0.1M acetic acid (pH 3.5) demonstrated a similar q_{e-TS} value to the control (pH 7) with a value of 10.9 mg-phenol/g-adsorbent. The adsorbents prepared with the base (pH 13.5) had the lowest maximum q_{e-TS} with a value of 9.0 mg-phenol/g-adsorbent. These results indicate that the q_{e-TS} values for treated TWAS increased with decreased pH values of the pretreatment solutions. Lu and Lau (1996) supported this observation where the micro-pore area and the result of BET surface area determined from nitrogen adsorption method increased to 80 and 150 m²/g-adsorbent respectively, with 3M H₂SO₄ as compared to the adsorbent with 1M H₂SO₄ that had values of 60 and 120 m²/g-adsorbent respectively. The adsorbent was prepared from the dried sludge with VS of 52 weight percent and pyrolysis at 650°C for 3 hours.

Figure 4.8: Adsorption Capacities of TWAS Adsorbents

Figure 4.9: Adsorption Capacities of Digested Sludge Adsorbents

Figure 4.9 presents the q_{e-TS} values from treated digested sludge. The behaviour of q_{e-TS} for digested sludges was similar to that of TWAS as lower pH resulted in higher adsorption. However, the differences in maximum adsorption capacities between the individual adsorbents were narrower (difference within 1.2 mg/g) than TWAS difference within 3.7 mg/g. Particularly, the adsorption capacities at lower phenol concentrations (50 and 100 mg/L) did not exhibit significant difference as the individual values overlapped in the error range. The relationship between the pH values of pretreatment solutions and the adsorption capacities was based upon the responses observed at the higher phenol concentrations (250 and 500 mg/L).

From Figure 4.9, the q_{e-VS} values of digested sludge were 7 to 9 mg/g higher than the q_{e-TS} values while the q_{e-VS} values of TWAS were higher than the q_{e-TS} values by 6 to 7 mg/g (Figure 4.8). From Figure 4.9, it can be seen that the rank of adsorption capacities based on VS was different as compared to the TS basis. In the case of the VS basis, the adsorption for NaOH-treated sludge was higher than the other sludges and the values for 3M HCl were lower than the other sludges at higher phenol concentrations (250 and 500 mg/L). The differences in behaviours between the q_{e-VS} from TWAS and digested sludge were due to the differing volatile fractions of the adsorbents. As mentioned earlier, the adsorption capacity was a function of VS fraction of the dried sludge. Hence, the q_{e-VS} values of digested sludge in Figure 4.9 presented the

overlapped behaviour and higher difference with q_{e-TS} as compared to TWAS due to the lower VS fractions than TWAS as demonstrated in Figure 4.8.

In conclusion, it was found that the pH value of sludge treatment solutions affected the adsorption capacity of the adsorbents. The affect of the pH of the solutions on adsorption capacities (q_{e-TS} and q_{e-VS}) was more distinct with the TWAS that had a higher volatile fraction than the digested sludge.

4.5 Adsorption Isotherms

Langmuir and Freundlich isotherms were employed to further characterize the adsorption behaviour of the adsorbents from the chars. All of the q_e values were analyzed to determine the appropriate isotherm theory. The q_e values of the adsorbents in subsequent sections were based on untreated or treated TS because these values were used to estimate the economic value.

4.5.1 Langmuir and Freundlich Isotherm

The equations describing the linearized form of the Langmuir and Freundlich isotherms are presented in Equations 4.7 and 4.8 respectively.

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q_{\max}b} \cdot \frac{1}{C_e} \quad (4.7)$$

where

q_e : concentration of solid phase, mg/g

C_e : concentration of liquid phase, mg/L

q_{max} : maximum adsorption amount, mg/g

b : Langmuir adsorption constant

Based on Equation 4.7, $1/q_e$ was plotted versus $1/C_e$, the constants b and q_{max} , were determined from the slope and intercept of the straight line.

$$\log q_e = \log K_f + n \log C_e \quad (4.8)$$

Where

q_e : concentration of solid phase, mg/g

C_e : concentration of liquid phase, mg/L

K_f : Freundlich adsorption constant

n : Freundlich exponent

The constants n and $\log K_f$ in Equation 4.8 were determined from the slope and intercept when $\log C_e$ was plotted versus $\log q_e$.

4.5.2 Data Analysis of Langmuir and Freundlich Isotherm

From Figures 4.10 to 4.13, the variability of slopes (b and n) and intercepts ($1/q_{max}$ and $\log K_f$) in both models associated with variation of individual data. Most of the data of 95 percent C.I were within 4 percent, hence the variability of slopes and intercepts would be acceptable.

Figure 4.10: Langmuir Isotherm of TWAS Adsorbents

Figure 4.11: Langmuir Isotherm of Digested Sludge Adsorbents

Figure 4.12 Freundlich Isotherm of TWAS Adsorbents

Figure 4.13 Freundlich Isotherm of Digested Adsorbents

Table 4.8 presents the Langmuir and Freundlich isotherm constants with their standard errors. As mentioned earlier, the $1/q_{\max}$ and $\log K_f$ value are the intercepts of the individual plot presented in Figures 4.10 to 4.13. From these values, Langmuir and Freundlich $q_{\max}$ and K_f constants were developed. The slopes of both isotherms were expressed as $1/q_{\max} \cdot b$ and n .

From Table 4.8, the Langmuir adsorption b constants of TWAS (0.71 to 1.018) were greater than digested sludge (0.52 to 0.708) over all the pretreatments. In general, the Langmuir adsorption $1/q_{\max}$ constants of TWAS ranged from 0.068 to 0.088 and were lower than the digested that ranged from 0.077 to 0.096. Each of the $1/q_{\max}$ constants of TWAS as compared to the digested sludge with the same pretreatment had lower values. In the Freundlich isotherm model, the K_f coefficients of TWAS and digested sludge ranged from 0.425 to 1.208 and from 0.515 to 1.041 respectively.

The n values of TWAS and digested sludge were 0.388 to 0.531 and 0.451 to 0.511 respectively. These results indicate that the Freundlich isotherm constants did not demonstrate any relationship between the various pretreatments and sludge types while the Langmuir b and $1/q_{\max}$ constants were influenced by pretreatments.

Table 4.8 Langmuir and Freundlich Isotherm Constants for Phenol

	Untreated	3M HCl	98% A.Acid	0.1M A.Acid	3M NaOH
TWAS					
Langmuir					
$1/q_{\max}$	0.072	0.069	0.068	0.068	0.088
SE for $1/q_{\max}$	0.006	0.006	0.003	0.003	0.002
b	0.860	0.718	0.716	1.018	0.710
SE for b	0.567	0.477	0.513	0.543	0.702
r^2	0.985	0.973	0.987	0.998	0.999
$q_{\max}$	13.9	14.5	14.7	14.8	11.4
Freundlich					
$\log K_f$	-0.283	0.08	0.082	-0.372	-0.317
SE for $\log K_f$	0.07	0.07	0.06	0.07	0.06
n	0.504	0.416	0.388	0.531	0.480
SE for n	0.015	0.012	0.012	0.018	0.014
r^2	0.974	0.971	0.968	0.979	0.979
K_f	0.521	1.001	1.208	0.425	0.482
Digested					
Langmuir					
$1/q_{\max}$	0.090	0.089	0.077	0.086	0.096
SE for $1/q_{\max}$	0.004	0.005	0.005	0.005	0.009
b	0.596	0.520	0.708	0.695	0.580
SE for b	0.37	0.46	0.47	0.42	0.76
r^2	0.991	0.977	0.990	0.992	0.974
$q_{\max}$	11.1	11.3	12.2	11.6	10.4
Freundlich					
$\log K_f$	-0.115	0.018	-0.269	-0.288	-0.252
SE for $\log K_f$	0.07	0.06	0.1	0.07	0.07
n	0.511	0.471	0.481	0.476	0.451
SE for n	0.03	0.03	0.04	0.03	0.03
r^2	0.965	0.967	0.954	0.975	0.970
K_f	0.768	1.041	0.538	0.515	0.560

SE: standard error

The standard error (SE) of the Langmuir and Freundlich constants refers to the random variation of the estimated values hence smaller values mean better replication [Berthouex and Brown, 1994]. From Table 4.8, it can be seen that in TWAS, the SE of the Langmuir b constants (0.477 to 0.702) was higher than that of Freundlich n constant ranging from 0.012 to 0.018. The SE of $1/q_{\max}$ ($SE_{-1/q_{\max}}$) value was 0.002 to 0.006. It presented lower than SE of $\log K_f$ ($SE_{-\log K_f}$) ranged from 0.06 to 0.07. However, normalization is needed to compare these different bases of parameters as divide by absolute value of $1/q_{\max}$ or $\log K_f$. The normalized $SE_{-1/q_{\max}}$ value (0.02 to 0.09) ranged lower than $SE_{-\log K_f}$ ranged from 0.24 to 0.875. In digested sludge, the SE of b and n presented small difference ranging from 0.52 to 0.708 and 0.451 to 0.511 respectively. The normalized $SE_{-1/q_{\max}}$ (0.04 to 0.09) had lower values than $SE_{-\log K_f}$ that ranged from 0.2 to 3.3. These results indicate that all of the SE values in both models were small enough to be acceptable, however the SE of the constants does not provide the information to determine the better appropriate model for this work.

In Table 4.8, the correlation coefficients (r^2) from Figures 4.10 to 4.13 present a measure of the variability of the data around the regression line in the Langmuir and Freundlich models. The r^2 values for the Langmuir isotherms (0.973 and 0.999) were slightly higher than those of the Freundlich isotherms (0.954 and 0.979). Hence, the Langmuir isotherm represents less variability of experiment data and present better fit to these results.

The r^2 parameter is the simplest and most commonly used regression parameter that is employed to estimate the goodness of fit. However, to properly determine the better model, this data analysis information is not enough [Berthouex and Brown, 1994]. Therefore, residual plots were employed to measure the quality of fit. The results of this analysis are presented in Appendix F.

The graphing of residuals is an important method that has applications in all areas of data analysis and model building. Residual plots for the TWAS and digested sludge adsorbents without pretreatment and generated at 500°C for both isotherms are presented in Figures 4.14 and 4.15. For the Langmuir isotherm, data from both sludges were randomly distributed against the concentrations of phenol solution. However, the data in the Freundlich model were not distributed randomly. In general, the residuals increased with the phenol concentration. A model needs to be modified to improve the residuals graphing a pattern is observed [Berthouex and Brown, 1994]. Therefore, the distribution of residuals supports the Langmuir isotherm as a better fit to the data than the Freundlich model.

From the analysis of the isotherm constants, the r^2 parameter and the residuals distribution, the Langmuir isotherm was selected as the better model for this work. Hence, the Langmuir adsorption constant $q_{\max}$ was employed to analyze the economic value of the individual adsorbents.

Langmuir Isotherm of TWAS Adsorbent at 500°C

Freundlich Isotherm of TWAS Adsorbent at 500°C

Figure 4.14: Residual Plots of TWAS Adsorbent

Langmuir Isotherm of Digested Sludge Adsorbent at 500°C

Freundlich Isotherm of Digested Sludge Adsorbent at 500°C

Figure 4.15: Residual Plots of Digested Sludge Adsorbent

Table 4.8 also presented the estimated $q_{\max}$ values of adsorbents from TWAS and digested sludge. The acid treated $q_{\max}$ values of TWAS and digested sludge were higher with values ranging from 14.5 to 14.8 and from 11.6 to 13.1 mg-phenol/g-adsorbent as compared the values without treatment (control) that were 13.9 and 11.1 mg-phenol/g-adsorbent respectively. The $q_{\max}$ values from TWAS and digested sludge with base were lower than the control values of 11.4 and 10.4 mg-phenol/g-adsorbent respectively.

4.6 Estimation of the Economic Values of Dried Sewage Sludge

In this section, economic values of the oils and chars as adsorbents from pyrolysis of dried sewage sludges were estimated using the information from previous sections. The energy costs for processes to produce oil and char such as drying, heating until target temperature and reaction energy for pyrolysis were estimated based on the current electricity cost because electricity was the actual energy used for this work (drying and operating pyrolysis process). The economic value of oil was evaluated based on the current crude oil prices and the residual char as an adsorbent was evaluated on the basis of relative value of adsorption capacity based on commercial activated carbon.

The analysis of the energy value of sewage sludges should consider energy consumption during dewatering, drying and pyrolysis of the sludges. However, calculating the energy consumption for dewatering

was difficult for this work because the energy cost of dewatering and drying of sewage sludge varies depending on the water content of the sludges. As mentioned previously, primary sludge and TWAS were collected as liquid and then dewatered using laboratory equipment, while the digested sludge was collected as cake after mechanical dewatering at the wastewater plant. Therefore, comparing energy consumption for dewatering was not factored into the calculations but should be considered when making future conclusions.

The energy consumption for drying (Q_{drying}) of dewatered sludge was calculated using Equation 4.9. The temperature difference employed in this equation was 80°C because the collected sludges (semi-liquids or cake) were kept at room temperature (25°C) in the laboratory after dewatering and were dried at 105°C.

$$Q_{drying} = M_{ws} \times W \times [(Cp_{water} \times \Delta T) + \Delta H_{vap}] + [M_{ws} \times (1 - W)] \times Cp_{sludge} \times \Delta T \quad (4.9)$$

where

M_{ws} : unit mass of wet sludge after dewatering, kg

W : fraction of water in sludge

ΔH_{vap} : latent heat for vaporization of water, 2090 kJ/kg

Cp_{water} : heat capacity of water, 4.18 kJ/kg·°C

Cp_{ds} : heat capacity of solids in sludge, 1.95 kJ/kg·°C

ΔT : temperature difference between initial and 105°C

The heat capacities of primary, TWAS and digested sludge are likely different due to the differing chemical contents of the individual sludge types. However, this study used a fixed value of 1.95 kJ/kg·°C because it was not possible to accurately estimate the heat capacities for the different sludges. This value was determined based upon the range of heat capacities of general organic and inorganic materials. The heat capacity of general organic material ranges between 2.1 and 2.5 kJ/kg·°C and the range for inorganic material is 0.8 to 1.3 kJ/kg·°C [Chemical engineer handbook, 1984]. The dried sewage sludge analyzed in this work contained 59 to 84 percent organic matter as presented in Table 4.1. Therefore, minimum and maximum values of heat capacity would be between 1.6 and 2.3 kJ/kg·°C based on the following calculations:

$$[2.1 \text{ kJ/kg}\cdot^{\circ}\text{C} \times 0.59 + 0.8 \text{ kJ/kg}\cdot^{\circ}\text{C} \times (1-0.59)] = 1.6 \text{ kJ/kg}\cdot^{\circ}\text{C}$$

$$[2.5 \text{ kJ/kg}\cdot^{\circ}\text{C} \times 0.84 + 1.3 \text{ kJ/kg}\cdot^{\circ}\text{C} \times (1-0.84)] = 2.3 \text{ kJ/kg}\cdot^{\circ}\text{C}$$

The average value of 1.6 kJ/kg·°C and 2.3 kJ/kg·°C is 1.95 kJ/kg·°C which is the value used for this study. This value is similar to the value of 2.1 kJ/kg·°C reported by Annadurai et al. (2003).

Water content has a major impact on the energy consumption predicted by Equation 4.9. As discussed in the previous paragraph, the water content of each sludge type depended on the mechanism of dewatering. The water contents after dewatering of primary, TWAS and digested

sludge as cake were 75, 91 and 70 percent respectively. Therefore, it was difficult to compare the energy cost of liquid sewage sludges due to these two factors. Therefore, the estimated energy consumption for drying the three sludge types was calculated using average water content of 80 percent after dewatering. The estimated energy value for drying the dewatered sludge samples was determined to be 1952 kJ per kg of dewatered sludge.

4.6.1 Energy Consumption for Pyrolysis

There were two components considered in the calculation of energy consumption for pyrolysis. One component involved heating the dried sludge from temperature after drying to the target temperature. The second component was the heat consumed to decompose the sewage sludge during the pyrolysis reaction.

The energy consumption to heat dried sludge to the target temperature (Q_{target}) can be calculated using Equation 4.10. The average value of heat capacity for dried sludges was used for this equation. The temperature of sludge after drying was considered as 105°C. The calculated energy consumption at 300 400 and 500°C to heat the sludge were 380, 575 and 770 kJ/kg-ds respectively.

$$Q_{target} = M_{ds} C_{p-ds} \Delta T_{target} \quad (4.10)$$

where

Q_{target} : energy required to heat sludge to reach target temperature, kJ

M_{ds} : mass of dried sewage sludge, kg

Cp_{ds} : heat capacity of solids in dried sludge (1.95 kJ/kg·°C)

ΔT_{target} : difference between target and 105°C

The second component is the heat of reaction for dried sludge pyrolysis (endothermic). The precise measurement of the heat of reaction for individual sewage sludges requires complex experimental work which was outside the scope of this work. Caballero et al. (1997) reported the reaction energy for sewage sludge pyrolysis as 300 kJ/kg. The reported value was measured at temperatures that ranged from 100 to 500°C. The carbon and hydrogen content of the sludges was approximately 32 and 5 weight percent respectively on a dry basis. They also revealed that the main decomposition for the sludge occurred between 250 and 500°C. Therefore, the total energy consumption (Q_{total}) pyrolysis could be calculated from Equation 4.11.

$$Q_{total} = Q_{drying} + Q_{target} + Q_{pyrolysis} \quad (4.11)$$

The energy consumption for drying (Q_{drying}) was 1952 kJ/kg and was the main energy consumption because it was about 2 to 3 times higher than summation of the other processes ($Q_{target} + Q_{pyrolysis}$) which ranged from 680 to 1070 kJ/kg although the energy for pyrolysis was assumed.

4.6.2 Evaluating the Economic Value of Pyrolysis Products

This section evaluates the economic value of oil as fuel and char as adsorbents based on the analysis presented in previous sections. The experimental results were used to determine the economic value of the dried sludges. The use of chars as fuel in combustion or incineration was not considered. Using chars or dried sludges as fuel is associated with environmental disadvantages. There is concern regarding the release of toxic gases such as dioxin in the emission or immobilized heavy metals in the ash. These concerns were raised in many literature sources. Hence, this work considered using the char as adsorbent for phenol adsorption in the liquid solution.

4.6.2.1 Economic Value of Bio-Oil

The economic value of bio-oil from pyrolyzed dried sludge was evaluated as a substitute for No.6 fuel that has a calorific value of 53 MJ/kg [Chemical engineer handbook, 1984] and the current crude oil price is CDN \$60/barrel. The average evaluated calorific value of bio-oil was 38 MJ/kg (Table 4.2). The calorific value of bio-oil would be 70 percent of the No.6 fuel oil with assumption that the oil from pyrolysis is used as a fuel. The economic value of bio-oil was evaluated as 70 percent of the current oil price and hence was determined to be CDN \$43/barrel. The density of the bio-oil was 0.9 kg/L, based on the preliminary experimental results obtained in this work as compared to a

reference value of 0.888 kg/L-crude oil [Chemical engineer handbook, 1984]. Therefore, the converted bio-oil value is approximately 35 ¢/kg-oil. An economic assessment of the value of producing bio-oil from dried sludge was performed and the results are presented in Table 4.9. In this table, the required energy for pyrolysis was calculated using Equation 4.11. The required energy cost for the operation of the laboratory-scale pyrolysis reactor and drying processes was evaluated based on CDN 4.3 ¢/kWhr as Ontario's current cost of electricity because electricity accounts for most of the operational costs of the processes. The energy cost was calculated using Equation 4.12 and a conversion of 3600 kJ/kWhr.

$$C_R = E_{consumed} \times C_E \quad (4.12)$$

where

C_R : cost of required energy, ¢

$E_{consumed}$: energy consumption for pyrolysis and drying, kJ

C_E : cost of electricity, CDN 4.3 ¢/kWhr

The economic value of the oil was determined by multiplying the oil yield by the estimated oil value (35 ¢/kg-oil). The economic value of oil was determined as the difference between the oil value and the energy cost for pyrolysis processes.

Table 4.9: Economic Value of Bio-Oil

Temperature °C	Oil		Energy		Economic
	Yield	Value	Required	Cost	Value of Oil
	kg-oil/kg-ds	¢/kg-ds	kJ/kg-ds	¢/kg-ds	¢/kg-ds
Primary					
250	8	2.8	2537	3.0	-0.2
300	26	9.1	2637	3.2	5.9
350	36	12.6	2730	3.3	9.3
400	39	13.7	2822	3.5	10.2
450	41	14.4	2925	3.7	10.7
500	42	14.7	3027	3.9	10.8
TWAS					
250	12	4.2	2537	3.0	1.2
300	18	6.3	2637	3.2	3.1
350	26	9.1	2730	3.3	5.8
400	33	11.6	2822	3.5	8.1
450	33	11.6	2925	3.7	7.9
500	32	11.2	3027	3.9	7.3
Digested					
250	4	1.4	2537	3.0	-1.6
300	14	4.9	2637	3.2	1.7
350	21	7.4	2730	3.3	4.1
400	24	8.4	2822	3.5	4.9
450	26	9.1	2925	3.7	5.4
500	28	9.8	3027	3.9	5.9

Based on the calculated economic value of the oil, the most valuable sludge was primary sludge pyrolyzed at 500°C which had a value of 10.8 ¢/kg-ds. Digested sludge was the least valuable at 5.9 ¢/kg-ds. The economic values of primary and digested sludge generated a negative economic value at 250°C because of the small oil yields (less than 10 weight percent). The economic values of primary and digested sludge increased with increasing pyrolysis temperature. In other words, both sludge types had the greatest economic value at the highest operation temperature (500°C). The economic value of TWAS had a peak value of 8.1 ¢/kg-ds at 400°C.

From the literature, the estimated cost of landfilling and land application for sludge was approximately \$1.3 to \$2 per kilogram of sludge [Simco Engineering, 1980; Bridgewater, 1989]. However, as shown on Table 4.9, the pyrolysis process provided economic benefit. Hence, the value of sewage sludge was economically positive in pyrolysis although it had been negative in traditional disposal process.

The economic value of oils from dried sludges treated with acid and base using the “untreated mass” calculation were evaluated to compare with value of untreated dried sludge and are presented in Table 4.10. Pretreated sludges included more production cost due to chemicals and additional energy requirements for washing and drying after pretreatment because the sludge were not pretreated in the wet condition in this work.

The commercial reagent chemical cost for this work varied. The costs of hydrochloric acid (37 weight percent), acetic acid (>98 weight percent) and sodium hydroxide (>97 weight percent) were CDN \$16, \$11 and \$11 per kilogram respectively. To treat one kilogram of dried sludge, samples were washed twice with the chemicals. The costs to treat one kilogram of dried sludge were approximately CDN \$8, \$22, \$0.13 and \$2.7 for 3M HCl, 98 percent acetic acid, 0.1M acetic acid and 3M NaOH respectively. Hence, the 98 percent acetic acid was the most expensive chemical. Meanwhile, 0.1 M acetic acid was the cheapest chemical for sludge treatment because it was used as a diluted solution. The reuse of used chemicals was not considered in this work.

The negative value indicates that the cost of producing the oil was greater than the economic value of the products after pretreatment. However, the oil values for weak acid presented more positive values as compared with the other pretreatment solutions because it was the cheapest pretreatment solution. This result supports the idea that only weak acid pretreatment has potential economic benefits in the pyrolysis of dried sludges. Table 4.10 illustrated that chemical cost was the major factor of pretreatment costs.

The additional energy required for washing and drying the treated sludges was estimated using Equation 4.9. The estimated additional energy for pretreatment of primary sludge was 1614 kJ/kg-ds (1.93 ¢/kg-ds),

Table 4.10: Economic Value of Oil from Pretreated Sludges

Temperature °C	Oil Yield kg-oil/kg-	Value of Oil ¢/kg-ds	Costs		Economic Value ¢/kg-ds
			Energy ¢/kg-ds	Chemical ¢/kg-ds	
3M HCl					
Primary					
300	12.39	4.3	5.2	800	-801
400	24.55	8.6	5.5	800	-797
500	24.57	8.6	5.7	800	-797
TWAS					
300	14.03	4.9	4.8	800	-800
400	22.65	7.9	5.1	800	-797
500	24.01	8.4	5.3	800	-797
Dgiested					
300	11.27	3.9	4.8	800	-801
400	17.96	6.3	5.1	800	-799
500	21.42	7.5	5.3	800	-798
98% Acetic Acid					
Primary					
300	15.4	5.4	5.2	22000	-22000
400	30.45	10.7	5.5	22000	-21995
500	30.56	10.7	5.7	22000	-21995
TWAS					
300	15.36	5.4	4.8	22000	-21999
400	27.24	9.5	5.1	22000	-21996
500	28.97	10.1	5.3	22000	-21995
Digested					
300	11.03	3.9	4.8	22000	-22001
400	20.45	7.2	5.1	22000	-21998
500	22.84	8	5.3	22000	-21997

Table 4.10 continued

Table 4.16 continued

Temperature °C	Oil yield kg-oil/kg-ds	Value of Oil ¢/kg-ds	Costs		Economic Value ¢/kg-ds
			Energy ¢/kg-ds	Chemical ¢/kg-ds	
0.1M Acetic Acid					
Primary					
300	16.52	5.8	5.2	13	-12
400	32.72	11.5	5.5	13	-7
500	32.11	11.2	5.7	13	-8
TWAS					
300	12.2	4.3	4.8	13	-14
400	25.26	8.8	5.1	13	-9
500	28.11	9.8	5.3	13	-9
Digested					
300	8.22	2.9	4.8	13	-15
400	20.49	7.2	5.1	13	-11
500	24.14	8.4	5.3	13	-10
3M NaOH					
Primary					
300	9.85	3.4	5.2	270	-272
400	12.04	4.2	5.5	270	-271
500	14.82	5.2	5.7	270	-271
TWAS					
300	12.28	4.3	4.8	270	-271
400	22.56	7.9	5.1	270	-267
500	23.29	8.2	5.3	270	-267
Dgiested					
300	9.75	3.4	4.8	270	-271
400	18.85	6.6	5.1	270	-269
500	19.64	6.9	5.3	270	-268

while pretreatment of TWAS and digested sludge required an additional 1275 kJ/kg (1.52 ¢/kg-ds). This difference cost is due to the higher water content of primary sludge. The energy costs listed in Table 4.10 include the costs of achieving and maintaining the target temperatures as outlined in Table 4.9 as well as the energy required to wash and dry the sample. However, the additional energy cost did not significantly affect the economic value change because of the relatively expensive chemical costs introduced.

4.6.2.2 Evaluation of the Economic Value of Char as an Adsorbent

The economic values of chars as adsorbents are shown in Table 4.11. The three factors considered in determining the value of the adsorbents were the adsorbent recovery fraction, the relative value of the adsorbent compared to commercial activated carbon and the chemical cost for char pretreatment.

The adsorbent recovery fraction was considered because not all of the char was converted to adsorbent. After adsorbent preparation, 40 percent and 50 percent of adsorbents were recovered at 400 and 500°C respectively. Therefore, these factors were applied for temperatures 400 and 500°C respectively.

The value of the adsorbents (V_{char}) was estimated using Equation 4.14 based on the Langmuir isotherm capacity of the adsorbents and the cost

of a commercial activated carbon by Fisher Scientific (CDN \$70/kg). The Langmuir adsorption capacity of the commercial activated carbon was approximately 150 mg-phenol/g-activated carbon based on the data from preliminary experiment. The adsorption capacity of the adsorbent from TWAS and digested sludges in this work ranged from 7.0 to 14.8 mg-phenol/g-adsorbent.

$$V_{char} = V_{ac} \times \frac{Q_{max, char}}{Q_{max, ac}} \quad (4.14)$$

where

V_{char} : value of adsorbent, ¢/kg

V_{ac} : value of commercial activated carbon ¢/kg

$Q_{max, char}$: Q_{max} of adsorbents, g-phenol/kg-adsorbent

$Q_{max, ac}$: Q_{max} of commercial activated carbon, g-phenol/kg-ac

Hydrochloric acid (3M) that was employed to wash and clean the chars following pyrolysis resulted in a cost of CDN \$8/kg-char. Deionized water was used to rinse the acid treated chars and then, it was dried in the oven. The water content of the char was approximately 50 percent after rinsing. Energy consumption for drying was estimated to 1.5 ¢/kg-char from Equations 4.9 and 4.13 for all of the values in Table 4.11.

From Table 4.11, it can be seen that the estimated economic values of adsorbents with (500°C) and without (400 to 500°C) pretreatment are all

Table 4.11: Evaluated Economic Value of Char as Adsorbent

Pretreatment	Char Yield wt. %	Recovered Adsorbent kg-ads / kg-ds	$q_{\max}$ g/kg-ads	Relative Value of Adsorbent ¢/kg-ads	Adsorbent Preparing Cost ¢	Economic Value of Adsorbent ¢/kg-ds
TWAS						
Without						
400°C	48	0.192	11.24	100.7	801.5	-700.8
500°C	43	0.215	13.9	139.5	801.5	-662.0
3M HCl	36	0.18	14.5	121.8	801.5	-679.7
98% A. Acid	38	0.19	14.7	130.3	801.5	-671.2
0.1M A. Acid	29	0.15	14.8	103.6	801.5	-697.9
3M NaOH	46	0.23	11.4	122.4	801.5	-679.1
Digested						
Without						
400°C	63	0.252	9.61	113.0	801.5	-688.5
500°C	54	0.27	11.1	139.9	801.5	-661.6
3M HCl	38	0.19	12.8	113.5	801.5	-688.0
98% A. Acid	50	0.25	12.2	142.3	801.5	-659.2
0.1M A. Acid	54	0.27	11.6	146.2	801.5	-655.3
3M NaOH	49	0.245	10.4	118.9	801.5	-682.6

ads: adsorbent

negative economic value due to the expensive chemical cost for preparation of adsorbent. The adsorbent from higher temperature was more economically valuable. The economic values of the adsorbents from pretreated digested sludge slightly increased with 98 percent and 0.1M acetic acid solutions when compared to those without pretreatment at

500°C. Other pretreatment solutions did not present any economic advantage. Therefore, the adsorbents from pyrolyzed sludges did not provide economic benefit.

4.7 Evaluation of the Optimum Pyrolysis Conditions

As mentioned in the previous sections for estimating economic values, acid and base pretreatment of dried sludge and char for use as an adsorbent provided no economic advantage due to the high chemical cost. Only oil produced from sludge that was not pretreated presented any economic benefit. Therefore, the pretreatment and use of char as an adsorbent did not positively impact the economic value of dried sludge.

As presented in Table 4.9, the optimum economic values of primary, TWAS and digested sludge were 10.9, 8.1 and 6.0¢ respectively. The optimum pyrolysis temperature for TWAS was 400°C and primary and digested sludges presented highest yield at 500°C. Overall, primary sludge pyrolyzed at 500°C produced the largest economic benefit.

Chapter 5

Conclusions and Recommendations

Pyrolysis temperature and VS content in sludge were the primary factors affecting oil and char yield. The oil yield in all sludge types steeply increased between 250 and 400°C due to VS decomposition in this temperature range. The reduced oil yields from digested sludge suggested that the VS destroyed during the sludge digestion process contained a higher fraction of oil precursors. The effect of temperature on char yield was very different from that on oil yield due to the different remaining VS in chars with the pyrolysis temperature.

The calorific value of dried sludge correlated with VS and did not present a significant difference between sludge types when expressed on the basis of VS content. The calorific values of the produced oil did not appear to differ between the pyrolysis temperatures and sludge types with the value ranging from 36 to 39 MJ/kg-oil.

The estimated yield of non-condensable gases as the difference between theoretical yield and actual yield of products ranged approximately 10 to 25 percent with sludge types and temperatures. The NCG yield increased with temperature in all sludge types.

A catalyst (zeolite) did not impact oil and char yields due to the increased conversion of VS to gas. The acid and base pretreatment reduced both VS and FS in the dried sludge. More VS was extracted with base than acids. The pretreatments did not improve the oil yield when based on the VS of the treated sludge.

The adsorption capacity of adsorbent from char was affected by the VS fraction of the raw sludge as well as pyrolysis temperature. A lower pH value of the sludge treatment solutions produced higher surface area for adsorption in some sludge types. The affect of the pH of the solutions on adsorption capacities based on TS and VS was more distinct with the TWAS that had a higher volatile fraction than the digested sludge.

The Langmuir isotherm was more appropriate than Freundlich for both sludge types based upon the correlation coefficients (r^2) and residual plots. Hence Langmuir adsorption constants were employed to analyze the economic value of the individual adsorbents.

Acid and base pretreatment of dried sludge and char for use as an adsorbent provided no economic advantage due to high chemical cost. Oil produced from sludge that was not pretreated presented more economic benefit than pretreated sludge.

The optimum economic values of primary, TWAS and digested sludge were 10.9, 8.1 and 6.0¢ respectively. The optimum pyrolysis temperature for TWAS was 400°C and primary and digested sludge presented highest value at 500°C. Overall, primary sludge pyrolyzed at 500°C produced the largest economic benefit.

Pyrolysis of sewage sludges from the wastewater treatment plant in Ottawa provided a potential economic benefit with bio-oil generation compared to traditional disposal processes of landfilling and land application with estimated costs of \$1.3 to 2 per kilogram of sludge quoted in the literature.

Some recommended objectives for future works include:

- 1) to determine optimum pyrolysis temperature (over 500°C) for primary and digested sludge to evaluate the maximum oil yield.
- 2) to identify an appropriate pretreatment solution in weak acids to improve the oil yields.
- 3) to investigate cheap and useful chemicals to improve the economic values of the adsorbents.

Appendixes

Appendix A: Oil and Char Yield

A. Oil Yields

a. Primary Sludge

Basis: 5g of Dried Primary Sludge

Temp. °C	Exp No	Oil & Reaction Water g	Oil g	Yield of Oil wt.%	Average wt.%	STD
250	27	0.403	0.36	7.3	7.80	0.49
	28	0.457	0.41	8.2		
	29	0.440	0.40	7.9		
300	9	1.498	1.35	27.0	26.05	1.30
	10	1.396	1.26	25.1		
350	20	1.933	1.74	34.8	35.48	1.84
	22	1.893	1.70	34.1		
	23	2.087	1.88	37.6		
400	13	2.144	1.93	38.6	39.24	0.67
	15	2.179	1.96	39.2		
	16	2.218	2.00	39.9		
450	17	2.234	2.01	40.2	40.79	0.68
	18	2.256	2.03	40.6		
	21	2.308	2.08	41.5		
500	24	2.364	2.13	42.6	41.84	1.01
	25	2.260	2.03	40.7		
	26	2.349	2.11	42.3		

Example Calculation: $(0.36/5) \times 100 = 7.3$

b. TWAS

Basis: 5g of Dried TWAS

Temp. °C	Exp No	Oil & Reaction Water g	Oil g	Yield of derived oil wt. %	Average wt. %	STD
250	41	0.609	0.55	10.96	12.20	1.75
	42	0.747	0.67	13.44		
300	39	0.970	0.87	17.46	17.55	0.13
	40	0.980	0.88	17.64		
350	37	1.457	1.31	26.23	26.44	0.29
	38	1.480	1.33	26.64		
400	35	1.780	1.60	32.04	33.11	1.51
	36	1.899	1.71	34.17		
450	32	1.815	1.63	32.66	33.11	0.63
	33	1.864	1.68	33.55		
500	30	1.799	1.62	32.39	32.44	0.08
	31	1.805	1.62	32.50		

c. Digested Sludge

Basis: 5g of Dried Digested Sludge

Temp. °C	Exp No	Oil & Reaction Water g	Oil g	Yield of derived oil wt. %t ,	Average wt. %	STD
250	49	0.236	0.21	4.20	4.33	0.18
	50	0.250	0.22	4.45		
300	51	0.744	0.66	13.24	13.84	0.84
	52	0.811	0.72	14.44		
350	53	1.111	0.99	19.78	20.48	0.99
	54	1.190	1.06	21.18		
400	55	1.359	1.21	24.19	23.56	0.89
	56	1.288	1.15	22.93		
450	57	1.449	1.29	25.79	25.36	0.62
	46	1.400	1.25	24.92		
500°C	58	1.480	1.32	26.34	26.08	0.38
	44	1.450	1.29	25.81		

B. Char Yields**a. Primary Sludge**

Basis: 5g of Dried Primary Sludge

Temp. C	Exp No	Char g	Yield of wt.%	Average wt.%	STD
250	27	4.292	85.83	84.60	1.07
	28	4.206	84.13		
	29	4.193	83.85		
300	9	2.938	58.76	59.91	1.63
	10	3.053	61.06		
350	20	2.369	47.39	46.06	1.36
	22	2.306	46.12		
	23	2.234	44.67		
400	13	2.096	41.92	41.55	0.36
	15	2.076	41.52		
	16	2.060	41.20		
450	17	1.914	38.28	38.25	0.43
	18	1.933	38.66		
	21	1.890	37.80		
500	24	1.639	32.77	32.66	0.23
	25	1.640	32.80		
	26	1.620	32.40		

Example Calculation: $(4.292/5) \times 100 = 85.83$ **b. TWAS**

Basis: 5g of Dried TWAS

250	41	3.94	78.83	77.08	2.49
	42	3.77	75.32		
300	39	3.28	65.60	66.50	1.27
	40	3.37	67.40		
350	37	2.94	58.87	58.91	0.06
	38	2.95	58.95		
400	35	2.50	50.00	48.14	2.63
	36	2.31	46.28		
450	32	2.29	45.77	45.96	0.27
	33	2.31	46.15		
500	30	2.12	42.47	42.68	0.29
	31	2.14	42.88		

c. Digested sludge

Basis: 5g of Dried Digested Sludge

Temp. °C	Exp No	Char g	Yield of Char wt.%	Average wt.%	STD
250	49	4.350	87.00	87.39	0.54
	50	4.389	87.77		
300	51	3.797	75.93	74.87	1.51
	52	3.690	73.80		
350	53	3.418	68.36	67.53	1.18
	54	3.335	66.70		
400	55	3.084	61.69	62.64	1.35
	56	3.180	63.59		
450	57	2.862	57.25	56.72	0.74
	46	2.810	56.20		
500	58	2.650	53.00	52.50	0.71
	44	2.600	52.00		

Appendix B: Calorific Values

The calculation procedure followed the operating instruction provided from manufacturer, Parr1341 Oxygen bomb calorimeter.

Example calculation:

Basis: using 2L of deionized water for measuring energy equivalent of the calorimeter

$$\frac{\{\Delta T_{totalmass} - (M_{diesel} \times \Delta T_{diesel})\} \times W}{M_{oil}}$$

$$= \frac{\{1.95^{\circ}C - (0.353g \times 4.8^{\circ}C/g)\} \times 8845J/^{\circ}C}{0.098g} = 23299J/g$$

W: energy equivalent of the calorimeter, determined under standardization,
8845 J/°C

ΔT_{diesel} : increased temperature by 1g of diesel fuel 4.8 °C/g-diesel

4.8 °C/g-diesel = 42500 J/g-diesel ÷ 8845 J/°C,

425000J/g is measured enthalpy of diesel.

A. Calorific Value of Dried Sludges

Exp No	Mass of diesel, g (a)	Mass of oil, g (b)	Total mass g (a+b)	Initial temp' °C (c)	Final temp' °C (d)	ΔT by total mass, °C (e) =(d) - (c)	ΔT by oil °C (e)- ΔT by diesel	Calorific value	Average J/g-oil	STD
								J/g		
Primary										
C1	0.353	0.098	0.451	20.22	22.16	1.95	0.259	23299		
C2	0.348	0.087	0.435	22.10	23.98	1.88	0.221	22395	22847	639
TWAS										
C3	0.356	0.144	0.500	23.55	25.57	2.02	0.323	19779		
C4	0.345	0.123	0.469	22.32	24.23	1.91	0.266	19043	19411	521
Digested										
C5	0.322	0.162	0.483	21.51	23.37	1.86	0.328	17948		
C6	0.335	0.153	0.488	23.13	25.02	1.89	0.293	16936	17442	715

B. Calorific Values of Oils

Exp No	Temp. °C	Diesel Mass g (a)	Oil Mass g (b)	Total mass g (a+b)	Temperature		ΔT Basis total mass, °C (e) = (d) - (c)	ΔT Basis oil, °C (e) - ΔT by diesel	Calorific value J/g	Average J/g-oil	STD
					Initial °C (c)	Final °C (d)					
Primary											
C7	300	0.243	0.112	0.355	23.10	24.73	1.63	0.470	37144		
C9	300	0.263	0.070	0.334	23.49	25.02	1.53	0.275	34569	35857	1821
C10	500	0.257	0.150	0.407	20.05	21.9	1.85	0.626	36789		
C12	500	0.276	0.132	0.408	19.71	21.6	1.89	0.574	38343	37566	1099
TWAS											
C14	300	0.264	0.084	0.348	22.24	23.86	1.62	0.361	37995		
C15	300	0.245	0.093	0.338	20.90	22.45	1.55	0.381	36270	37132	1220
C18	500	0.275	0.119	0.395	21.14	22.97	1.83	0.518	38361		
C20	500	0.279	0.148	0.428	21.09	23.04	1.95	0.619	36871	37616	1053
Digested											
C21	300	0.268	0.072	0.340	19.47	21.08	1.61	0.332	41055		
C22	300	0.263	0.087	0.350	21.90	23.51	1.61	0.354	36000	38528	3574
C23	500	0.283	0.124	0.406	21.51	23.4	1.89	0.543	38739		
C24	500	0.273	0.152	0.424	20.96	22.89	1.93	0.630	36709	37724	1435

C. Calorific Values of Chars

Exp No	Temp. °C	Diesel Mass g (a)	Char Mass g (b)	Total mass g (a+b)	Temperature Initial °C (c) Final °C (d)		ΔT Basis Total mass, °C (e) = (d) - (c)	ΔT Basis Char, °C (e) - ΔT by diesel	Calorific value J/g	Average J/g-oil	STD
Primary											
	300	0.389	0.090	0.479	22.45	24.510	2.06	0.209	20458		
	300	0.340	0.091	0.431	21.13	22.970	1.84	0.222	21565	21011	783
	500	0.255	0.072	0.327	26.60	27.950	1.35	0.133	16276		
	500	0.284	0.073	0.357	26.69	28.190	1.50	0.146	17704	16990	1010
TWAS											
	300	0.345	0.132	0.476	22.81	24.730	1.92	0.279	18704		
	300	0.354	0.109	0.463	23.26	25.200	1.94	0.254	20563	19634	1314
	500	0.311	0.144	0.455	27.10	28.780	1.68	0.199	12235		
	500	0.358	0.136	0.494	21.80	23.700	1.90	0.196	12682	12459	316
Digested											
	300	0.363	0.174	0.537	21.95	23.980	2.03	0.299	15218		
	300	0.334	0.112	0.446	23.54	25.340	1.80	0.207	16396	15807	833
	500	0.332	0.154	0.487	20.97	22.710	1.74	0.156	8958		
	500	0.363	0.145	0.508	21.57	23.470	1.90	0.172	10489	9723	1083

Appendix C: Elemental Analysis

A. Elemental Analysis of Dried Sludge

Sample Name	Weight (µg)	% N	% C	% H	% S	Hatch Lab ID
Primary	2.05	2.5	43.1	6.4	0.3	B04-071-004
Primary-d	3.27	2.0	41.0	5.6	0.6	B04-103-001
Primary-t	2.08	3.5	48.0	6.5	0.4	B04-103-002
Average		2.7	44.1	6.1	0.4	
TWAS	3.04	6.9	36.5	5.8	0.5	B04-071-005
TWAS-d	2.18	7.1	37.0	5.4	0.5	B04-103-003
TWAS-t	2.21	6.4	36.7	5.2	0.5	B04-103-004
Average		6.8	36.7	5.4	0.5	
Digested	2.21	4.7	31.1	4.9	0.7	B04-071-006
Digested-d	2.51	4.8	31.3	4.5	0.7	B04-103-005
Digested-t	2.85	4.8	30.9	4.5	0.7	B04-103-006
Average		4.8	31.1	4.6	0.7	

B. Elemental Analysis of Oil

Sample Name	Weight (µg)	% N	% C	% H	% S	Hatch Lab ID
Primary						
PO-300C	2.77	2.51	65.11	9.89	0.51	B04-089-001
PO-300C-d	2.53	2.82	65.23	9.33	0.50	B04-071-007
Average		2.67	65.17	9.61	0.51	
PO-500C	2.69	3.91	71.98	9.69	0.36	B04-089-017
PO-500C-d		3.91	71.95	9.57	0.30	B04-089-018
Average		3.91	71.97	9.63	0.33	
TWAS						
TO-300C	2.55	6.69	63.50	9.76	0.45	B04-089-005
TO-300C-d	2.80	6.89	62.14	9.64	0.50	B04-089-006
Average		6.79	62.82	9.70	0.47	

continue

Sample Name	Weight, μg	% N	% C	% H	% S	Hatch Lab ID
TO-500C	3.18	8.53	64.85	9.33	0.43	B04-089-007
TO-500C-d	2.92	8.53	64.27	9.40	0.42	B04-089-008
Average		8.53	64.56	9.37	0.42	
Digested						
DO-300C	2.19	5.47	69.93	9.63	0.58	B04-089-009
DO-300C-d	2.86	5.62	68.94	9.73	0.64	B04-089-010
Average		5.55	69.44	9.68	0.61	
DO-500C	2.09	6.33	74.41	9.82	1.21	B04-089-011
DO-500C-d	2.37	6.30	74.45	9.91	0.86	B04-089-012
Average		6.31	74.43	9.87	1.04	

C. Elemental Analysis of Char

Sample Name	Weight, μg	% N	% C	% H	% S	Hatch Lab ID
Primary						
PC-300C	2.02	3.33	42.38	4.11	0.86	B04-089-031
PC-300C-d	2.25	3.40	42.82	3.90	0.57	B04-089-032
Average		3.37	42.60	4.00	0.72	
PC-400C	2.133	3.93	42.16	2.97	0.39	B04-089-033
PC-400C-d	2.16	3.82	42.60	3.02	0.43	B04-089-034
Average		3.87	42.38	3.00	0.41	
PC-500C	2.55	3.73	41.35	2.05	0.27	B04-089-035
PC-500C-d	2.045	3.81	43.94	2.21	0.22	B04-089-036
Average		3.77	42.64	2.13	0.24	
TWAS						
TC-300C	2.51	6.05	34.79	3.82	0.47	B04-089-037
TC-300C-d	2.04	7.14	40.63	4.60	0.38	B04-089-038
Average		6.60	37.71	4.21	0.43	
TC-400C	2.176	5.97	33.41	3.17	0.22	B04-089-039
TC-400C-d	2.24	4.66	25.85	2.01	0.24	B04-089-040
Average		5.31	29.63	2.59	0.23	

continue

Sample Name	Weight, μg	% N	% C	% H	% S	Hatch Lab ID
TWAS						
TC-500C	2.366	5.13	26.62	1.77	0.73	B04-089-041
TC-500C-d	3.02	5.41	27.94	2.10	0.43	B04-089-042
	Average	5.27	27.28	1.93	0.58	
Digested						
DC-300C	2.174	4.84	32.77	3.72	0.72	B04-089-043
DC-300C-d	2.163	4.82	32.68	3.78	0.64	B04-089-044
	Average	4.83	32.73	3.75	0.68	
400C	2.53	3.56	25.66	2.38	0.58	B04-089-045
400C-d	2.74	3.59	25.59	2.30	0.55	B04-089-046
	Average	3.57	25.62	2.34	0.56	
DC-500C	2.01	3.18	21.39	1.21	0.43	B04-089-047
DC-500C-d	2.23	3.63	21.22	1.31	0.49	B04-089-048
	Average	3.40	21.31	1.26	0.46	

Appendix D: Yields of Oil and Char with Pretreatment

A. Pretreatment with 3M HCl

a. Primary

Basis: 5g of Dried Primary Sludge, Mass Reduction by Pretreatment: 38.2 wt.%

Temp. °C	Yield		Basis of treated		Basis of untreated		Average of untreated		STD	
	Oil g / 5g-ds	Char g / 5g-ds	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil	Char
300	1.01	3.15	20.18	63.00	12.47	38.93				
	1.00	3.30	19.93	66.00	12.32	40.79	12.39	39.86	0.11	1.31
400	1.98	2.10	39.59	42.00	24.46	25.96				
	1.99	2.15	39.86	43.00	24.63	26.57	24.55	26.27	0.12	0.44
500	1.98	1.99	39.58	39.86	24.46	24.63				
	2.00	2.01	39.95	40.10	24.69	24.78	24.57	24.71	0.16	0.10

Example Calculation: $20.18 = \{1.01/(5 \times 38.2\%)\} \times 100$, $12.47 = (1.01/5) \times 100$

b. TWAS

Basis: 5g of Dried TWAS, Mass Reduction by Pretreatment: 25.5 wt.%

300	0.96	3.66	19.17	73.10	14.28	54.46				
	0.93	3.71	18.50	74.20	13.78	55.28	14.03	54.87	0.35	0.58
400	1.55	2.63	30.91	52.54	23.02	39.14				
	1.50	2.68	29.90	53.50	22.28	39.86	22.65	39.50	0.53	0.51
500	1.65	2.39	33.06	47.79	24.63	35.61				
	1.57	2.41	31.40	48.25	23.40	35.95	24.01	35.78	0.87	0.24

c. Digested Sludge

Basis: 5g of Dried Digested Sludge, Mass Reduction by Pretreatment: 28.8 wt.%

Temp. °C	Yield		Basis of treated		Basis of untreated		Average of untreated		STD	
	Oil g / 5g-ds	Char g / 5g-ds	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil wt.%	Char wt.%	Oil	Char
300	0.82	3.92	16.34	78.40	11.63	55.82	11.27	56.11	0.52	0.40
	0.77	3.96	15.31	79.20	10.90	56.39				
400	1.25	2.93	24.98	58.57	17.79	41.70	17.96	41.39	0.24	0.44
	1.27	2.89	25.45	57.70	18.12	41.08				
500	1.53	2.66	30.57	53.24	21.76	37.91	21.42	38.05	0.49	0.20
	1.48	2.68	29.59	53.63	21.07	38.19				

B. Pretreatment with 98percent Acetic Acid

a. Primary Sludge

Basis: 5g of Dried Primary Sludge, Mass Reduction by Pretreatment: 21.8 wt.%

300	1.01	3.15	20.18	63.00	15.78	49.27	15.40	51.22	0.54	2.76
	0.96	3.40	19.20	68.00	15.02	53.18				
400	1.94	2.13	38.75	42.58	30.30	33.30	30.45	33.66	0.21	0.51
	1.96	2.18	39.13	43.50	30.60	34.02				
500	1.95	2.10	38.95	41.99	30.46	32.83	30.56	33.03	0.15	0.28
	1.96	2.13	39.22	42.50	30.67	33.24				

b. TWAS

Basis: 5g of Dried TWAS, Mass Reduction by Pretreatment: 12.4 wt.%

Temp. °C	Yield		Basis of treated		Basis of untreated		Average of untreated		STD	
	Oil g / 5g-ds	Char g / 5g-ds	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil wt.%	Char wt.%	Oil	Char
300	0.86	3.75	17.25	75.00	15.12	65.70	15.36	65.04	0.35	0.93
	0.89	3.68	17.82	73.50	15.61	64.39				
400	1.59	2.54	31.81	50.86	27.86	44.55	27.24	45.05	0.88	0.71
	1.52	2.60	30.39	52.00	26.62	45.55				
500	1.70	2.22	33.96	44.30	29.75	38.81	28.97	37.80	1.09	1.42
	1.61	2.10	32.19	42.00	28.20	36.79				

c. Digested Sludge

Basis: 5g of Dried Digested Sludge, Mass Reduction by Pretreatment: 12.2 wt.%

300	0.61	3.69	12.14	73.78	10.66	64.78	11.03	67.55	0.53	3.92
	0.65	4.01	12.99	80.10	11.41	70.33				
400	1.17	3.21	23.45	64.25	20.58	56.41	20.45	56.08	0.19	0.46
	1.16	3.18	23.14	63.50	20.32	55.75				
500	1.32	2.86	26.44	57.19	23.21	50.22	22.84	49.74	0.53	0.68
	1.28	2.81	25.59	56.10	22.47	49.26				

C. Pretreatment with 0.1M Acetic Acid**a. Primary**

Basis: 5g of Dried Primary Sludge, Mass Reduction by Pretreatment: 15.4 wt.%

Temp. °C	Yield		Basis of treated		Basis of untreated		Average of untreated		STD	
	Oil g / 5g-ds	Char g / 5g-ds	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil wt.%	Char wt.%	Oil	Char
300	0.99	3.42	19.86	68.32	16.80	57.80	16.52	58.64	0.39	1.18
	0.96	3.52	19.20	70.30	16.24	59.47				
400	1.98	2.20	39.57	43.90	33.47	37.14	32.72	36.25	1.07	1.26
	1.89	2.09	37.78	41.80	31.96	35.36				
500	1.88	1.75	37.60	35.00	31.81	29.61	32.11	29.10	0.42	0.72
	1.92	1.69	38.31	33.80	32.41	28.59				

b. TWAS

Basis: 5g of Dried TWAS, Mass Reduction by Pretreatment: 8.9 wt.%

300	0.65	3.85	13.00	77.00	11.84	70.15	12.20	68.37	0.51	2.51
	0.69	3.66	13.79	73.10	12.56	66.59				
400	1.38	2.87	27.51	57.34	25.06	52.24	25.26	50.40	0.28	2.60
	1.40	2.67	27.95	53.30	25.46	48.56				
500	1.53	2.44	30.57	48.80	27.85	44.46	28.11	42.91	0.37	2.19
	1.56	2.27	31.14	45.40	28.37	41.36				

c. Digested Sludge

Basis: 5g of Dried Digested Sludge, Mass Reduction by Pretreatment: 8.4 wt.%

Temp. °C	Yield		Basis of treated		Basis of untreated		Average of untreated		STD	
	Oil g / 5g-ds	Char g / 5g-ds	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil wt.%	Char wt.%	Oil	Char
300	0.43	4.13	8.51	82.60	7.79	75.66	8.22	74.93	0.60	1.04
	0.47	4.05	9.43	81.00	8.64	74.20				
400	1.14	3.22	22.83	64.32	20.92	58.92	20.49	57.40	0.61	2.15
	1.09	3.05	21.89	61.00	20.05	55.88				
500	1.29	2.95	25.82	59.00	23.65	54.04	24.14	54.42	0.69	0.54
	1.34	2.99	26.89	59.83	24.63	54.80				

D. Pretreatment with 3M NaOH

a. Primary Sludge

Basis: 5g of Dried Primary Sludge, Mass Reduction by Pretreatment: 53.3 wt.%

300	0.88	3.25	17.64	65.06	10.00	36.89	9.85	37.18	0.21	0.42
	0.86	3.31	17.11	66.10	9.70	37.48				
400	1.05	2.82	21.01	56.31	11.91	31.93	12.04	31.64	0.19	0.41
	1.07	2.77	21.48	55.30	12.18	31.36				
500	1.30	2.41	26.05	48.10	14.77	27.27	14.82	27.53	0.06	0.36
	1.31	2.45	26.21	49.00	14.86	27.78				

b. TWAS

Basis: 5g of Dried TWAS, Mass Reduction by Pretreatment: 12.4 wt.%

Temp. °C	Yield		Basis of treated		Basis of untreated		Average of untreated		STD	
	Oil g / 5g-ds	Char g / 5g-ds	Oil Yield wt.%	Char Yield wt.%	Oil Yield wt.%	Char Yield wt.%	Oil wt.%	Char wt.%	Oil	Char
300	0.72	3.66	14.37	73.10	12.59	64.04	12.28	64.08	0.43	0.06
	0.68	3.66	13.68	73.20	11.98	64.12				
400	1.29	2.95	25.86	59.04	22.66	51.72	22.56	52.18	0.13	0.66
	1.28	3.01	25.65	60.10	22.47	52.65				
500	1.33	2.56	26.53	51.21	23.24	44.86	23.29	45.64	0.07	1.11
	1.33	2.65	26.64	53.00	23.34	46.43				

c. Digested

Basis: 5g of Digested Dried Sludge, Mass Reduction by Pretreatment: 16.2 wt.%

300	0.57	4.05	11.42	80.92	9.57	67.81	9.75	68.39	0.25	0.82
	0.59	4.12	11.84	82.30	9.92	68.97				
400	1.11	3.43	22.29	68.66	18.68	57.54	18.85	56.42	0.24	1.58
	1.13	3.30	22.70	66.00	19.02	55.31				
500	1.16	2.99	23.28	59.80	19.51	50.11	19.64	49.40	0.18	1.01
	1.18	2.91	23.59	58.10	19.76	48.69				

Appendix E: Measurement of Phenol Adsorption Capacity

A. Char from TWAS

Basis: 50mL of phenol standard solution and 0.25g of Adsorbent

Conc. Of Standard mg/L	UV reading at 270nm	Measured Phenol mg/L	Fraction of Adsorption percent	Mass of Phenol Basis 50mL mg/50mL	Adsorption Basis 0.25g mg/0.25g	q_e mg/g	Average q_e mg/g	STD
A	b	c	$d=((a-c)/a) \times 100$	$e=a \times (50/1000)$	$f=d \times e$	$g=f \times 4$		
400°C without Pretreatment								
Blank	0.18							
50	0.80	38.8	22.4	2.5	0.56	2.2		
100	1.36	78.6	21.4	5.0	1.07	4.3		
250	3.35	220.5	11.8	12.5	1.47	5.9		
500	4.09	462.9	7.4	25.0	1.85	7.4		
Blank	0.16							
50	0.79	39.7	20.7	2.5	0.52	2.1	2.15	0.12
100	1.34	79.86	20.2	5	1.01	4.03	4.31	0.40
250	3.36	222.5	11.0	12.5	1.38	5.5	5.70	0.27
500	4.07	458.8	8.2	25.0	2.06	8.2	7.83	0.58
500°C without Pretreatment								
Blank	0.104							
50	0.62	31.6	36.9	2.5	0.92	3.7		
100	1.20	72.5	27.5	5.0	1.38	5.5		
250	3.04	203.7	18.5	12.5	2.32	9.3		
500	4.01	446.6	10.7	25.0	2.67	10.7		
Blank	0.13							
50	0.66	32.6	34.9	2.5	0.87	3.5	3.59	0.14
100	1.21	75.7	24.3	5.0	1.22	4.9	5.19	0.45
250	3.06	207.1	17.2	12.5	2.15	8.6	8.92	0.48
500	3.98	444.0	11.2	25.0	2.80	11.2	10.94	0.38

Conc. Standard mg/L	UV reading at 270nm	Measured Phenol mg/L	Fraction of Adsorption percent	Mass of Basis 50mL mg/50mL	Adsorption Basis 0.25g mg/0.25g	q_e mg/g	Average q_e mg/g	STD
A	b	c	$d = ((a-c)/a) \times 100$	$e = a \times (50/1000)$	$f = d \times e$	$g = f \times 4$		
3M HCl at 500 °C								
Blank	0.076							
50	0.53	27.0	46.0	2.5	1.15	4.6		
100	1.10	67.3	32.7	5.0	1.63	6.7		
250	2.98	201.4	19.4	12.5	2.43	9.7		
500	3.97	437.4	12.5	25.0	3.13	12.5		
Blank	0.1121							
50	0.53	24.7	50.5	2.5	1.26	5.1	4.83	0.32
100	1.05	61.6	38.4	5.0	1.92	7.7	7.2	0.52
250	2.98	198.8	20.5	12.5	2.56	10.2	9.98	0.36
500	4.01	436.0	12.8	25.0	3.20	12.8	12.66	0.20
500°C with 98percent Acetic Acid								
Blank	0.11							
50	0.51	23.3	53.4	2.5	1.33	5.3		
100	1.05	61.9	38.1	5.0	1.91	7.6		
250	2.89	192.6	23.0	12.5	2.87	11.5		
500	4.01	438.7	12.3	25.0	3.06	12.3		
Blank	0.12							
50	0.53	23.7	52.7	2.5	1.32	5.3	5.30	0.05
100	1.10	64.6	35.4	5.0	1.77	7.1	7.35	0.38
250	2.95	196.1	21.5	12.5	2.69	10.8	11.13	0.50
500	4.01	434.8	13.0	25.0	3.26	13.0	12.65	0.55

continue

Conc. of STD Solution mg/L	UV reading at 270 nm	Measured Phenol mg/L	Fraction of Adsorption percent	Mass of Basis 50mL mg/50mL	Adsorption Basis 0.25g mg/0.25g	q_c mg/g	Average q_c mg/g	STD
A	b	c	$d = ((a-c)/a) \times 100$	$e = a \times (50/1000)$	$f = d \times e$	$g = f \times 4$		
0.1M Acetic Acid at 500°C								
Blank	0.2147							
50	0.77	34.2	31.7	2.5	0.79	3.2		
100	1.31	72.7	27.3	5.0	1.37	5.5		
250	3.21	207.9	16.8	12.5	2.11	8.4		
500	4.12	445.7	10.9	25.0	2.72	10.9		
Blank	0.32							
50	0.88	34.4	31.3	2.5	0.78	3.1	3.15	0.03
100	1.44	73.9	26.1	5.0	1.30	5.2	5.34	0.18
250	3.34	209.2	16.3	12.5	2.04	8.2	8.29	0.18
500	4.23	445.6	10.9	25.0	2.72	10.9	10.88	0.02
3M NaOH at 500°C								
Blank	0.078							
50	0.64	35.0	30.0	2.5	0.75	3.0		
100	1.23	77.0	23.0	5.0	1.15	4.6		
250	3.16	214.1	14.4	12.5	1.80	7.2		
500	3.99	454.7	9.1	25.0	2.27	9.1		
Blank	0.1123							
50	0.68	35.4	29.2	2.5	0.73	2.9	2.96	0.06
100	1.26	76.2	23.8	5.0	1.19	4.8	4.68	0.11
250	3.19	213.8	14.5	12.5	1.81	7.2	7.22	0.04
500	4.02	455.6	8.9	25.0	2.22	8.9	8.97	0.13

B. Char from Digested sludge

Basis: 50mL of phenol standard solution and 0.25g of Adsorbent

Conc. of Standard Soln. mg/L	UV reading at 270nm	Measured Phenol Conc. mg/L	Fraction of Adsorption percent	Mass of Phenol Basis 50mL mg/50mL	Adsorption Basis 0.25g mg/0.25g	q_e mg/g	Average q_e mg/g	STD
A	b	c	$d=((a-c)/a) \times 100$	$e=a \times (50/1000)$	$f=d \times e$	$g=f \times 4$		
without at 400 °C								
Blank	0.169							
50	0.8645	44.33	11.34	2.50	0.28	1.13		
100	1.502	89.67	10.33	5.00	0.52	2.07		
250	3.482	230.49	7.80	12.50	0.98	3.90		
500	4.09	474.15	5.17	25.00	1.29	5.17		
Blank	0.12							
50	0.81	43.94	12.12	2.50	0.30	1.21	1.17	0.06
100	1.44	88.75	11.25	5.00	0.56	2.25	2.16	0.13
250	3.43	230.27	7.89	12.50	0.99	3.95	3.92	0.03
500	4.04	471.32	5.74	25.00	1.43	5.74	5.45	0.40
Without at 500 °C								
Blank	0.058							
50	0.57	31.28	37.44	2.50	0.94	3.74		
100	1.149	72.46	27.54	5.00	1.38	5.51		
250	3.072	209.22	16.31	12.50	2.04	8.16		
500	3.965	454.69	9.06	25.00	2.27	9.06		
Blank	0.062							
50	0.59	32.42	35.16	2.50	0.88	3.52	3.63	0.16
100	1.18	74.38	25.62	5.00	1.28	5.12	5.32	0.27
250	3.09	210.22	15.91	12.50	1.99	7.96	8.06	0.14
500	3.97	453.34	9.33	25.00	2.33	9.33	9.20	0.19

continue

Conc. of STD Solution mg/L	UV reading at 270 nm	Measured Phenol mg/L	Fraction of Adsorption percent	Mass of Phenol Basis 50mL mg/50mL	Adsorption Basis 0.25g mg/0.25g	q_e mg/g	Average q_e mg/g	STD
A	b	c	$d=((a-c)/a) \times 100$	$e=a \times (50/1000)$	$f=d \times e$	$g=f \times 4$		
3M HCl at 500 °C								
Blank	0.012							
50	0.473	27.65	44.69	2.50	1.12	4.47		
100	1.061	69.47	30.53	5.00	1.53	6.11		
250	2.98	205.95	17.62	12.50	2.20	8.81		
500	3.915	449.29	10.14	25.00	2.54	10.14		
Blank	0.025							
50	0.51	29.36	41.28	2.50	1.03	4.13	4.30	0.24
100	1.11	72.03	27.97	5.00	1.40	5.59	5.85	0.36
250	3.01	207.30	17.08	12.50	2.13	8.54	8.67	0.19
500	3.93	451.98	9.60	25.00	2.40	9.60	9.87	0.38
98percent Acetic Acid at 500 °C								
Blank	0.17							
50	0.72	33.98	32.03	2.50	0.80	3.20		
100	1.301	75.30	24.70	5.00	1.23	4.94		
250	3.161	207.59	16.97	12.50	2.12	8.34		
500	4.075	451.98	9.60	25.00	2.40	9.33		
Blank	0.165							
50	0.70	32.85	34.31	2.50	0.86	3.70	3.45	0.35
100	1.27	73.10	26.90	5.00	1.35	5.38	5.16	0.31
250	3.13	205.60	17.76	12.50	2.22	8.71	8.53	0.26
500	4.07	450.63	9.87	25.00	2.47	9.60	9.47	0.19

continue

Conc. of STD Solution mg/L	UV reading at 270 nm	Measured Phenol mg/L	Fraction of Adsorption percent	Mass of Phenol Basis 50mL mg/50mL	Adsorption Basis 0.25g mg/0.25g	q_e mg/g	Average q_e mg/g	STD
a	b	c	$d=((a-c)/a) \times 100$	$e=a \times (50/1000)$	$f=d \times e$	$g=f \times 4$		
0.1M Acetic Acid at 500 °C								
Blank	0.098							
50	0.646	33.84	32.32	2.50	0.81	3.23		
100	1.25	76.80	23.20	5.00	1.16	4.64		
250	3.124	210.08	15.97	12.50	2.00	7.98		
500	4.004	453.34	9.33	25.00	2.33	9.33		
Blank	0.2343							
50	0.79	34.25	31.51	2.50	0.79	3.15	3.19	0.06
100	1.38	76.35	23.65	5.00	1.18	4.73	4.69	0.06
250	3.27	211.00	15.60	12.50	1.95	7.80	7.89	0.13
500	4.14	454.28	9.14	25.00	2.29	9.14	9.24	0.13
3M NaOH at 500 °C								
Blank	0.098							
50	0.64	33.41	33.17	2.50	0.83	3.32		
100	1.24	76.09	23.91	5.00	1.20	4.78		
250	3.16	212.64	14.95	12.50	1.87	7.47		
500	4.006	456.05	8.79	25.00	2.20	8.79		
Blank	0.112							
50	0.68	34.91	30.18	2.50	0.75	3.02	3.17	0.21
100	1.29	78.86	21.14	5.00	1.06	4.23	4.51	0.39
250	3.19	213.77	14.49	12.50	1.81	7.25	7.36	0.16
500	4.02	457.42	8.52	25.00	2.13	8.52	8.65	0.19

Appendix F: Langmuir and Freundlich Isotherm

A. Langmuir Isotherm Analysis

a. TWAS at 500°C

C_e	q_{e-1}	q_{e-2}	$1/C_e$	$1/q_{e-1}$	$1/q_{e-2}$	Average	STD
without							
50	3.69	3.49	0.02	0.27	0.29	0.28	0.008
100	5.51	4.87	0.01	0.18	0.21	0.19	0.012
250	9.26	8.58	0.004	0.11	0.12	0.11	0.004
500	10.68	11.21	0.002	0.09	0.09	0.09	0.002
3M HCl							
50	4.60	5.05	0.02	0.22	0.20	0.21	0.010
100	6.53	7.69	0.01	0.15	0.13	0.14	0.011
250	9.72	10.23	0.004	0.10	0.10	0.10	0.003
500	12.52	12.81	0.002	0.08	0.08	0.08	0.001
98% Acetic Acid							
50	5.34	5.27	0.02	0.19	0.19	0.19	0.001
100	7.62	7.09	0.01	0.13	0.14	0.14	0.005
250	11.48	10.77	0.004	0.09	0.09	0.09	0.003
500	12.26	13.04	0.002	0.08	0.08	0.08	0.002
0.1M Acetic Acid							
50	3.17	3.13	0.02	0.32	0.32	0.32	0.002
100	5.46	5.21	0.01	0.18	0.19	0.19	0.004
250	8.42	8.17	0.004	0.12	0.12	0.12	0.002
500	10.86	10.89	0.002	0.09	0.09	0.09	0.000
3M NaOH							
50	3.00	2.92	0.02	0.33	0.34	0.34	0.005
100	4.60	4.76	0.01	0.22	0.21	0.21	0.004
250	7.19	7.25	0.004	0.14	0.14	0.14	0.001
500	9.06	8.87	0.002	0.11	0.11	0.11	0.001

b. Digested Sludge at 500°C

C_e	q_e-1	q_e-2	$1/C_e$	$1/q_e-1$	$1/q_e-2$	Average	STD
without							
50	3.74	3.52	0.02	0.27	0.28	0.28	0.009
100	5.51	5.12	0.01	0.18	0.20	0.19	0.007
250	8.16	7.53	0.004	0.12	0.13	0.13	0.005
500	9.06	9.33	0.002	0.11	0.11	0.11	0.002
3M HCl							
50	4.47	4.13	0.02	0.22	0.24	0.23	0.009
100	6.11	5.59	0.01	0.16	0.18	0.17	0.007
250	8.81	8.54	0.004	0.11	0.12	0.12	0.002
500	10.14	9.60	0.002	0.10	0.10	0.10	0.003
98% Acetic Acid							
50	3.20	3.70	0.02	0.31	0.29	0.30	0.010
100	4.94	5.38	0.01	0.20	0.19	0.19	0.008
250	8.34	8.71	0.004	0.12	0.11	0.12	0.003
500	9.33	9.60	0.002	0.11	0.10	0.10	0.003
0.1M Acetic Acid							
50	3.23	3.15	0.02	0.31	0.32	0.31	0.004
100	4.64	4.73	0.01	0.22	0.21	0.21	0.002
250	7.98	7.80	0.004	0.13	0.13	0.13	0.001
500	9.60	8.60	0.002	0.10	0.12	0.11	0.006
3M NaOH							
50	3.32	3.02	0.02	0.30	0.33	0.32	0.015
100	4.78	4.23	0.01	0.21	0.24	0.22	0.014
250	7.47	7.25	0.004	0.13	0.14	0.14	0.002
500	8.79	9.06	0.002	0.11	0.11	0.11	0.002

B. Freundlich Isotherm Analysis

a. TWAS at 500 °C

C_e	q_{e-1}	q_{e-2}	$\log C_e$	$\log q_{e-1}$	$\log q_{e-2}$	Average	STD
without							
50	3.69	3.49	1.70	0.57	0.54	0.55	0.012
100	5.51	4.87	2.00	0.74	0.69	0.71	0.027
250	9.26	7.87	2.40	0.97	0.90	0.93	0.035
500	10.68	11.21	2.70	1.03	1.05	1.04	0.011
3M HCl							
50	3.17	3.13	1.70	0.50	0.50	0.50	0.003
100	5.46	5.21	2.00	0.74	0.72	0.73	0.010
250	8.42	8.17	2.40	0.93	0.91	0.92	0.007
500	10.86	10.89	2.70	1.04	1.04	1.04	0.001
98% Acetic Acid							
50	5.34	5.27	1.70	0.73	0.72	0.72	0.003
100	7.62	7.09	2.00	0.88	0.85	0.87	0.016
250	11.48	10.77	2.40	1.06	1.03	1.05	0.014
500	12.26	13.04	2.70	1.09	1.12	1.10	0.013
0.1M Acetic Acid							
50	4.60	5.05	1.70	0.66	0.70	0.68	0.021
100	6.53	7.69	2.00	0.82	0.89	0.85	0.035
250	9.72	10.23	2.40	0.99	1.01	1.00	0.011
500	12.52	12.81	2.70	1.10	1.11	1.10	0.005
3M NaOH							
50	3.00	2.92	1.70	0.48	0.47	0.47	0.006
100	4.60	4.76	2.00	0.66	0.68	0.67	0.007
250	7.19	7.25	2.40	0.86	0.86	0.86	0.002
500	9.06	8.87	2.70	0.96	0.95	0.95	0.005

b. Digested Sludge at 500°C

C_e	q_e-1	q_e-2	$1/C_e$	$1/q_e-1$	$1/q_e-2$	Average	STD
without							
50	3.74	3.52	1.70	0.57	0.55	0.56	0.014
100	5.51	5.12	2.00	0.74	0.71	0.73	0.016
250	8.16	7.53	2.40	0.91	0.88	0.89	0.017
500	9.06	9.33	2.70	0.96	0.97	0.96	0.006
3M HCl							
50	3.23	3.15	1.70	0.51	0.50	0.50	0.006
100	4.64	4.73	2.00	0.67	0.67	0.67	0.004
250	7.98	7.80	2.40	0.90	0.89	0.90	0.005
500	9.60	8.60	2.70	0.98	0.93	0.96	0.024
98% Acetic Acid							
50	3.20	3.43	1.70	0.51	0.54	0.52	0.015
100	4.94	5.38	2.00	0.69	0.73	0.71	0.019
250	8.48	8.88	2.40	0.93	0.95	0.94	0.010
500	9.33	9.87	2.70	0.97	0.99	0.98	0.012
0.1M Acetic Acid							
50	4.47	4.13	1.70	0.65	0.62	0.63	0.017
100	6.11	5.59	2.00	0.79	0.75	0.77	0.019
250	8.81	8.54	2.40	0.94	0.93	0.94	0.007
500	10.14	9.60	2.70	1.01	0.98	0.99	0.012
3M NaOH							
50	3.32	3.02	1.70	0.52	0.48	0.50	0.020
100	4.78	4.23	2.00	0.68	0.63	0.65	0.027
250	7.47	7.25	2.40	0.87	0.86	0.87	0.007
500	8.79	9.06	2.70	0.94	0.96	0.95	0.007

C. Residual Plots with Langmuir Isotherm

Residual plot is an important method that has applications in all areas of data analysis and model building. Random distribution of residuals is better model.

a. TWAS

a) Untreated at 500°C

b) 3M HCl at 500°C

c) 98% Acetic Acid at 500°C

d) 0.1M Acetic Acid at 500°C **e) 3M NaOH at 500°C** **b. Digested Sludge****a) Untreated at 500°C**

b) 3M HCl at 500°C **c) 98% Acetic Acid at 500°C** **d) 0.1M Acetic Acid at 500°C**

e) 3M NaOH at 500°C **D. Residual Plots with Freundlich Isotherm****a. TWAS****a) Untreated at 500°C** **b) 3M HCl 500°C**

c) 98% Acetic Acid at 500°C **d) 0.1M Acetic Acid at 500°C** **e) 3M NaOH at 500°C**

b. Digested Sludge**a) Untreated at 500°C** **b) 3M HCl at 500°C** **c) 98% Acetic Acid at 500°C**

d) 0.1M Acetic Acid at 500°C **e) 3M NaOH at 500 °C**

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