

**Impact of Operating Conditions on Thermal Hydrolysis Pre-Treated
Digestion Return Liquor**

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Abstract

Return liquor from thermal hydrolysis process (THP) can significantly add to the nitrogen load of a wastewater treatment plant (WWTP) and introduce UV quenching substances to the wastewater stream when recycled. While there are mature technologies in place to handle the inorganic nitrogen produced due to the thermal pretreatment, organic nitrogen remains a parameter of concern for utilities employing THP pretreatment. The impact of operating conditions of the THP on dissolved organic nitrogen (DON) and UV absorbance in return liquor was investigated. Operating conditions studied were (1) operating temperature (2) solids retention time (SRT) in the anaerobic digester (3) THP flash pressure (4) the effect of co-digestion of sewage sludge with food waste and, (5) polymer conditioning. Operating temperature and polymer dose had the most significant impact on DON and UV quenching. It was found that an increase in operating temperature resulted in an increase in DON, which was primarily contributed by the hydrophilic fraction. An increase in temperature also resulted in increased UV_{254} absorbance. However, this trend was not linear and the increase was more pronounced when the temperature was increased from 150°C to 170°C. Increasing flash pressure from 25 psi to 45 psi did not have a significant impact on the return liquor. However, increasing the flash pressure to 75 psi increased the DON and UV_{254} absorbing compounds. Co-digesting the sludge with food waste resulted in a slight increase in DON and a decrease in dissolved organic carbon (DOC) and UV quenching compounds. Increasing the SRT from 10 days to 15 days resulted in a slight decrease in DON but did

not have any impact on UV₂₅₄ absorbance. Overall, it can be concluded that optimizing operating conditions of thermal hydrolysis process can result in decreased DON and UV quenching compounds in the recycle stream.

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List of Abbreviations

AD: Anaerobic digestion

COD: Chemical Oxygen Demand

DON: Dissolved organic nitrogen

DON: Dissolved organic nitrogen

FA: Fulvic acids

FP: Flash pressure

HA: Humic acids

Hpi: Hydrophilic fraction

MAD: Mesophilic anaerobic digestion

MWCO: Molecular weight cut-off

SRT: Solids retention time

THP: Thermal hydrolysis process

TKN: Total Kjeldahl Nitrogen

TMDL: Total Maximum Daily Load

TN: Total Nitrogen

UF: Ultrafiltration

UV: Ultraviolet

UVT: Ultraviolet transmittance

WWTP: Wastewater treatment plant

Chapter 1 : Introduction

Research and technological advancements in the field of biosolids/sludge management have gained momentum in the last few decades. This growing interest is primarily driven by stricter regulations being passed for disposal of treated sludge, increasing hauling costs associated with its disposal, decreasing land availability and prioritizing of energy efficiency (Odegaard 2004, Pérez-Elvira et al. 2006). Pre-treatment of sludge at high pressure and high temperature is called thermal hydrolysis process (THP). This is one such technological advancement being adopted by several wastewater treatment plants across Europe and North America. THP as a pre-treatment to anaerobic digestion has been reported to achieve better cake dewaterability, increased methane production, increased digester loading rates and produce Class A bio-solids fit for land disposal (Carrère et al. 2010, Haug et al. 1978, Jolis 2008, Kepp et al. 2000, Low and Chase 1999, Neyens and Baeyens 2003, Ødeby et al. 1996). Adoption of this process has led to increasing concerns with regards to the downstream impact of THP.

The dewatered side stream from the THP (after mesophilic anaerobic digestion or MAD), also referred to as the THP return liquor, contains a higher concentration of ammonium, dissolved organic nitrogen (DON) and UV_{254} quenching substances than that from a conventional MAD process (Constantine 2006, Dwyer et al. 2008, Figdore et al. 2011, Phothilangka 2008, Wilson et al. 2011). This THP return liquor is usually recycled back to the wastewater treatment plant and can significantly impact the nitrification and total nitrogen (TN) removal performance of secondary treatment units (Constantine 2006). The biological nutrient removal (BNR) systems employed for removal of phosphorous and nitrogen in wastewater can effectively reduce dissolved inorganic nitrogen (DIN) in

the effluent with removal efficiencies of up to 95%. However, the excess DON formed during THP is mostly refractory in nature and is not effectively removed by BNR processes (Dwyer et al. 2008, Phothilangka 2008).

Although the recycled centrate contributes only about 1% of the volumetric load it can contribute up to 15-30% of the nitrogen load of the wastewater treatment plant (WWTP) (Constantine 2006). Thus, the DON being contributed by the THP return liquor could significantly impact the DON in the final effluent from the WWTP. Stricter regulations are now in place to limit the total nitrogen being released by WWTPs into surface water (USEPA 2010). Thus, minimizing the DON in THP return liquor has become important due to problems associated with eutrophication.

Subsequently, THP pre-treatment has also been reported to increase formation of recalcitrant UV quenching organic compounds in the return liquor (Dwyer et al. 2008, Neyens and Baeyens 2003, Stuckey and McCarty 1984, Wilson et al. 2011). Dwyer et al. (2008) identified these highly colored compounds formed during THP as melanoidins (brown high molecular weight polymers). Presence of these compounds in the return liquor could be of particular problem for WWTPs employing UV disinfection, as these compounds could quench the UV light and decrease the effectiveness of UV treatment.

Thus, the objective of this research is to understand the impact of the sludge treatment operating conditions on the DON and formation of UV quenching substances in the THP return liquor. The findings of this research would be helpful in further optimizing the THP to minimize the DON and the formation of UV quenching compounds being contributed by the side-stream to the downstream processes.

The impact of operating temperature on DON and UV quenching substances in THP return liquor is discussed in **Chapter 3**. Dewatered sludge samples thermally pretreated at operating temperatures of 130°, 150°C and 170°C were fractionated based on particle size and on the basis of hydrophobic nature into humic acids (HA), fulvic acids (FA) and hydrophilic fraction (Hpi). An increase in operating temperature resulted in an increase in DON, which was primarily contributed by the hydrophilic fraction. An increase in temperature also resulted in increased UV₂₅₄ absorbance. However, this trend was not linear and the increase was more pronounced when the temperature was increased from 150°C to 170°C.

The impact of varying (1) solids retention time (SRT) in the anaerobic digester (2) THP flash pressure (3) the effect of co-digestion of sewage sludge with food waste, and, (4) polymer conditioning, on DON and UV quenching substances in THP return liquor is discussed in **Chapter 4**. SRT and polymer dose had the greatest impact on DON and UV quenching compounds among the operating conditions considered. Increasing flash pressure from 25 psi to 45 psi did not have a significant impact on the return liquor. However, increasing the flash pressure to 75 psi increased the DON and UV₂₅₄ absorbing compounds. Co-digesting the sludge with food waste resulted in a slight increase in DON and a decrease in dissolved organic carbon (DOC) and UV quenching compounds. Overall, it can be concluded that optimizing operating conditions of thermal hydrolysis process can result in decreased DON and UV quenching compounds in the recycle stream.

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Chapter 2 : Literature Review

Treatment and disposal of sludge produced during treatment of wastewater is one of the major challenges faced by municipal wastewater treatment plants. These problems continue to increase with increasing hauling cost, decreasing land availability due to urbanization and stricter regulations for its treatment and application. There have been several advancements in the field of biosolids treatment over the past few decades to reduce the excess sludge produced by the activated sludge process (Low and Chase 1999, Metcalf & Eddy et al. 2003, Odegaard 2004, Wei et al. 2003, Yasui and Shibata 1994). Studies have shown that the major limitation in mechanical dewatering of polymer conditioned sludge is its inability to remove bound water (water within the flocs, molecules on the surface of solids and water of hydration) (Novak 2006, Novak and Novak 2006, Vesilind 1994). Thus, most efforts in the field of biosolids treatment have been aimed at changing the floc structure of the sludge and releasing the bacterial cell content in order to improve digestibility and dewaterability (Neyens and Baeyens 2003). The sludge pre-treatment mechanisms attempted in the past include those based on thermal treatment pre and post treatment, thermochemical treatment, chemical treatment, mechanical disintegration, freezing and thawing and biological hydrolysis with or without enzyme addition (Neyens and Baeyens 2003, Odegaard 2004).

2.1 Thermal Hydrolysis Process (THP)

Thermal hydrolysis process (THP) is a high-pressure and high temperature pretreatment of sludge prior to mesophilic anaerobic digestion (MAD). The high pressure and high temperature treatment increases the hydrolysis rate and yield, which has been identified

as the rate limiting step in anaerobic digestion (AD) of sludge (Eastman and Ferguson 1981). While high temperature thermal hydrolysis treatment technologies such as Porteous (185°C-220°C) and Zimpro (~250°C) had been employed as early as 1960s, the plants based on these technologies had to shut down due to operational problems and odors associated with treatment at such high temperatures (Neyens and Baeyens 2003). Another, THP based technology, Cambi, was introduced in the 1990s with its first plant commissioned in 1995 in Hamar, Norway (Kepp et al. 2000). Since then Cambi THP process has gained much attention in Europe and North America due to its ability to increase cake dewaterability between 60-80% and production of class A biosolids (Agency 1992, Ødeby et al. 1996). Commissioned in 2015, Blue Plains Wastewater Treatment Plant (WWTP) in Washington DC is the first THP plant in North America and the largest in the world in terms of its solids handling capacity.

Process Description

The THP is a two stage process comprising of heating and flashing. In the process, dewatered sludge is first preheated to ~97°C and homogenized in the pulper as shown in Figure 2-1. It is then passed through the reactor chamber where it is heated to a temperature of ~165°C and pressure of ~6 bar/87 psi. The retention time in the reactor chamber is about 30 minutes. Treating the sludge at 165°C for 30 minutes results in sterilization. The pressure is then gradually reduced to 1.5-2 bar prior to flashing at atmospheric pressure in the flash tank. This flashing generates shear forces causing the cell walls to rupture and release of cell content. This availability of cell biomass previously inaccessible to microorganisms results in better digestibility of the sludge. The hydrolyzed sludge is then anaerobically

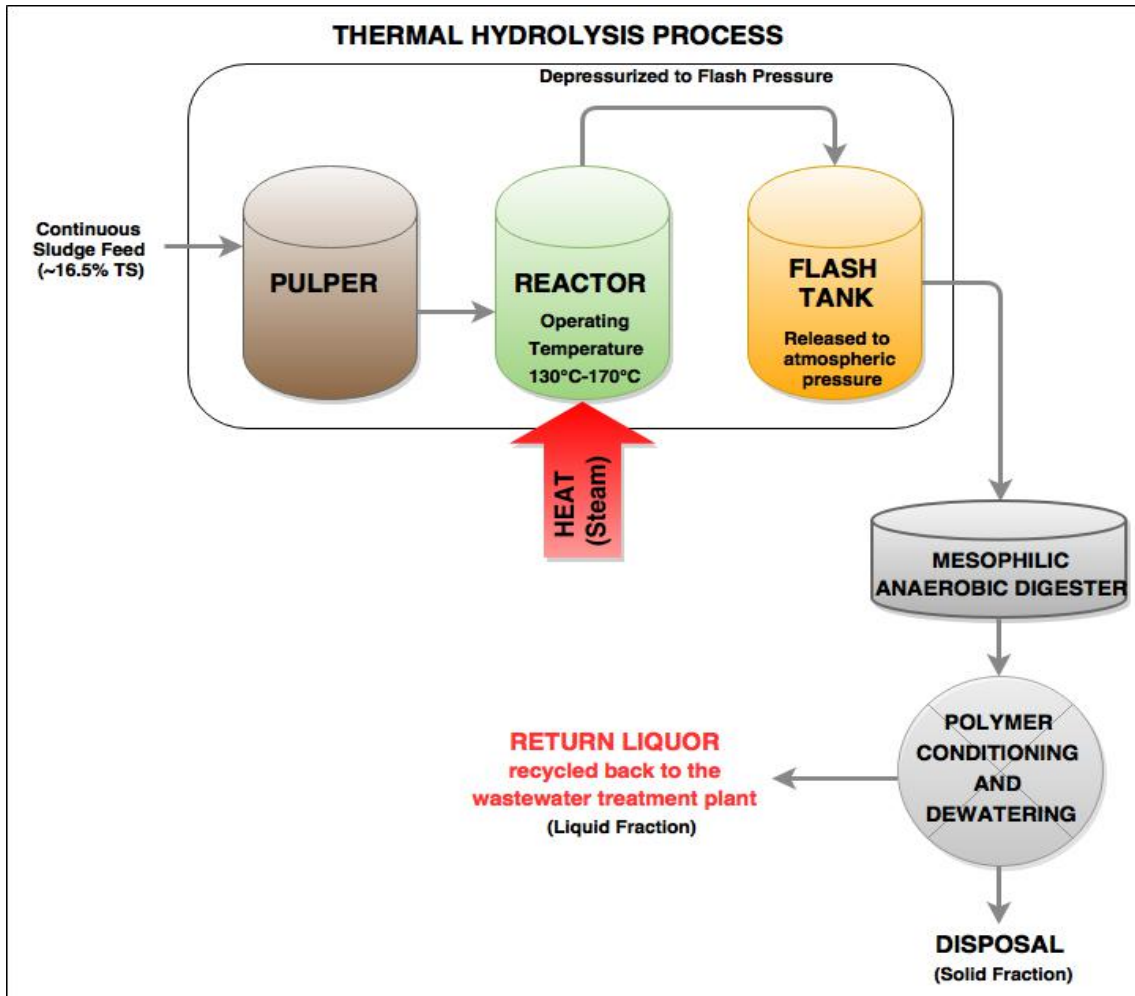


Figure 2-1: Process flow diagram of sludge treatment involving thermal hydrolysis process (THP) digested using conventional MAD (35°C-43°C). This treatment results in higher volatile solids reduction, higher digester loadings rate and higher dewatered cake solids (Cambi). The improved dewaterability and increase in cake solids in thermally hydrolysed sludge is attributed to the release of bound water as a result of degradation of extracellular polymeric substances (Neyens et al. 2004).

THP Operating Conditions

System optimization studies on THP have been primarily focused on sludge characteristics such as dewaterability, COD solubilization, methane production and solids

content of the dewatered cake. Operating temperature and time being significant parameters in driving the energy balance and operational cost have been of primary focus to the research efforts in this field (Donoso-Bravo et al. 2011).

Haug et al. (1978) in their study analyzed the impact of operating temperatures of 100°C, 135°C and 175°C, 225°C on COD solubilization in the feed, methane production and volatile solids destruction in WAS, and reported the highest yield at 175°C. They also observed a positive correlation between temperature and sludge dewaterability.

However, an increase in temperature also resulted in higher volatile acids in the effluent. They also reported a negative effect on COD solubilization at 225°C, which they suggested could be due to formation of humic substances or due to maximum achievable organic destruction by thermal treatment.

In another a study by Stuckey and McCarty (1978) where the operating temperatures ranged between 150°C and 275°C, indicated an optimum temperature of 175°C for maximum bioconvertibility of mesophilic WAS for an operating time of 60 minutes. The study also reported a decrease in bioconvertibility of nitrogen compounds and mixtures upon thermal pretreatment, in comparison to samples without thermal pretreatment resulting from conversion of biodegradable organics to refractory substances.

A study by Valo et al. (2004) found COD solubilization and volatile solids solubilization to be sensitive to the temperature of thermal pre-treatment. They proposed the optimum temperature for pre-treatment at 170°C to achieve maximum COD solubilization. They also reported an insignificant effect of operating time on COD solubilization.

Donoso-Bravo et al. (2011) also reported that operating temperature had a greater influence than operating time on COD solubilization. They also revealed a positive correlation between operating time and protein solubilization.

A study conducted by (Wilson and Novak 2009) at operating temperatures of 130°C - 220°C on primary sludge and WAS showed a dramatic increase in total ammonia nitrogen in treated sludge from 170°C to 190°C and soluble proteins from 130°C - 150°C. They also reported an increase in UV₂₅₄ absorbance with increase in operating temperature.

While most studies indicate an increase in COD solubilization with an increase in temperature, a study by Dwyer et al. (2008) reported no significant impact of change in operating temperature from 165°C to 140°C on the rate and extent of COD degradation. The study reported a significant decrease in the colored recalcitrant product resulting from thermal pretreatment with a decrease in operating temperature, which was identified as melanoidins.

These studies along with several other similar studies have concluded the optimum operating temperature to be between 160°C -180°C with 30-60 minutes of operation time Carrère et al. (2010). While most of these research efforts focused on improving digestibility of sludge and dewaterability of sludge, there is limited understanding about the impact of operating conditions on the recycled return liquor from the THP. Additionally, there is limited understanding of impact of flash pressure on the digestibility, dewaterability, and return liquor from the THP.

Recycled Sidestream

The dewatered side stream from the THP (after MAD), also referred to as the THP return liquor, contains a higher concentration of ammonium, dissolved organic nitrogen (DON) and UV_{254} quenching substances than that from a conventional MAD process (Constantine 2006, Dwyer et al. 2008, Figdore et al. 2011, Phothilangka 2008, Wilson et al. 2011). The higher ammonium concentration is due to the higher solids concentration in the feed and better degradation of N-containing organic compounds during the thermal hydrolysis (Figdore et al. 2011). Wilson et al. (2011) demonstrated in their study that the total ammonia released per mass of volatile solids destroyed was equivalent for mesophilic digestion with and without THP pretreatment. This THP return liquor is usually recycled back to the wastewater treatment plant and can significantly impact the nitrification and total nitrogen (TN) removal performance of secondary treatment units (Constantine 2006). The biological nutrient removal (BNR) systems employed for removal of phosphorous and nitrogen in wastewater can effectively reduce dissolved inorganic nitrogen (DIN) in the effluent with removal efficiencies of up to 95%. However, the excess dissolved organic nitrogen (DON) observed during THP is mostly refractory in nature and is not effectively removed by BNR processes (Dwyer et al. 2008, Phothilangka 2008). Simulations by Phothilangka (2008) indicate that increasing the THP temperature beyond 170°C can significantly increase the refractory organics produced which is similar to observations made by (Haug et al. 1978).

Although the recycled centrate contributes about 1% of the volumetric load it can contribute up to 15-30% of the nitrogen load (Constantine 2006). The higher DIN removal efficiencies in the return liquor result in DON being the major contributor to the

total nitrogen concentration in the effluent. Past studies indicate that DON can contribute between 20-85% of the TN in the effluents (Bronk et al. 2010, Dwyer et al. 2008, Pagilla 2006, Pehlivanoglu-Mantas and Sedlak 2006, Qasim 1999, Shouliang et al. 2013) making it important to study the impact of THP on DON in the recycled stream.

Additionally, with the increasing popularity of UV treatment for disinfection of wastewater, the presence of UV quenching substances in the THP return liquor can significantly decrease the efficiency of the UV disinfection system (Dwyer et al. 2008, Zhao et al. 2012). Thus, making it a parameter of concern in the recycled stream.

2.2 Impact of DON in wastewater effluent

Nitrogen and phosphorus are primary nutrients responsible for eutrophication in surface water bodies. Effluents from wastewater treatment plants are major contributors of point source nutrient pollution in surface water bodies (Howarth 2008) and hence require a high degree of treatment efficiency of TN removal prior to disposal. Increasing problems of eutrophication in bays and estuaries have resulted in implementation of stricter total nitrogen (TN) limits in Total Maximum Daily Load (TMDLs) for receiving waters in the United States (EPA 2015b). DON being a significant part of the effluent TN has become an important parameter to understand. Although regulations are applicable to all forms of nitrogen in the effluent, the eutrophication potential of DON is different than that of DIN depending on its bioavailability. A review by Pehlivanoglu-Mantas and Sedlak (2006) suggests that the bioavailability of DON may vary as much as 2-70% of the total DON, with compounds such as amino acids, nucleic acids and urea present in effluents being

readily bioavailable. Bioavailability of DON can also be altered negatively or positively by photochemical reactions after being discharged to the water bodies.

Additionally, direct potable water reuse or indirect potable water reuse downstream of the wastewater discharge has the potential for forming nitrogen based disinfection byproducts (N-DBPs) when chlorine based compounds are used for disinfection in the drinking water treatment train (Pehlivanoglu-Mantas and Sedlak 2006). N-DBPs such as haloacetonitriles (HANs), haloacetaldehydes, and N-nitrosodimethylamine (NDMA) are more potent carcinogens and mutagens than the DBPs that are currently being regulated (trihalomethanes and haloacetic acids). Studies indicate that DON in wastewater effluent serves as a precursor to formation of these N-DBPs and is thus of significant concern (Krasner et al. 2009, Lee et al. 2007, Mitch et al. 2003).

2.3 Challenges with DON measurement

Several researchers have attempted characterization of compounds in DON in wastewater but have not been able to account for a large fraction (Pehlivanoglu-Mantas and Sedlak 2008, Shouliang et al. 2013). This unidentified matrix of multiple organic compounds constituting DON in wastewater makes its direct analysis difficult. Traditional approaches to indirect measurements include bulk measurements combined with ammonia and ammonium using Total Kjeldahl Method (TKN). DON is then estimated by subtracting ammonia and ammonium concentration from TKN. These indirect measurements result in higher error margins especially when higher concentrations of inorganic compounds are present. An alternative to eliminate the interference by DIN, the DIN could be distilled prior to the distillation step (Pehlivanoglu-Mantas and Sedlak

2006). However, due to larger sample volumes required for analysis using TKN method, this approach may not be feasible.

Another commonly used method for DON measurement is the persulphate method. In this method all forms of nitrogen are oxidized to nitrates and total nitrogen (TN) is analyzed using colorimetry, ion chromatography or ion selective electrode and each inorganic form is subtracted from TN. However, higher DIN concentration limits the accuracy of this method as well (APHA et al. 2012, Pehlivanoglu-Mantas and Sedlak 2006).

While dialysis pretreatment is another technique proposed by (Lee and Westerhoff 2005) for measurement of DON in surface water and drinking water, it is not suitable for wastewater application due to adsorption of organics on the membranes

As an alternate to identifying individual compounds comprising of the DON fraction, characterization based on size and hydrophobicity has been widely used by researchers. Hydrophobicity is determined by segregating the hydrophobic compounds or humic substances and hydrophilic compounds (non-humic substances). Humic substances are poly-functional high molecular weight compounds formed by disintegration of plant and microbial tissues and/or products of their biochemical and chemical transformations (IHSS 2007). Methods developed by Leenheer (1981) and Thurman and Malcolm (1981) have been extensively used by researchers to isolate humics, fulvics and hydrophilic fractions in wastewater and landfill leachates. Aquatic humic substances have been long identified as a concern due to their potential of forming DBPs (Rook 1974) and are thus

of interest to researchers studying the humics in DON fractions and of relevance to this study.

Ultrafiltration (UF) has been widely used for size based characterization of dissolved organic matter in water and wastewater (Kilduff and Weber 1992, Tadanier et al. 2000). Ultrafiltration membranes are classified by molecular weight cut-offs (MWCO), which is determined by its capability to reject macromolecules of a given size. Understanding of the size distribution of DON can give important insight into the structural characteristics and its treatability.

2.4 Specific Ultraviolet Absorbance (SUVA) in THP return liquor

UV absorbance at wavelength of 254 nm indicates the presence of aromatic compounds and unsaturated double bonds. Specific UV absorbance at 254 nm ($SUVA_{254}$) is also used to determine aromaticity of DOM (Edzwald et al. 1985). SUVA is determined by normalizing the UV absorbance at 254 nm by the non-purgeable organic carbon (NPOC)/total organic carbon (TOC). Thus it has been used as a bulk parameter surrogate for TOC and DBP precursors (Kitis et al. 2001) A study by (Weishaar et al. 2003) shows that although SUVA is not a good indicator of DOC as a whole, a strong co-relation exists between SUVA and reactivity of aquatic humic substances. It is thus a significant parameter indicative of DBP formation potential (Kitis et al. 2001) .

2.5 Co-Digestion

Co-digestion is a process of digesting two substrates together, mostly involving digestion of municipal solid waste or agricultural waste with energy rich organic waste. The energy rich organic fraction mainly comprises of food waste and fats, oils and grease which is easily degradable (EPA 2015a). Food waste primarily consisting of waste from household kitchens, cafeterias, canteens, restaurants, commercial or institutional establishments, etc. is diverted from the landfills and sewer lines to the anaerobic digesters at municipal WWTP. Co-digestion is gaining popularity among utilities due its potential benefits of improved digestibility, increased methane production, toxicity dilution and improved balance of nutrients in the digesters (Dai et al. 2013, EPA 2015a). Addition of food waste results in improving the C:N ratio in the digester, due to the high C:N ratio in the food waste resulting in high methane yields. The additional energy production makes for an economically lucrative way for utilities with excess digester capacity to reduce their carbon footprint (Iacovidou et al. 2012).

As more and more utilities explore the co-digestion option, several research efforts are being focused towards understanding its feasibility and operation. While there is sizeable amount of literature available to understand various aspects of co-digestion of food waste with sludge from wastewater treatment plants, very little is understood about its impact on the recycled liquor stream from the digesters. Thus, as part of this study the impact of co-digestion on thermally pre-treated return liquor from mesophilic digestion is studied.

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Chapter 3 : Impact of operating temperature on dissolved organic nitrogen and UV absorbance in thermal hydrolysis pretreated digestion return liquor

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Abstract

Return liquor from thermal hydrolysis process (THP) can significantly add to the nitrogen load of a wastewater treatment plant (WWTP) and introduce UV quenching substances to the wastewater stream. While there are mature technologies in place to handle the inorganic nitrogen produced due to the thermal pretreatment, organic nitrogen remains to be a parameter of concern for utilities employing THP pretreatment. In this study, the impact of operating temperature of THP on dissolved organic nitrogen (DON) and UV absorbance in return liquor was studied at operating temperatures of 130°C, 150°C and 170°C. An increase in operating temperature resulted in an increase in DON, which was primarily contributed by the hydrophilic fraction. An increase in temperature also resulted in increased UV₂₅₄ absorbance. However, this trend was not linear and the increase was more pronounced when the temperature was increased from 150°C to 170°C.

Keywords: dissolved organic nitrogen, UV absorbance, thermal hydrolysis, return liquor, operating temperature

3.1 Introduction

Anaerobic digestion is the oldest technique for treatment of sludges produced from wastewater treatment processes. The primary purpose of anaerobic digestion is stabilization of solids and vector inactivation prior to disposal (Metcalf & Eddy et al. 2003). There have been several advancements in the field of biosolids treatment over the past few decades to reduce the excess sludge produced by the activated sludge process (Low and Chase 1999, Metcalf & Eddy et al. 2003, Odegaard 2004, Wei et al. 2003, Yasui and Shibata 1994). The thermal hydrolysis process (THP) is one of them. THP is a high-pressure and high temperature pretreatment of sludge prior to mesophilic anaerobic digestion (MAD). The high pressure and high temperature treatment increases the hydrolysis rate and yield, which has been identified as the rate limiting step in anaerobic digestion (AD) of sludge (Eastman and Ferguson 1981). This treatment results in higher volatile solids reduction, higher digester loadings rate and higher dewatered cake solids.

The dewatered side stream from the THP (after MAD), also referred to as the THP return liquor, contains a higher concentration of ammonium, dissolved organic nitrogen (DON) and UV_{254} quenching substances than that from a conventional MAD process (Constantine 2006, Dwyer et al. 2008, Figdore et al. 2011, Phothilangka 2008, Wilson et al. 2011). The higher ammonium concentration is due to the higher solids concentration in the feed and better degradation of N-containing organic compounds during the thermal hydrolysis (Figdore et al. 2011). Wilson et al. (2011) demonstrated in their study that the total ammonia released per mass of volatile solids destroyed was equivalent for mesophilic digestion with and without THP pretreatment. This return liquor is usually

recycled back to the wastewater treatment plant and can significantly impact the nitrification and total nitrogen removal performance of secondary treatment units (Constantine 2006). The biological nutrient removal (BNR) systems employed for removal of phosphorous and nitrogen in wastewater can reduce the dissolved inorganic nitrogen (DIN) in the wastewater effectively. However, the DON is mostly refractory in nature and is not effectively removed by BNR processes (Dwyer et al. 2008, Phothisilangka 2008). This results in DON being the major contributor to the total nitrogen concentration in the wastewater effluent (Bronk et al. 2010, Pagilla et al. 2006).

Effluents from wastewater treatment plants are major contributors of point source nutrient pollution in surface water bodies (Howarth 2008) and hence require a high degree of treatment efficiency of TN removal prior to disposal in water bodies. Increasing problems of eutrophication in bays and estuaries have resulted in implementation of stricter total nitrogen (TN) limits in Total Maximum Daily Load (TMDLs) for receiving waters in the United States (EPA 2015b). DON being a significant part of the effluent TN, especially in plants employing THP systems, has become an important parameter to understand. Additionally, with the increasing popularity of UV treatment for wastewater effluent disinfection, the presence of UV quenching substances in the THP return liquor can significantly decrease the efficiency of the UV disinfection system (Dwyer et al. 2008, Zhao et al. 2012). Thus, UV quenching compounds have become parameter of concern in the recycled stream.

System optimization studies on THP have been primarily focused on sludge characteristics such as dewaterability, COD solubilization, methane production and solids content in the cake. Operating temperature and time being significant parameters in

driving the energy balance and operational cost, have been of primary focus to the research efforts in this field (Donoso-Bravo et al. 2011, Neyens and Baeyens 2003). However, limited literature is available on the effect of operating temperature on DON and UV quenching compounds. Pagilla et al. (2006) identified research on characteristics of wastewater derived DON as one of the major gaps that need to be filled.

This study focuses on analysis and molecular weight based characterization of DON and UV quenching compounds in the THP return liquor for different operating temperatures of the THP. The results will provide useful information for optimization of operating temperature for THP with respect to DON and UV quenching substances and the possible treatment options that could be explored based on their molecular weight distribution and hydrophobic characteristic.

3.2 Materials and Methods

THP Return Liquor

The samples were received from the THP pre-treated anaerobic sludge treatment pilot plant at the Blue Plains Advanced Wastewater Treatment Plant, Washington DC, USA. The thermal hydrolysis reactor at the pilot plant was operated at three different temperature conditions: 130°C, 150°C and 170°C. Thermally hydrolyzed sludge was then transported to the laboratory at Bucknell University, Pennsylvania, USA where it was anaerobically digested at 38°C at a SRT of 15 days. This was followed by transportation of the digested sludge to the laboratory at Virginia Tech, Virginia, USA. This sludge was conditioned with polymer Clarifloc-3258 followed by dewatering using a funnel fitted with a belt filter cloth. Filtrate from the dewatering process for these three operating

temperatures was then analyzed. The pH of the samples was decreased using laboratory grade hydrochloric acid to 6.7 ± 0.3 to reduce volatilization of ammonia prior to fractionation.

Molecular size based fractionation

The return liquor samples were centrifuged at 4000 rpm for 30 minutes to aid the subsequent filtration process. The centrate was passed through 0.45 μ m cellulose nitrate membrane (Millipore, Billerica, MA) to separate the dissolved solids fraction from the suspended solids fraction. The filtrate obtained was then sequentially passed through ultrafiltration (UF) membrane disks (Millipore, Billerica, MA) of molecular weight cut-off (MWCO) 100k Da, 3k Da and 1k Da using 200 mL stirred dead end batch UF cells (Amicon model # 8200). The UF cells were pressurized at 120 kPa using nitrogen gas.

Fractionation based on hydrophobicity

The samples were characterized into Humic Acids (HA), Fulvic Acids (FA) and Hydrophilic Acids (Hpi) based on the methods described by (Leenheer 1981, Thurman and Malcolm 1981). The samples were first acidified to pH 2 using concentrated hydrochloric acid to precipitate the HAs. The precipitated HA fraction was settled by centrifuging (make) the acidified sample for 30 minutes. The precipitated HAs were re-dissolved in 0.1 M sodium hydroxide (NaOH) solution and used for analysis. The supernatant from the centrifuged fraction was passed through a column of XAD-8 resin (currently Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO). The FAs were sorbed on the resin and re-dissolved in 0.1 M NaOH solution. The eluted fraction contained the Hpi. Cleaning of XAD-8 resin and preparation of the column prior to fractionation was

carried out following the procedures described by (Leenheer 1981). The three fractions were subject to size-based fractionation as described in the previous section.

Analysis

Organic nitrogen in the samples was estimated by subtracting ammonium from total Kjeldahl nitrogen. Total Kjeldahl nitrogen was measured by semi micro-Kjeldahl Method per Standard Method 4500-C (APHA et al. 2012). Ammonium was determined by the salicylate method (Hach, Loveland, CO) and measured using a spectrophotometer (DR 2800, Hach, Loveland, CO).

Total Organic Carbon (DOC) was analyzed using a high temperature combustion DOC analyzer (Shimadzu TOC- 5000A, Japan). The UV absorbance at 254 nm (UV_{254} abs) was measured with a spectrophotometer (Beckman Coulter, Brea, CA). The samples were diluted 50 times prior to UV_{254} absorbance and TOC measurement. Specific UV absorbance at 254 nm (SUVA) is calculated as UV_{254} abs divided by TOC. UV transmittance (UVT) was calculated using the relation: UV_{254} abs = $2 - \log_{10}$ UVT.

HA-DON, FA-DON, Hpi-DON refers to DON in humic acids fraction, fulvic acids fraction and hydrophilic acids fraction respectively. Similarly, HA-DOC, FA-DOC, Hpi-DOC refers to DOC in humic acids fraction, fulvic acids fraction and hydrophilic acids fraction respectively.

Statistics

Data was graphed using Microsoft Office Excel 2011. Linear regression analysis was performed using JMP 11.0.0 (SAS, Cary, NC) and is provided in Appendix B.

3.3 Results

Impact of operating temperature on DON

From Figure 3-1 it is observed that DON concentration in the samples (0.45 μm fraction) increase with increase in operating temperature. Linear regression analysis of DON yields a linear trend between 130°C and 170°C with a R^2 value of 0.997. However, no such trend is observed between 100k, 3k and 1k Da fraction sizes among these samples.

At 130°C and 150°C almost all the DON produced is less than 100k Da in size. However, at 170°C, 51% of the DON is greater than 100k Da. Significant removal of DON occurs when passed through 1k Da UF membranes for temperatures of 130°C (62%), 150°C (62%) and 170°C (83%). The highest DON <1k Da is produced at 150°C, which could be difficult to remove due to its small size.

Characterization of DON based on hydrophobic nature

Figure 3-2 shows the size-based distribution of HA-DON. While there is no linear trend observed with respect to temperature, there is decrease in HA-DON when the temperature is increased from 130°C to 150°C and 170°C. At higher temperatures of 150°C and 170°C, the HA-DON is primarily >1k Da in size with removal of 84% and 90% respectively when passed through 1k Da MWCO UF.

A significant increase in FA-DON is observed when temperature is increased from 130°C to 150°C (135%) as shown in Figure 3-3. Increase in temperature beyond 150°C does not appear to have a significant impact on the FA-DON with an increase of only 13%. The trend observed in FAs is opposite to that observed in HA fraction. Increase in DON in

combined humics fraction (FA+HA) is 16% (10 mg/L) and 6% (4 mg/L) between 130 °C and 150°C and 150°C and 170°C. This increase is less drastic than that observed in FA-DON indicating that the increase in temperatures results in conversion of higher molecular weight HA to lower molecular weight FA.

MWCO based distribution of Hpi shown in Figure 3-4, clearly indicates an increase in Hpi-DON with increase in temperature. This linear trend is similar to that observed in the total DON (combined HA, FA and Hpi) ($R^2=0.954$). For temperatures of 170, 58% of the Hpi-DON is >100k Da. At operating temperature of 150, 53% of Hpi-DON is in the 100 k Da-3k Da fraction and 38% is <1k Da.

Impact of operating temperature on DOC

Figure 3-5 shows an increase in DOC with increase in temperature between 130°C and 170°C. The increase in DOC with increase in temperature is not linear as observed with DON. The increase in DOC observed between 130°C and 150°C is only 7% in comparison to the increase of 52% between the operating temperature of 150°C and 170°C.

Size distribution trend across DOC fractions is similar at 130°C and 150°C. Nearly half of the DOC present in the return liquor at 130°C (51%), 150°C (44%) and 170°C (56%) is in the fraction <1k Da. Similar size distribution trends are observed in the FA-DOC and Hpi-DOC fraction as shown in Figure 3-7 and Figure 3-8, respectively.

The HA-DOC and FA-DOC trends across the varying temperatures are similar to that observed for DON i.e. HA-DOC has an inverse correlation with temperature as seen in

Figure 2(b) and FA-DOC has a positive correlation with temperature as shown in Figure 2(c). This suggests conversion of high molecular weight compounds to smaller MW compounds (FAs). However, it is to be noted that there is decrease in humics (HA+FA) from 130°C to 150°C of about 4% whereas the increase between 130°C and 170°C is about 45%. While, the decrease could be attributed to the variations in measurement, the increase is significant and indicates increase in formation of Humics-DOC when the temperature is increased to 170°C.

About 73% 48% and 63% humics are smaller than 1k Da in size at 130°C, 150°C and 170°C, respectively indicating that humics produced during THP are significantly smaller in size.

Similar to DON, the increase in DOC is primarily attributed to the increase in Hpi as shown in Figure 2(d) thus indicating production of recalcitrant organic compounds with increase in operating temperature.

UV₂₅₄ abs, SUVA and UVT

Figure 3-9 shows the UV₂₅₄ absorbance of size-based fractions for the different operating temperatures. A clear increasing trend is observed in UV₂₅₄ abs with increase in operating temperature with an increase of 29% and 73% at 150°C and 170°C, respectively. The trend is similar to that observed with TOC indicating increase in UV quenching compounds with increasing temperature. At 130°C the presence of UV quenching substances is almost evenly distributed across all size fraction. However, with increasing temperature there is an increase in UV quenching substances between size 0.45 µm and 3k Da.

Table 3-1 shows the SUVA values for the same fractions. The increase in SUVA with temperature at 150°C and 170°C is 18% and 26% in comparison to that observed at 130°C indicating an increase in aromaticity of organic compounds with increase in temperature. While, there is an increase in SUVA in all fractions except the fraction with MWCO <1k Da across the temperature increase, there is no trend observed among these values.

Figure 3-11 shows the UV transmittance vs. dilution for return liquor at the different operating temperatures. The graph is constructed to indicate the dilution necessary for efficient working of UV disinfection systems employed at the end of wastewater treatment train when the return liquor is recycled back into the wastewater treatment train. The dilution of return liquor required to achieve UVT of 67% would be 41%, 52% and 81% for 130°C, 150°C and 170°C respectively.

Correlation between DON, DOC and UV₂₅₄ abs

Figure 3-10 shows the correlation between DON, DOC and UV₂₅₄ abs for all fractions across the three operating temperature conditions. The linear correlation between DON and UV₂₅₄ abs is not very strong with $R^2=0.74$ but UV₂₅₄ abs could be used as a bulk parameter to indicate DON trend when expected DON is less than 150 mg/L as the correlation is stronger at lower concentrations. On the other hand, correlation between DOC and UV₂₅₄ abs is stronger than that for DON ($R^2=0.83$).

3.4 Discussion

A positive linear correlation exists between temperature and DON in the return liquor from the THP. These results are somewhat contradictory to those observed by (Dwyer et al. 2008). They observed an increase in DON in sludge with increase temperature between 140°C and 155°C. However, the increase plateaued beyond 155°C and 165°C and the increase was not as dramatic as observed in the samples used in this study. There could be three probable reasons contributing to this increase in DON: (1) It could be due to increased cell lysis at higher temperature resulting in cell content and cell wall containing organically bound N being released into the fluid and its partial metabolism, (2) decreased bio-convertibility with increase in temperature as observed by (Stuckey and McCarty 1978), or (3) production of poorly degradable compounds with an increase in temperature (Phothilangka 2008). While, these factors are not mutually exclusive, further studies would be required to determine the exact mechanism(s)/process(es) responsible for the increase in DON.

An increase in DON with temperature results in increase of DON greater than 1k Da in size. At operating temperature of 170°C, 51% of DON is greater than 100k Da in size. Thus, for THP systems operated at 170°C, a membrane bio-reactor with MWCO of 100k Da could be explored for treatment of DON in THP return liquor. Operating at THP temperature of 150°C could result in a higher concentration of small sized (<1k Da) DON in the return liquor. This could be difficult to remove through coagulation (bioflocculation), and/or membrane bioreactors due to operational problems associated with operating membranes with small MWCOs.

Although there exists a positive correlation between DOC and temperature, it does not follow a linear trend as observed in DON. Thus, DOC/DON ratio decreased from 4.58 at 130 to 2.57 and 2.54 at 150°C and 170°C indicating presence of more organically bound nitrogen at higher temperatures.

An increase in DON and DOC with an increase in temperature is mostly contributed by the Hpi fraction, which follows the same trend across all fractions as that of total DON and total DOC. A decrease in HA-DON and increase in FA-DON with increase in temperature between 130°C and 170°C could indicate breakdown of high molecular weight HAs into low molecular weight FAs.

The trends observed in HA-DOC and FA-DOC fractions are similar to that of HA-DON and FA-DON. The increase in DOC (45%) in humics is much higher at 170°C from 150°C, with no increase in HA-DOC. This indicates an increase in formation of FAs with increase in temperature. An increase in FA-DON (13%) for the same temperature change is much lower indicating formation of humic DON with a higher DOC/DON ratio.

A positive correlation between temperature and UV_{254} abs observed in this study is similar to the results observed by Wilson et al. (2011) for operating temperatures of 150°C and 170°C and Dwyer et al. (2008). This could be due to increase in production of highly colored recalcitrant melanoidins as reported by Dwyer et al. (2008).

The samples indicate an increase in SUVA values with increase in temperature at 150°C (18%) and 170°C (26%). However, this increase is not as dramatic as that observed in UV_{254} abs of 29% and 73% at 150°C and 170°C respectively. This indicates that while

there is an increased production of UV quenching substances with increase in temperature, these compounds do not have high aromaticity.

While this study gives an understanding of the impact of operating temperatures on DON and UV quenching substances in the return liquor from THP, the areas of treatability and bioavailability of DON in the THP return liquor remain to be explored further.

Overall impact of return liquor

The ratio of the return liquor to the wastewater stream when recycled back to the wastewater treatment units is an important factor to be considered in the studies involving return liquor. This recycle ratio may vary from plant to plant. For the purpose of this study, which was conducted using sludge samples from Blue Plains Wastewater Treatment Plant, the recycle ratio was about 0.33% (1:300). Thus, at operating temperatures of 130°C, 150°C and 170°C the DON recycled back is 0.37 mg/L, 0.71 mg/L and 1.09 mg/L respectively for the recycle ratio of 0.33%. With effluent TN limits as low as 4.2 mg/L for the plant, this increase in DON in the return liquor with increase in THP operating temperature could have a significant impact on the effluent.

3.5 Conclusions

- Positive linear correlation exists between increase in temperature and DON between 130°C and 170°C. This increase is primarily contributed by the hydrophilic fraction of DON.
- At 170°C about 51% of DON present had MWCO greater than 100k Da.

- DOC also increases with increase in temperature and the increase is primarily contributed by the hydrophilic fraction. However, the trend is not the same as that observed for DON. The increase is much sharper between 150°C and 170°C.
- DOC/DON ratio decreases with increase in temperature i.e. more organically bound nitrogen present at higher operating temperatures.
- Increase in operating temperature resulted in break-down of of humic acids to fulvic acids. Increase in temperature from 150°C to 170°C resulted in formation of fulvic acids in addition to those that formed by degradation of humic acids. However, DOC/ DON ratio decreased in the fulvic acids fraction from 150°C and 170°C
- There is an increased production of UV quenching substances with increase in temperature.
- For a recycle ratio of 0.33%, the DON contributed by the return liquor to the wastewater treatment plant for operating temperature of 130°C, 150°C and 170°C could be as high as 0.37 mg/L, 0.71 mg/L and 1.09 mg/L respectively. Thus, making operating temperature an important operating parameter to be considered.

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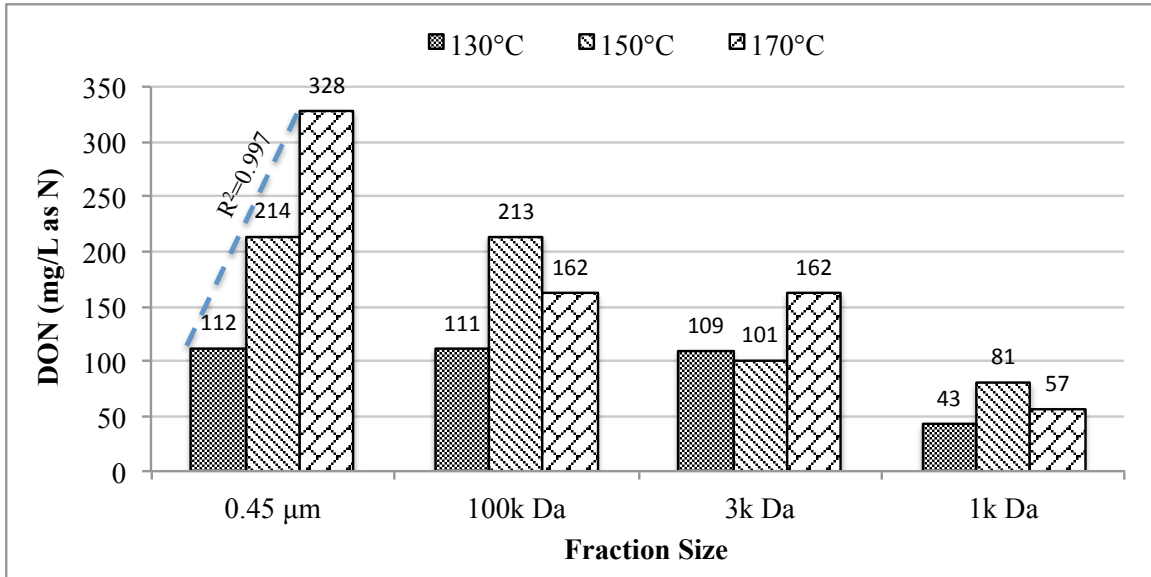


Figure 3-1: Molecular size based distribution of dissolved organic nitrogen in thermal hydrolysis/anaerobic digestion return liquor for different operating temperatures

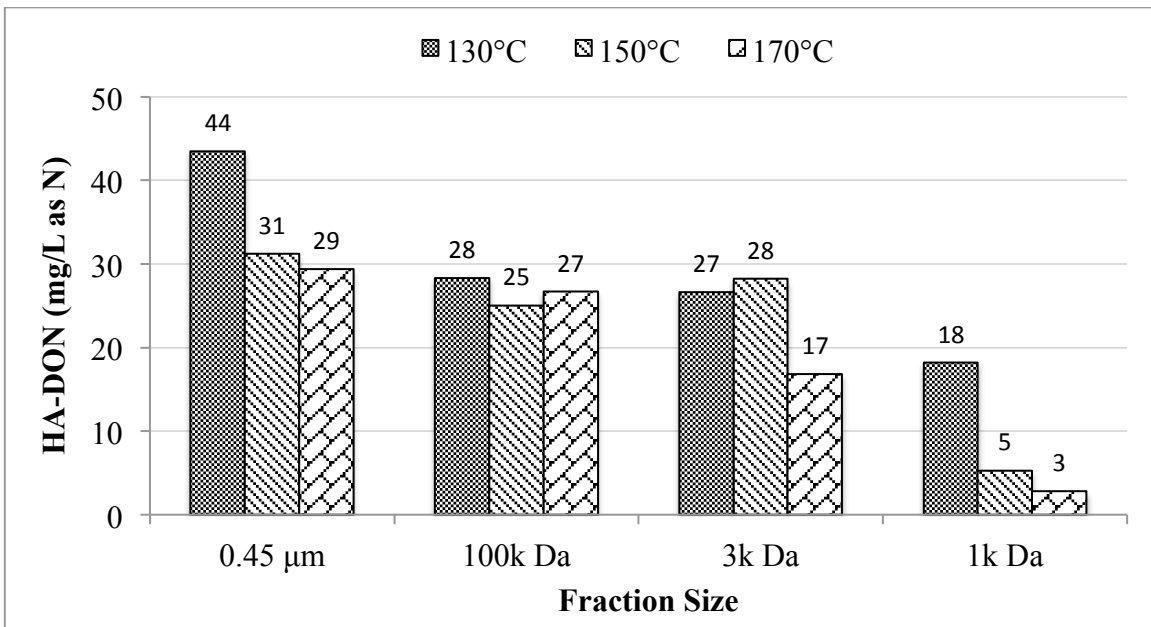


Figure 3-2: Molecular size based distribution of dissolved organic nitrogen in humic acids fraction thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

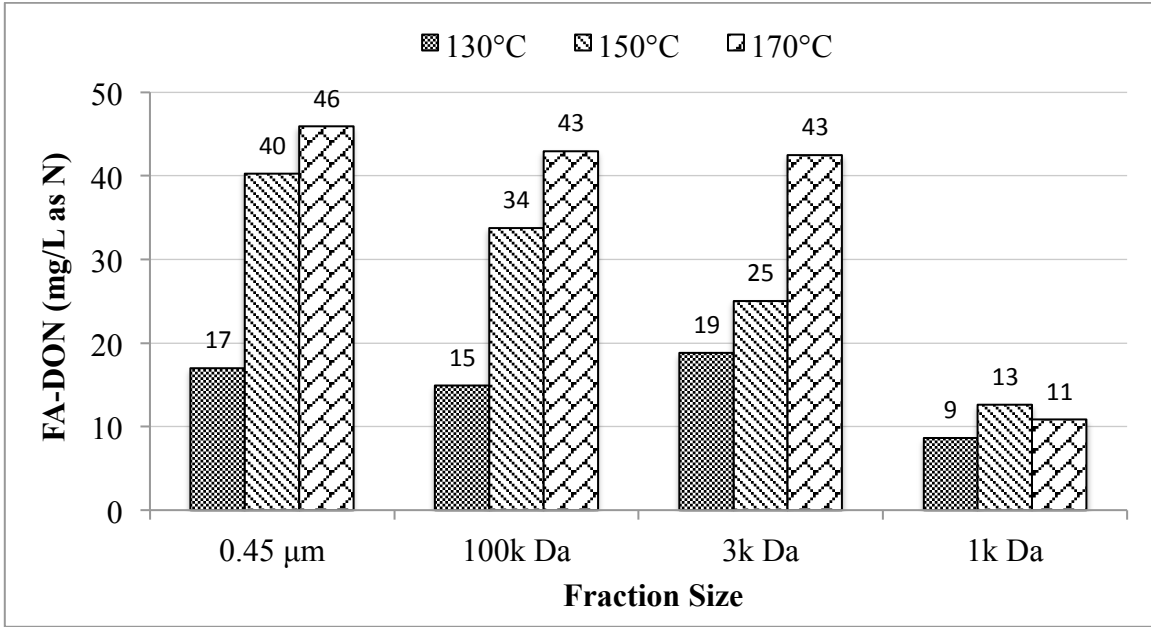


Figure 3-3: Molecular size based distribution of dissolved organic nitrogen in fulvic acids fraction of thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures.

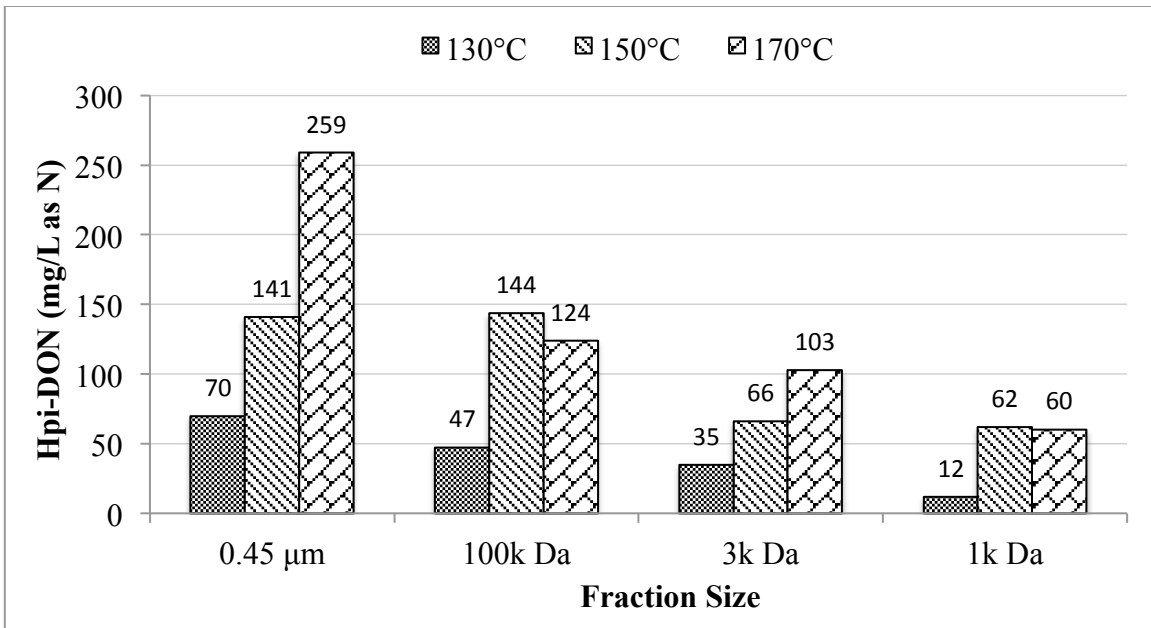


Figure 3-4: Molecular size based distribution of dissolved organic nitrogen in hydrophilic fraction of thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures.

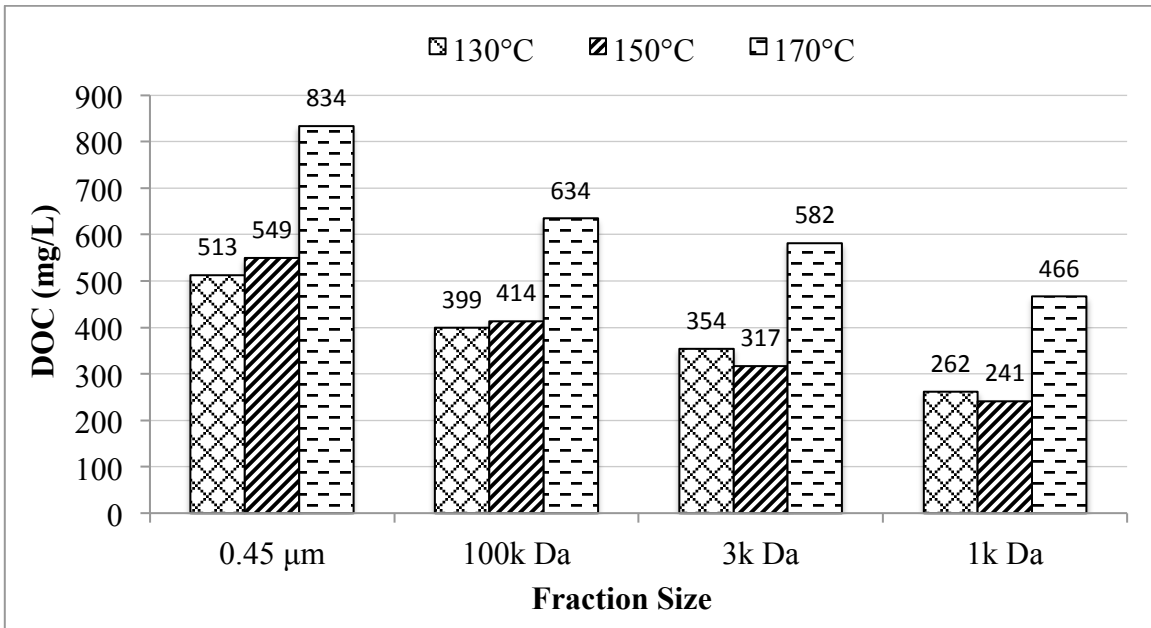


Figure 3-5: Molecular size based distribution of dissolved organic carbon in thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

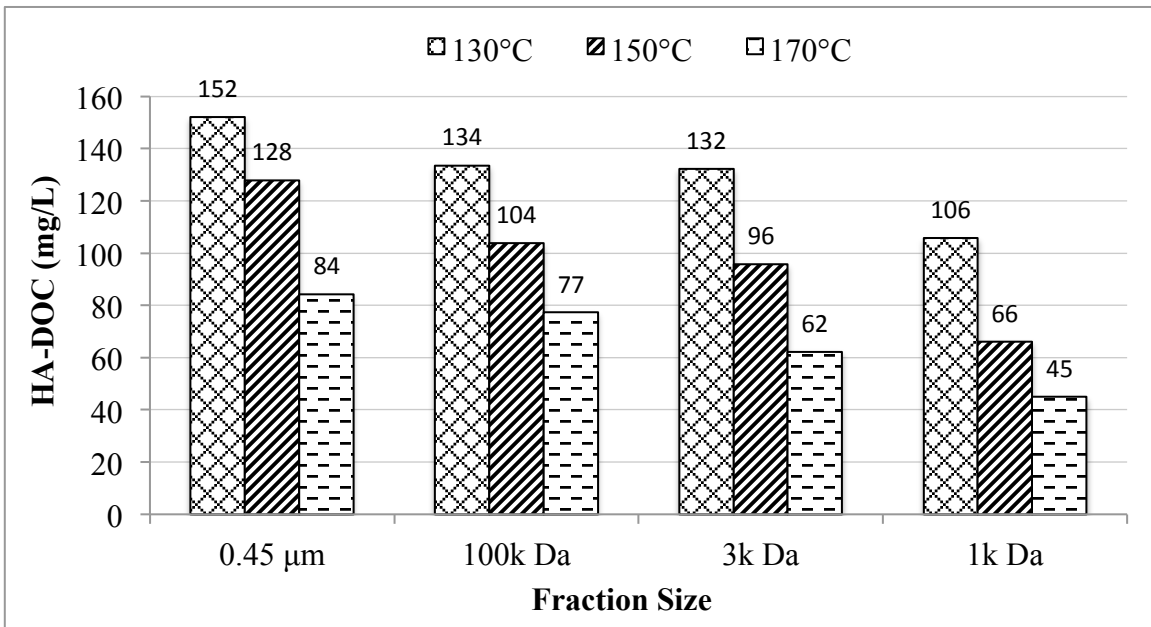


Figure 3-6: Molecular size based distribution of dissolved organic carbon in humic acids fraction of thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

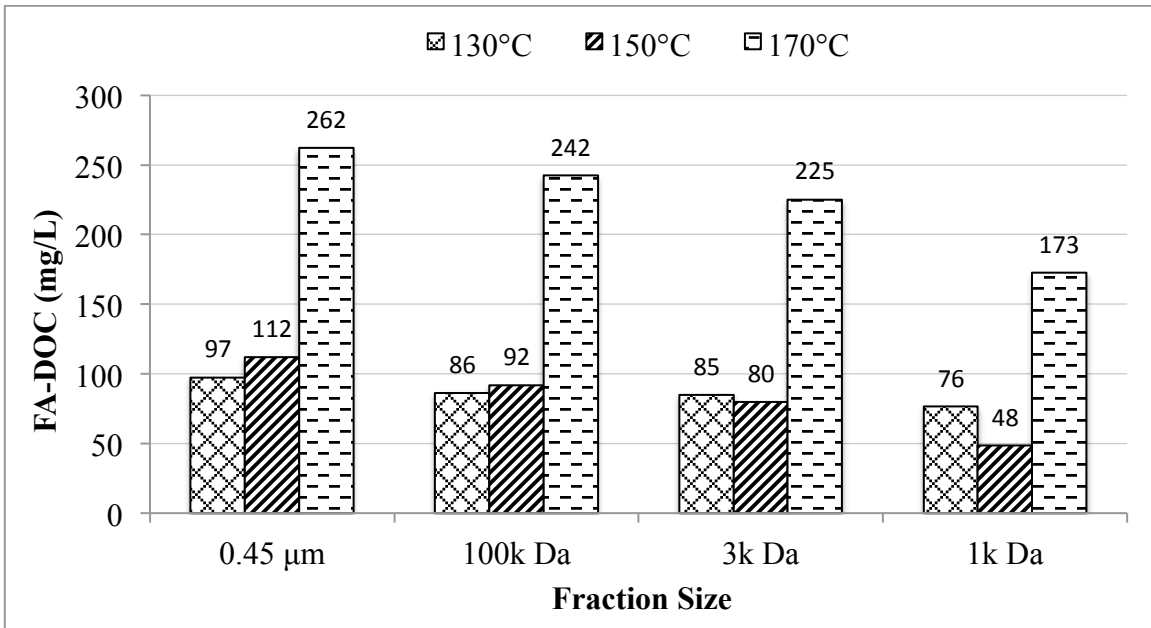


Figure 3-7: Molecular size based distribution of dissolved organic carbon in fulvic acids fraction of thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

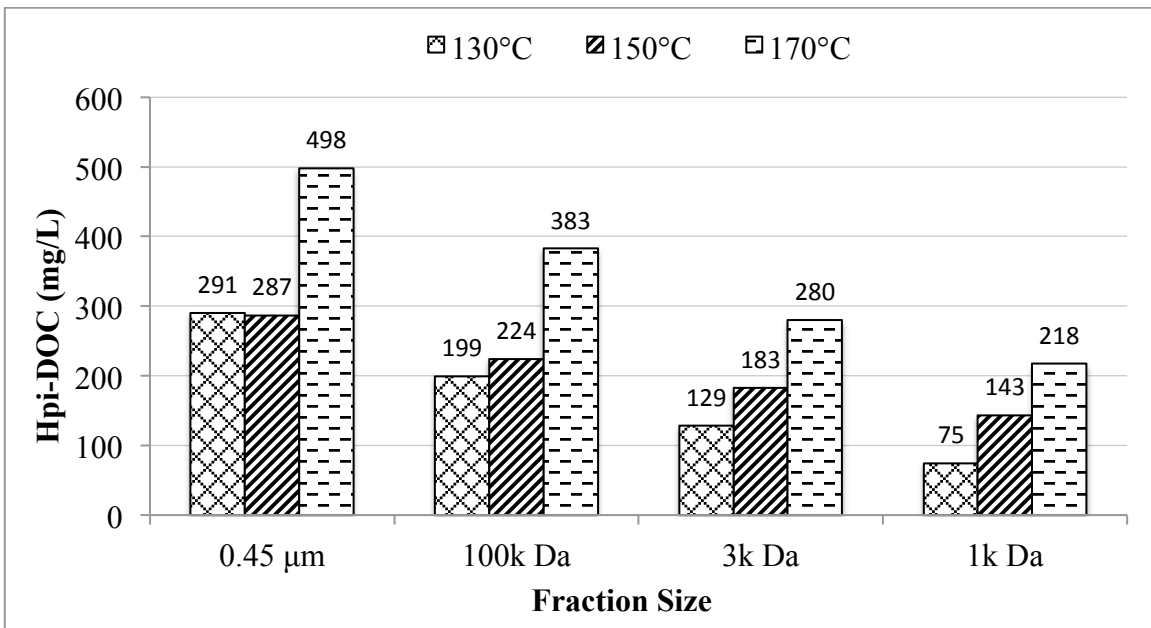


Figure 3-8: Molecular size based distribution of dissolved organic carbon in hydrophilic fraction of thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

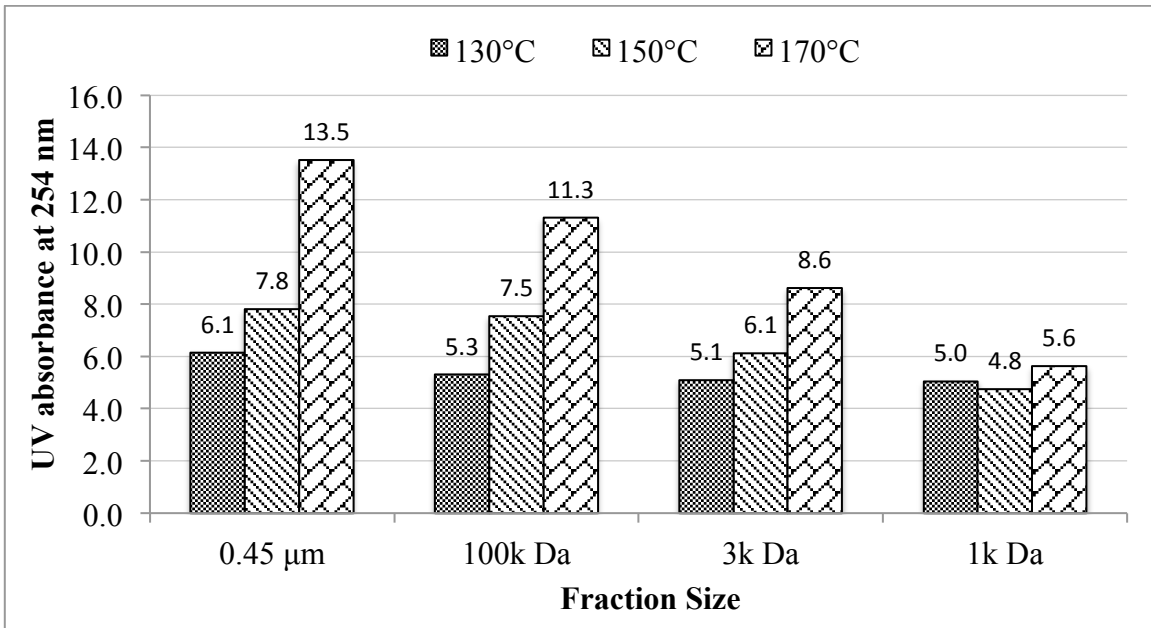


Figure 3-9: Molecular size based distribution of UV₂₅₄ absorbance in thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

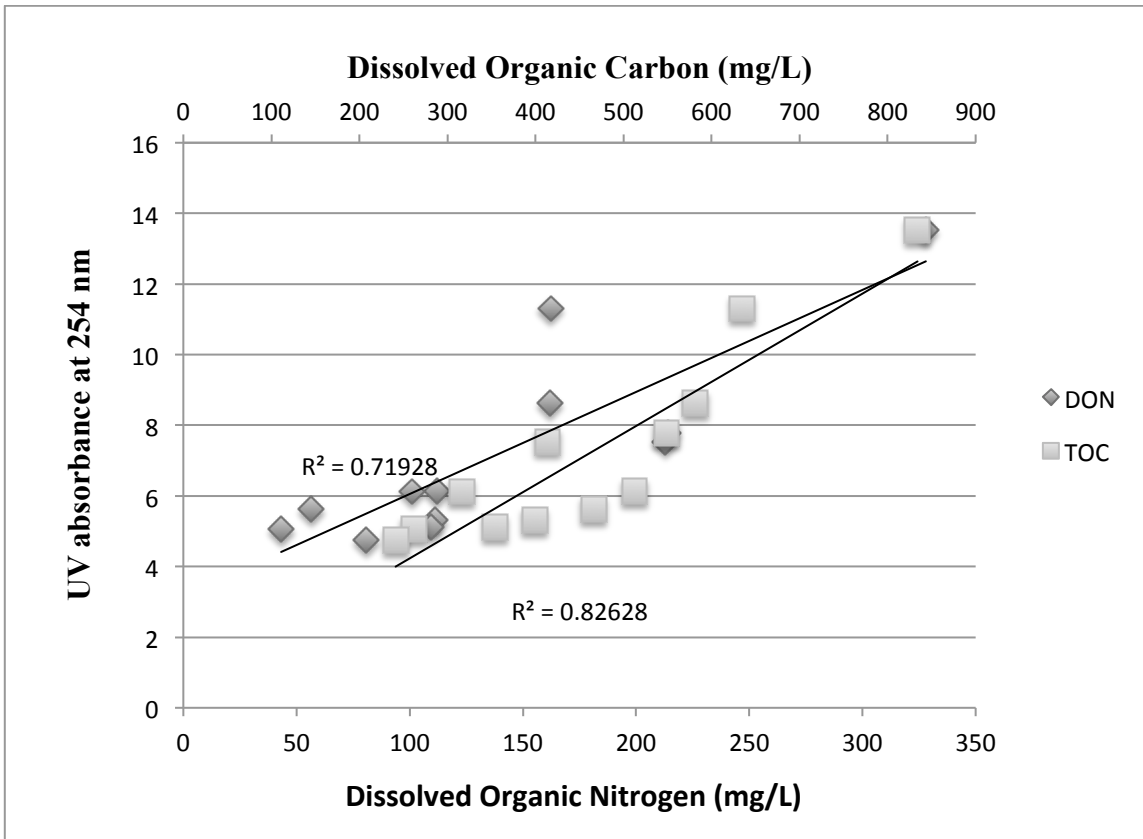


Figure 3-10: Relationship between dissolved organic carbon, dissolved Organic Nitrogen and UV_{254} absorbance across all operating temperatures and molecular size based fractions.

Table 3-1: Molecular size based distribution of Specific UV Absorbance (SUVA) in thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures

| Operating Temperature | $SUVA_{254}$ (L/mg-m) | | |
|-----------------------|-----------------------|-------|-------|
| | 130°C | 150°C | 170°C |
| Sample Fraction | | | |
| 0.45 μ m | 1.20 | 1.42 | 1.62 |
| 100k Da | 1.33 | 1.82 | 1.78 |
| 3k Da | 1.44 | 1.93 | 1.48 |
| 1k Da | 1.93 | 1.97 | 1.21 |

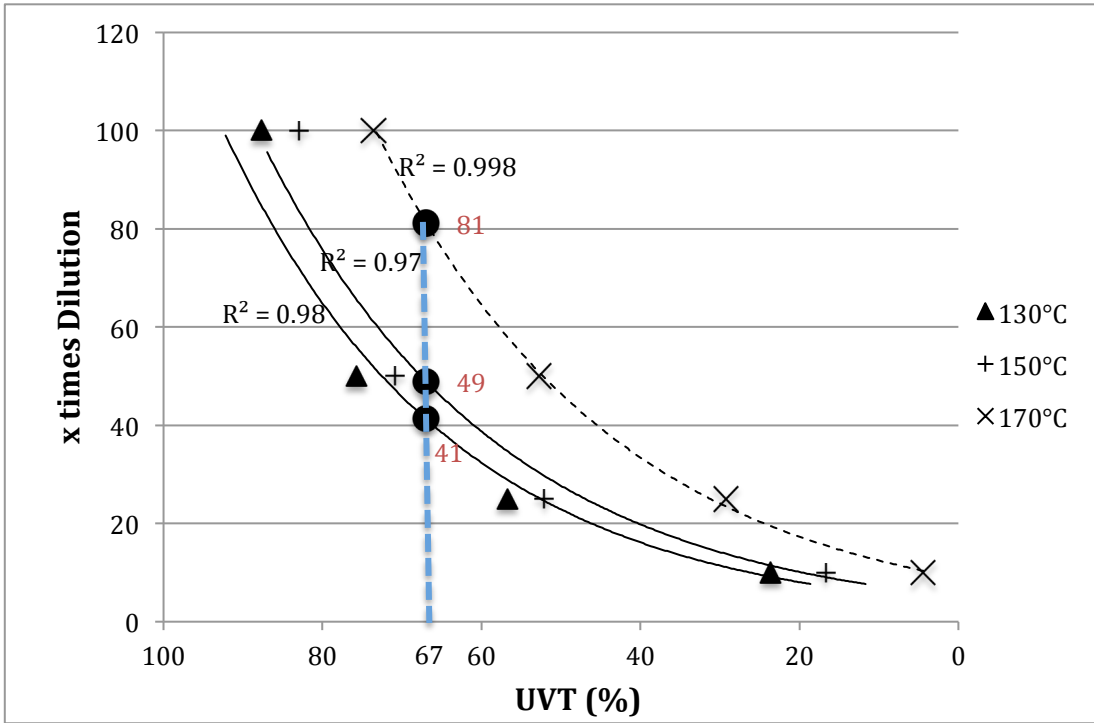


Figure 3-11: UVT in thermal hydrolysis/ anaerobic digestion return liquor for different operating temperatures with different dilutions

Chapter 4 : Impact of operating conditions on thermal hydrolysis pre-treated digestion return liquor

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Abstract

Impact of varying operating conditions on dissolved organic nitrogen (DON) and UV quenching compounds in the return liquor from mesophilic anaerobic digestion of thermally hydrolyzed sewage sludge (primary and waste activated) was assessed in this study. Operational parameters studied were (1) solids retention time (SRT) in the anaerobic digester (2) Thermal hydrolysis process (THP) flash pressure (3) the effect of co-digestion of sewage sludge with food waste, and, (4) polymer conditioning. Polymer dose had the greatest impact on DON and UV quenching compounds among the operating conditions considered. Increasing the SRT from 10 d to 15 d resulted in a slight decrease in DON but did not have any impact on UV_{254} absorbance. Increasing flash pressure from 25 psi to 45 psi did not have a significant impact on the return liquor. However, increasing the flash pressure to 75 psi increased the DON and UV_{254} absorbing compounds. Co-digesting the sludge with food waste resulted in a slight increase in DON and a decrease in dissolved organic carbon (DOC) and UV quenching compounds. Overall, it can be concluded that optimizing operating conditions of thermal hydrolysis process can result in decreased DON and UV quenching compounds in the recycle stream.

4.1 Introduction

Treatment and disposal of excess sludge produced during treatment of wastewater is one of the major challenges faced by municipal wastewater treatment plants. These problems continue to increase with increasing hauling cost, decreasing land availability due to urbanization and stricter regulations for its treatment and application (Pérez-Elvira et al. 2006). There have been several advancements in the field of biosolids treatment over the past few decades to reduce the excess sludge produced by the activated sludge process (Low and Chase 1999, Metcalf & Eddy et al. 2003, Odegaard 2004, Wei et al. 2003, Yasui and Shibata 1994). Studies have shown that the major limitation in mechanical dewatering of polymer-conditioned sludge is its inability to remove bound water i.e., water within floc, molecules on surface of solids and water of hydration (Novak 2006, Vesilind 1994). Most efforts in the field of biosolids treatment have been aimed at changing the floc structure of the sludge and releasing the bacterial cell content in order to improve digestibility and dewaterability (Neyens and Baeyens 2003).

The Thermal Hydrolysis Process (THP) is one of the sludge minimization technologies gaining much attention in North America, Europe and China (primarily CambiTHP) due to its ability to increase cake dewaterability between 60-80% and produce class A biosolids (Agency 1992, Ødeby et al. 1996). The improved dewaterability and increase in cake solids in thermally hydrolysed sludge is attributed to the release of bound water as a result of degradation of extracellular polymeric substances (Neyens et al. 2004).

The dewatered side stream from the THP (after MAD), also referred to as the THP return liquor, contains a higher concentration of ammonium, dissolved organic nitrogen (DON)

and UV₂₅₄ quenching substances, than that from a conventional MAD process (Constantine 2006, Dwyer et al. 2008, Figdore et al. 2011, Phothilangka 2008, Wilson et al. 2011). The higher ammonium concentration is due to the higher solids loading to the digester and better degradation of N-containing organic compounds during the thermal hydrolysis (Figdore et al. 2011). Wilson et al. (2011) demonstrated in their study that the total ammonia released per mass of volatile solids destroyed was equivalent for mesophilic digestion with and without THP pretreatment. This THP return liquor is usually recycled back to the wastewater treatment plant and can significantly impact the nitrification and total nitrogen (TN) removal performance of secondary treatment units (Constantine 2006). The biological nutrient removal (BNR) systems employed for removal of phosphorous and nitrogen in wastewater can effectively reduce dissolved inorganic nitrogen (DIN) in the effluent with removal efficiencies of up to 95%. However, the excess dissolved organic nitrogen (DON) observed during THP is mostly refractory in nature and is not effectively removed by BNR processes (Dwyer et al. 2008, Phothilangka 2008). Thus most of it has a potential of ending up in the effluent of wastewater treatment plants.

Although the recycled centrate contributes only about 1% of the volumetric load¹ it can contribute up to 15-30% of the nitrogen load (Constantine 2006). The higher DIN removal efficiencies in the return liquor result in DON being the major contributor to the total nitrogen concentration in the effluent. Past studies indicate that DON can contribute between 20-85% of the TN in the effluents (Bronk et al. 2010, Dwyer et al. 2008, Pagilla

¹ Blue Plains Wastewater Treatment Plant, Washington D. C. has a volumetric loading rate of 0.3% for the recycled return liquor from the THP

2006, Pehlivanoglu-Mantas and Sedlak 2006, Qasim 1999, Shouliang et al. 2013) making it important to study the impact of THP on DON in the recycled stream.

Increasing problems of eutrophication in bays and estuaries have resulted in implementation of stricter total nitrogen (TN) limits in Total Maximum Daily Load (TMDLs) for receiving waters in the United States (EPA 2015b). DON being a significant part of the effluent TN has become an important parameter to understand. Although regulations are applicable to all forms of nitrogen in the effluent, the eutrophication potential of DON is different than that of DIN depending on its bioavailability.

Additionally, direct potable water reuse or indirect potable water reuse downstream of the wastewater discharge has the potential for forming nitrogen based disinfection byproducts (N-DBPs) when chlorine based compounds are used for disinfection in the drinking water treatment train (Pehlivanoglu-Mantas and Sedlak 2006). N-DBPs such as haloacetonitriles (HANs), haloacetaldehydes, and N-nitrosodimethylamine (NDMA) are more potent carcinogens and mutagens than the DBPs that are currently being regulated (trihalomethanes and haloacetic acids). Studies indicate that DON in wastewater effluent serves as a precursor to formation of these N-DBPs and is thus of significant concern (Krasner et al. 2009, Lee et al. 2007, Mitch et al. 2003).

While there is a growing body of literature on optimization of THP for improved digestibility and dewaterability of sludge, the understanding about the impact of operating conditions on the recycled return liquor from the THP is very limited. This research aims at understanding the impacting of operating conditions on DON and UV quenching

substances in the return liquor from the THP. The operational parameters studies are (1) solids retention time (SRT) in the anaerobic digester (2) THP flash pressure (3) co-digestion of sewage sludge with food waste, and, (4) polymer conditioning.

4.2 Materials and Methods

Sludge samples used in this study were subjected to different operating conditions listed in Table 4-1. SRT varied from 10-15 days, flash pressure from 170-520 kPa and polymer doses ranged from 6.8×10^{-3} – 15.9×10^{-3} kg polymer/ kg dry sludge (15-35 lb/ton) in the combinations presented.

Thermal pretreatment

The samples used in this study were subject to a series of treatment processes at different locations prior to its analysis. The primary sludge (PS) and waste activated sludge (WAS) from Blue Plains Advanced Wastewater Treatment Plant, Washington DC, USA was thermally treated at the THP pilot treatment plant located on the plant premises. The ratio of PS:WAS in the THP feed was roughly 1:1 and the feed was subjected to pre-dewatering to achieve total solids (TS) concentration ~16.5% prior to thermal treatment. The thermal hydrolysis reactor at the pilot plant was operated at temperature of 160°C and corresponding pressure of 520 kPa for samples C-I to C-V and operating temperature of 150°C (370 kPa) and 170°C (690 kPa) for samples C-VI and C-VII respectively. Thermal treatment was provided for a duration of 30 minutes. After thermal treatment, the temperature of the sludge was gradually decreased till the pressure was reduced to a predetermined value and then released at atmospheric pressure. This process is termed as flashing and the predetermined pressure set point is called flash pressure (FP). FP for this

study was varied at 170 kPa, 310 kPa and 520 kPa to study its impact on the return liquor.

Anaerobic Digestion

Thermally pretreated sludge was then transported to the laboratory at Bucknell University, Pennsylvania, USA, where it was anaerobically digested in laboratory reactors operated at 38°C and water head pressure of 10 inches. A three-blade propeller rotated at a speed of 200 rpm carried out mixing in the digesters. The digesters were operated at an SRT of 15 days for all samples except one, which was digested at an SRT of 10 days. This was done to understand the impact of SRT on the THP return liquor. Sludge samples were collected once the digesters reached a steady operation. Since, daily organic loading rate was same for the digesters operated at SRT of 10 days and 15 days. The results obtained for SRT of 10 days have been corrected by a factor of 1.5 to account for the difference in overall organic loading in the digester over the retention period in comparison to the digester operated at SRT of 15 days.

Co-digestion

To observe the impact of co-digestion on the return liquor from the feed, one of the reactors was operated with combined feed of PS+WAS along with food waste (FW). Waste Management, Inc. provided the FW procured from multiple sources such as cafeteria, restaurants, kitchens, etc. FW was added in the form of homogenized slurry in the ratio of 107 mL per 560 mL of combined sludge (PS+WAS).

Polymer conditioning and dewatering

The digested sludge samples were then received by the laboratory at Virginia Tech,

Virginia, USA where, they were subjected to polymer conditioning. The polymer used for this study was a 35% charge linear polyacrylamide polymer (Clarifloc C-3258). The choice of the polymer is based on its selection for use at the full scale THP plant at Blue Plains WWTP. The samples used for investigating the impact of SRT, flash pressure and co-digestion were subject to a polymer dose of 35 lb/ton each. To study the impact of polymer dose, the samples for operating temperature of 150°C and 170°C were subject to polymer dose of 15, 20, 25, 30 and 35 lb/ton. Dewatering of sludge was carried out using a centrifuge and a modified centrifuged cup to simulate the tension of a belt press following the polymer conditioning. The liquor from the dewatered sludge samples was then used for analysis and is referred as THP return liquor in this paper.

The pH of the samples was decreased using laboratory grade hydrochloric acid to 6.7 ± 0.3 to reduce volatilization of ammonia prior to fractionation.

Analysis

Organic nitrogen in the samples was estimated by subtracting ammonium from total Kjeldahl nitrogen. Total Kjeldahl nitrogen was measured by semi micro-Kjeldahl method per Standard Method 4500-C (APHA et al. 2012). Ammonium was determined by the salicylate method (Hach, Loveland, CO) and measured using a spectrophotometer (DR 2800, Hach, Loveland, CO). While inaccuracy in DON analysis associated with wastewater containing higher concentrations of inorganic nitrogen is well understood (Pehlivanoglu-Mantas and Sedlak 2006), this method of analysis was chosen based on a supporting study (Appendix A) carried out to determine the possibility of errors associated with using this method.

Dissolved Organic Carbon (DOC) in the samples was analyzed using a high temperature combustion TOC analyzer (Shimadzu TOC- 5000A, Japan). The UV absorbance at 254 nm (UV_{254} abs) was measured with a spectrophotometer (Beckman Coulter, Brea, CA). The samples were diluted 50 times prior to UV_{254} absorbance and DOC measurement. Specific UV absorbance at 254 nm (SUVA) is calculated as UV_{254} abs divided by DOC.

Molecular size based fractionation

The return liquor samples were centrifuged (IEC HN0SII, International Equipment Company, USA) at 4000 rpm for 30 minutes to aid in separation of the dissolved solids fraction. The centrate was then passed through 0.45 μ m cellulose nitrate membrane (Millipore, Billerica, MA), to separate the dissolved solids fraction from the suspended solids fraction. The filtrate obtained was then sequentially passed through ultrafiltration (UF) membrane disks (Millipore, Billerica, MA) of molecular weight cut-off (MWCO) 100k Da, 3k Da and 1k Da using 200 mL stirred dead end batch UF cells (Amicon model # 8200). The UF cells were pressurized at 120 kPa using nitrogen gas.

Fractionation based on hydrophobicity

The samples were characterized into humic acids (HA), fulvic acids (FA) and hydrophilic acids (Hpi) based on the methods described by (Leenheer 1981, Thurman and Malcolm 1981).

The samples were first acidified to pH 2 using concentrated hydrochloric acid to precipitate the HAs. The precipitated HA fraction was settled by centrifugation for 30 minutes. The precipitated HAs were re-dissolved in a 0.1 M sodium hydroxide (NaOH)

solution and used for analysis. The supernatant from the centrifuged fraction was passed through a column of XAD-8 resin (currently Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO). The FAs were sorbed on the resin and redissolved in 0.1 M NaOH solution. The eluted fraction contained the Hpi fraction. Cleaning of XAD-8 resin and preparation of column prior to fractionation was carried out following the procedures described by (Leenheer 1981). The three fractions were subject to size-based fractionation as described in the previous section.

Statistics

Data was graphed using Microsoft Office Excel 2011. Linear regression analysis was performed using JMP 11.0.0 (SAS, Cary, NC) and is provided in Appendix B.

4.3 Results and Discussions

Impact of SRT

Figure 4-1 shows size-based distribution of DON observed for SRT of 10 d (C-I) and 15 d (C-II) maintaining all other operating conditions. A decrease of 12% from 326 mg/L to 288 mg/L is observed in DON from C-I to C-II. This decrease is almost entirely contributed by the DON >1k Da in size. Approximately, 43% and 46% of DON is <1k Da in size for C-I and C-II respectively. The trend observed in DOC (Figure 4-2) is opposite to that for DON. There is a slight increase in DOC of 8% from 767 mg/L to 827 mg/L from C-I to C-II. The increase of DOC/DON ratio from 2.35 to 2.87 indicates presence of more organically bound nitrogen at SRT of 10 d. The increase in DOC/DON ratio is more pronounced for fractions <100k Da in size.

The increase observed in DOC for C-II is indicative of slightly improved degradation of particulate and colloidal organic compounds into smaller sized compounds in the dissolved fraction when retained in the digester for a longer duration. This is supported by the improved digestibility of sludge observed by (Dwyer et al. 2008) for an increase in retention time for similar thermal pre-treatment conditions. An increase of about 20% in methane yield was reported at 160°C between SRT of 10 d and 15 d. The decrease in DON and increase in DOC/DON ratio could be explained by improved degradation of organic nitrogen in the dissolved fraction.

From Figure 4-3 it can be seen that increasing SRT from 10 d to 15 d did not impact the UV_{254} abs observed. However, an increase in SRT did result in a decrease in the SUVA values (Table 4-2) across all fractions, This decrease in SUVA without any changes in UV_{254} abs indicates presence of compounds with higher aromaticity for a shorter SRT of 10 days. This is an additional indicator of improved digestibility and degradation of compounds at higher digester retention times.

While, increasing the SRT does not result in a very significant difference in DON, DOC and UV_{254} abs it may impact the overall sludge digestibility and may lead to improved biogas production as demonstrated by Dwyer et al. (2008). The impact that SRT has on biogas yield, volatile fatty acids destruction, sludge dewaterability and DON would vary depending on the sludge feed characteristics. Thus, benefits and drawbacks of decreasing SRT may have to be further evaluated on case-to-case basis.

Impact of flash pressure

Figure 4-1 shows an increase in DON with an increase in flash pressure for operating

conditions C-II, C-III, C-IV. The DON observed for C-II, C-III and C-IV is 288 mg/L, 293 mg/L and 334 mg/L, respectively. This increase of 1.4% between C-II and C-III is insignificant in comparison to the increase of 16% in DON between C-II and C-IV. This increase is mostly contributed by DON in fractions with MWCO between 0.45 μm and 100k Da. The trend observed in overall DON is not followed across all size-based fractions instead DON is highest at FP of 310 kPa across all fractions <100k Da in size. There is also an increase of 29% and 23% observed in DON <1k Da when FP is increase to 310 kPa and 520 kPa respectively. This indicates that not only is there an increase in production of DON with increase in FP, increasing FP also results into breakdown of larger dissolved fractions into smaller molecular weight DON compounds. These compounds with MWCO <1 k Da are thought to be hard to remove owing to their smaller size while the increase in DON in the 0.45 μm and 100k Da fraction should be removed in the activated sludge system when the sludge is recycled back to the treatment plant.

The increase in DOC is similar to that observed in DON with negligible change in DOC between DOC at C-II (827 mg/L) and C-III (828 mg/L) and a 7% increase between C-II to C-IV (885 mg/L) (Figure 4-2). Approximately, 60%, 54% and 50% of the DOC is present in fraction <1k Da in size at C-II, C-III and C-IV respectively. The majority of the remaining DOC is contributed the fractions 100k Da-3k Da in size.

UV₂₅₄ abs and SUVA of the dissolved solids fraction follows the same trend as that followed by DOC (Figure 4-3 and Table 4-2). SUVA trends are similar across all fractions at the three FP with the highest SUVA values observed in the fraction 3k Da-1k Da and the lowest SUVA values observed for the fraction <1k Da.

The increase observed in DOC and DON is thought to be due to better cell lysis resulting from increased shear force created at higher FP. However, it is to be noted that the magnitude of increase is not very high. This could indicate that: (1) there is increased cell lysis and breakdown of larger compounds (mostly in the particulate and colloidal fraction) to smaller sized compounds resulting in improved bio-convertibility. Thus most of the disintegration products are completely degraded resulting in lower concentrations ending up in the return liquor, or, (2) majority of the disintegration is achieved at a FP of 170 kPa or lower. This raises an important question: Does the flashing process have any role to play in improving digestibility of sludge? The answer to this question is critical because flashing can result in operational problems associated with accumulation of compounds on the walls of the flash tank. Thus, eliminating the flashing process could eliminate these operational problems altogether. Further studies on FP with sampling done after each unit operation i.e. THP, anaerobic digestion and dewatering, are currently being conducted by the research team at Bucknell University which would be helpful in further understanding the impact of FP in the THP process.

Impact of Co-digestion

DON observed for co-digestion of food waste and sludge (C-V) and without co-digestion (C-II) is 288 mg/L and 305 mg/L, respectively (Figure 1) when all other operating conditions are the same. A slight increase (6%) in DON is observed between C-II and C-V. The distribution of DON across all size fractions is similar except the fraction <1k Da. About 46% and 18% of DON is present in fraction <1k Da for samples without and with co-digestion, respectively.

The distribution of DON in the HA, FA (Figure 4-4) and Hpi (Figure 4-5) fractions shows the increase in DON is contributed by the Hpi fraction and the decrease in DON in the fraction <1k Da upon co-digestion is also primarily a consequence of decrease of DON in the Hpi fraction.

DOC data represented in Figure 4-2 shows that co-digestion resulted in a decrease in DOC from 827 mg/L to 644 mg/L (22%). About 60% and 36% of the DOC is <1k Da in size at C-II and C-V respectively. More than half of the remaining fraction is present in the 100k Da-3k Da fraction for C- II, and, in 0.45um-100k Da fraction for C-V. This indicates that not only does co-digestion result in production of less organic compounds; the organic compounds formed are higher molecular weight compounds. The opposing TOC and DON trends for samples with and without co-digestion result in a decrease in DOC/ DON ratio from 2.87 to 2.11 indicating an increase in organically bound nitrogen upon co-digestion.

The decrease in DOC is contributed somewhat proportionately by a decrease in Humics (HA+FA)-DOC (25%) as well as in the Hpi-DOC fraction (20%) as shown in Figure 4-6 and Figure 4-7 respectively. This trend is similar across all fractions of humics and Hpi fraction. While there is decrease in humics-DOC observed upon co-digestion, it also results in an increase in HAs and a decrease in FAs. This could be a result of (1) introduction of difficult to degrade HAs present in the food waste, (2) reduced degradability of HAs into FAs upon co-digestion and/or (3) better degradation of FAs.

Figure 4-3 shows a decrease of UV₂₅₄ abs in return liquor from 11.5 to 5.5 (52%) upon co-digestion from . The trend of decreasing UV₂₅₄ abs is similar for C-II and C-V across all

fractions. SUVA also decreases by 38% upon co-digestion indicating decrease in aromaticity of compounds in the return liquor (Table 4-2). The decrease SUVA is also observed across all fractions of the co-digested sample. The decrease in DOC, UV quenching substances and aromaticity of compounds is indicative of better digestibility of sludge when it is co-digested with food waste.

Impact of polymer conditioning

The impact of polymer dose on DON in return liquor is illustrated in Figure 4-8 and Figure 4-9 for the THP operating temperature of 150°C (C-VI) and 170°C (C-VII) respectively. It is to be noted that the sludge substrate used for this analysis is different than that used for C-I - C-V. Thus, the results obtained are not directly comparable.

From Figure 4-8 and 4-9 it can be seen that increasing polymer dose results in a decrease in DON in return liquor up to polymer dose of 13.6×10^{-3} kg/kg (30 lb/ton) followed by an increase in DON when polymer dose is increased to 15.9×10^{-3} kg/kg (35 lb/ton). A possible explanation for this increase in DON could be that increasing the polymer dose beyond 13.6×10^{-3} kg/kg (30 lb/ton) results in excess polymer being available which does not bind to organic compounds. The organic nitrogen present in this excess polymer itself contributes to the DON in the return liquor resulting in an overall increase in DON observed.

While the DON trends observed across polymer doses are similar for operating temperatures of 150°C and 170°C the decrease observed when the polymer dose is increased from 6.8×10^{-3} kg/kg (15 lb/ton) to 9.1×10^{-3} kg/kg (20 lb/ton) is much more steep at 150°C than at 170°C. For both the operating temperatures the decreasing DON

trend with increase in polymer dose is observed across all fractions up till 13.6×10^{-3} kg/kg (30 lb/ton). Increasing the dose beyond 13.6×10^{-3} kg/kg (30 lb/ton) resulted in an increase in DON for both C-VI and C-VII. A significant decrease of 55% and 36% in DON for fraction <1k Da for C-VI and C-VII respectively is observed when the polymer dose is increased from 9.1×10^{-3} kg/kg (20 lb/ton) to 11.3×10^{-3} kg/kg (25 lb/ton). This indicates that polymer dose can have a significant impact even on the DON in the smallest fraction.

Trends followed by DOC for C-VI and C-VII are similar to that observed for DON (Figure 4-10 and Figure 4-11) for polymer dose between 6.8×10^{-3} kg/kg (15 lb/ton)- 13.6×10^{-3} kg/kg (30 lb/ton). While the trends are similar for C-VI and C-VII the magnitude of decrease in DOC in the return liquor is not the same for the conditions. Upon increasing the polymer dose to 15.9×10^{-3} kg/kg (35 lb/ton) there is a decrease observed in DOC for both C-VI and C-VII as opposed to the increase in DON observed for the same sample. However, for C-VII the decrease in DOC at 13.6×10^{-3} kg/kg (35 lb/ton) polymer dose is marginal. The decrease in DOC with increasing polymer dose is observed across all fractions >1k Da for C-VI and >3k Da for C-VII. For fraction <1k Da lowest DOC is observed for the polymer dose of 13.6×10^{-3} kg/kg (30 lb/ton) for both C-VI and C-VII.

Figure 4-12 shows the UV_{254} abs observed with increasing polymer dose for C-VI. The UV_{254} abs decreases with increase in polymer dose for all polymer doses except at 13.6×10^{-3} kg/kg (30 lb/ton) where a slight increase (1%) in UV_{254} abs is observed. Figure 4-13 shows the distribution of UV_{254} abs with increasing polymer dose for C-VII. Similar to the trend observed in C-V, increasing polymer dose results in a decrease in UV_{254} abs in

C-VI except for polymer dose of 15.9×10^{-3} kg/kg (35 lb/ton) where an increase of 4% in UV_{254} abs is observed. The decreasing UV_{254} abs trends observed for both C-VI and C-VII are not as steep as that observed for DON and DOC indicating that polymer dose does not have as strong an impact on removal of dissolved UV quenching substances as it does on DOC and DON. More than 35% and 45% of the UV quenching substances are present in fractions $>1k$ Da across all polymer doses for C-VI and C-VII respectively. This indicates that a significant fraction of UV quenching substances are smaller in size ($<1k$ Da) and are not impacted by polymer conditioning.

The higher UV_{254} abs and DON observed across all polymer doses for C-VII in comparison to that observed C-VI affirms the conclusions drawn by (Ahuja N. et al. 2015) that increasing operating temperature results in formation of UV quenching substances.

Correlation between DOC, UV abs and DON

A significant correlation ($\alpha=0.05$) exists between DOC and UV_{254} abs and DON and UV_{254} abs as seen in Figure 4-14(a) and (b). The data for C-VI to C-VII is plotted separately due to difference in sludge feed. It can be seen that a stronger correlation exists between DOC and UV_{254} abs for both the conditions in comparison to that between DON and UV_{254} abs. It should also be noted that the correlation between DON and UV_{254} abs is much weaker ($R^2=0.38$) for C-VI and C-VII than for the other conditions indicating UV_{254} abs to be a poor indicator of DON for comparison between samples of varying polymer doses.

A correlation between DON and DOC is shown in Figure 4-15(a) and 4-15(b) for C-I to

C-IV and C-VI and C-VII respectively. From these figures it can be seen that DON is directly proportional to DOC (significant linear correlation, $\alpha=0.05$) with $R^2=0.65$ and $R^2=0.56$.

Overall impact of return liquor

The ratio of the return liquor to the wastewater stream when recycled back to the wastewater treatment units is an important factor to be considered in the studies involving return liquor. This recycle ratio may vary from plant to plant. For the purpose of this study, which was conducted using sludge samples from Blue Plains Wastewater Treatment Plant, the recycle ratio was about 0.33% (1:300). Table 4-3 summarizes the expected concentration of DON in the wastewater treatment train contributed by the THP return liquor. The expected concentration of DON ranges from 0.5-1.1 mg/L. With effluent TN limits as low as 4.2 mg/L for the plant, these variations could significantly impact the DON in the effluent. Thus, altering operating conditions for sludge treatment could be an effective way of controlling DON being recycled back into the plant by the THP return liquor.

4.4 Conclusions

- Increase in SRT from 10 d to 15 d resulted in a slight decrease in DON and a slight increase in DOC. Increasing SRT also resulted in a decrease in SUVA indicated a probable decrease in aromaticity of the UV quenching compounds without much impact on UV_{254} abs.
- Increase in FP from 170 kPa to 310 kPa did not have a very significant impact on DON, DON or UV_{254} abs. Increasing the FP to 520 kPa psi did result in an

increase in DON, DOC, UV₂₅₄ abs and SUVA. However, the increase was not very significant indicating that increasing FP beyond 170 kPa may not improve disintegration of compounds.

- Co-digestion resulted in a slight increase in DON, which was contributed by the hydrophilic fraction of DON. This was accompanied by a decrease in DOC, UV quenching substances and aromaticity of compounds indicative of better digestibility of sludge when it is co-digested with food waste. UV₂₅₄ abs was most significantly impacted by co-digestion among all the operational parameters considered.
- Polymer dose had the most significant impact on the DON, DOC and UV₂₅₄ abs among all the operational parameters studied. Increasing polymer dose resulted in a decrease in DON in return liquor up to polymer dose of 13.6×10^{-3} kg/kg (30 lb/ton) followed by an increase in DON when polymer dose is increased to 15.9×10^{-3} kg/kg (35 lb/ton) for THP operating temperature of both 150°C and 170°C. However, DOC followed a decreasing trend even beyond a polymer dose of 13.6×10^{-3} kg/kg (30 lb/ton) for both the operating temperatures. Polymer conditioning did not impact UV₂₅₄ abs as much as it impacted DON and DOC in the return liquor.

Overall, findings of this study indicate that operating conditions can have a significant impact on DON and UV quenching substances in the return liquor from the THP process. While the findings of this study are a significant addition to the growing body of literature on managing DON and UV quenching compounds downstream of biosolids

treatment units, further research on understanding the mechanisms involved would be helpful in better optimization of the THP.

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Table 4-1: Nomenclature of operating conditions for sludge treatment considered in this study

| Operating Condition | Operating Temperature (°C) | Solids Retention Time (SRT) (d) | Flash Pressure (kPa) | Feed | Polymer Dose (x 10⁻³ kg polymer/ kg dry sludge) |
|----------------------------|-----------------------------------|--|-----------------------------|-------------------|---|
| C-I[#] | 160 | 10 | 170 | PS+WAS (1:1) | 15.9 |
| C-II | 160 | 15 | 170 | PS+WAS (1:1) | 15.9 |
| C-III | 160 | 15 | 310 | PS+WAS (1:1) | 15.9 |
| C-IV | 160 | 15 | 520 | PS+WAS (1:1) | 15.9 |
| C-V | 160 | 15 | 170 | PS+WAS+Food Waste | 15.9 |
| C-VI* | 150 | 15 | 170 | PS+WAS (1:1) | 6.8, 9.1, 11.3, 13.6, 15.9 |
| C-VII* | 170 | 15 | 170 | PS+WAS (1:1) | 6.8, 9.1, 11.3, 13.6, 15.9 |

[#] All results obtained for C-I corrected by a factor of 1.5 to account for the difference in SRT

* Different sludge feed than that for C-I – C-V

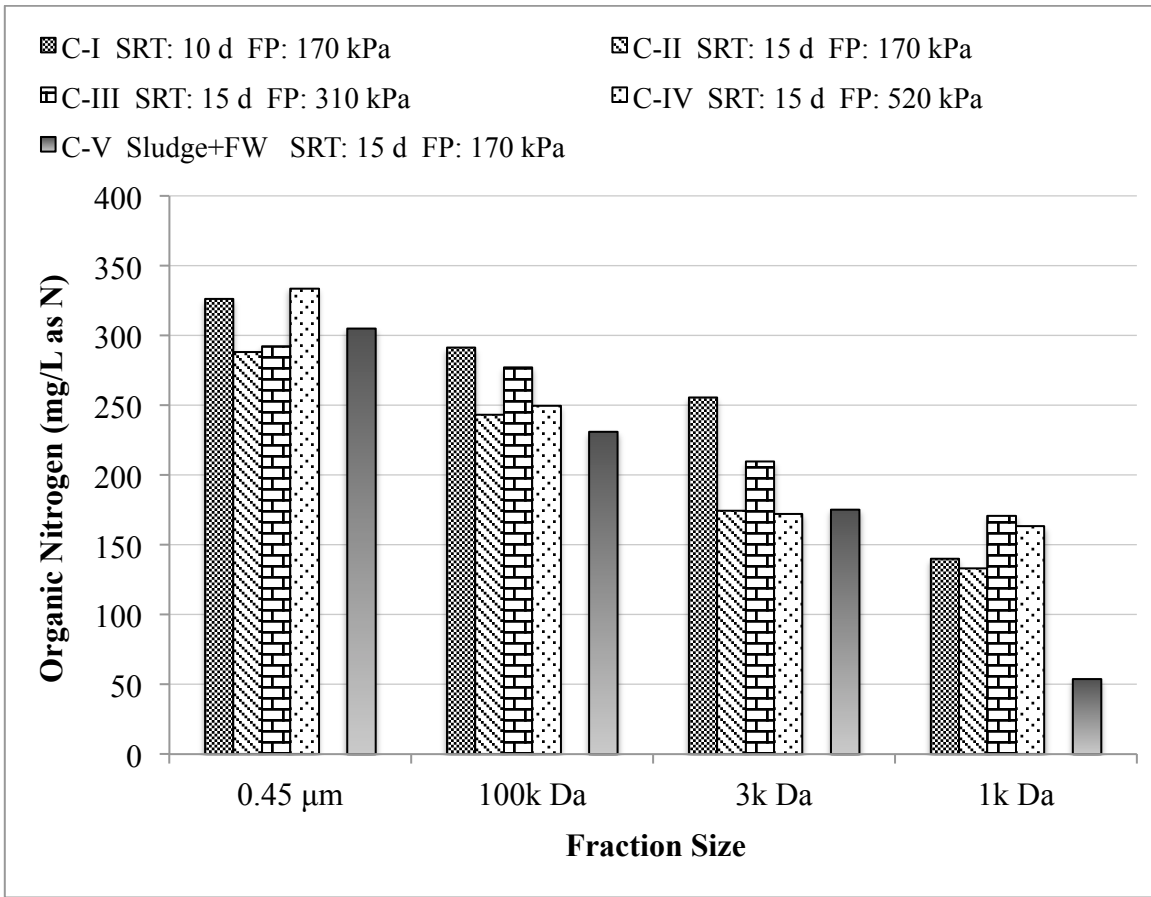


Figure 4-1: Molecular size based distribution of DON for operating conditions C-I to C-V

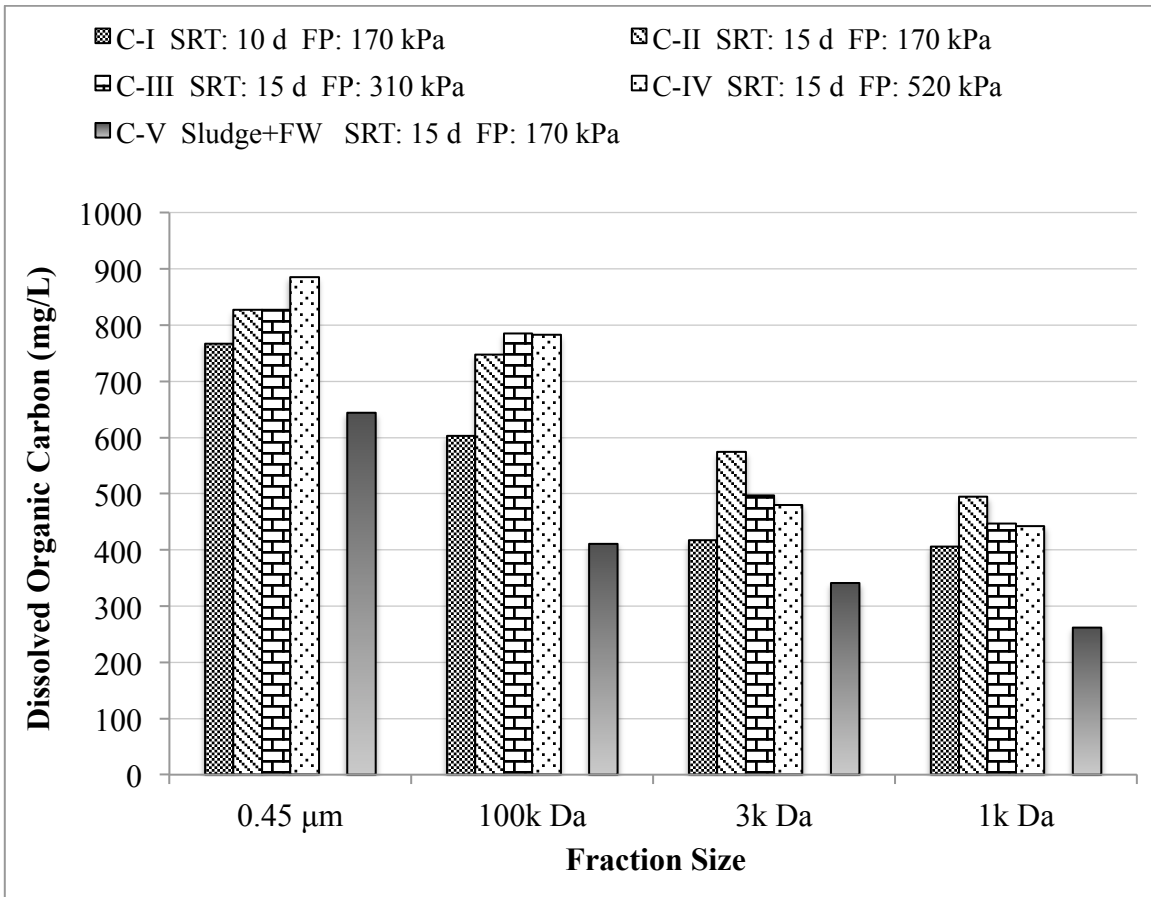


Figure 4-2: Molecular size based distribution of DOC for operating conditions C-I to C-V

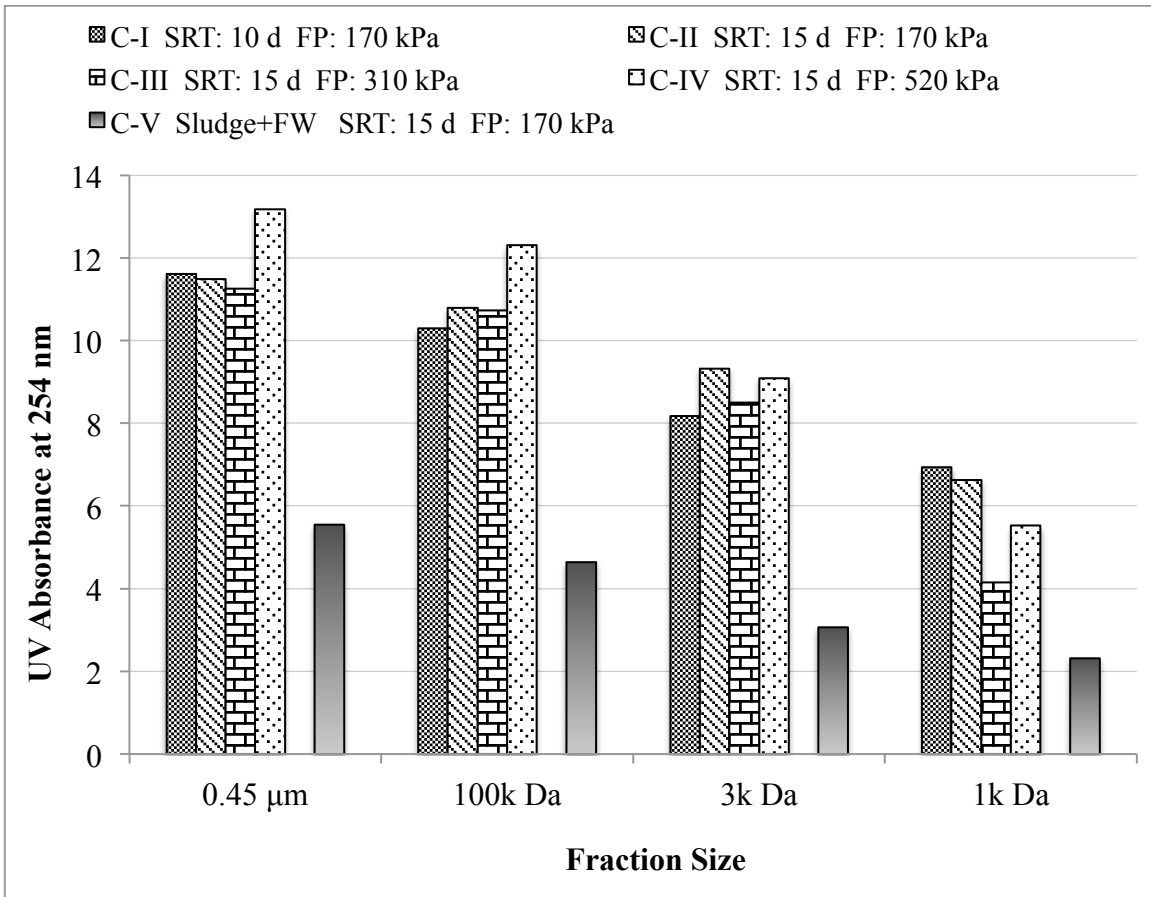


Figure 4-3: Molecular size based distribution of UV₂₅₄ absorbance for operating conditions C-I to C-V

Table 4-2: Molecular size based distribution of specific UV absorbance (SUVA) for operating conditions C-I to C-V

| SUVA (m⁻¹ mg/L) | | | | | |
|-----------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------------------|
| Operating Condition | C-I | C-II | C-III | C-IV | C-V |
| | SRT: 10 d FP: 170 kPa | SRT: 15 d FP: 170 kPa | SRT: 15 d FP: 310 kPa | SRT: 15 d FP: 520 kPa | Sludge+FW SRT: 15 d FP: 170 kPa |
| Sample Fraction | | | | | |
| 0.45 μm | 1.51 | 1.39 | 1.36 | 1.49 | 0.86 |
| 100k Da | 1.71 | 1.44 | 1.37 | 1.57 | 1.13 |
| 3k Da | 1.96 | 1.62 | 1.71 | 1.89 | 0.90 |
| 1k Da | 1.71 | 1.34 | 0.93 | 1.25 | 0.88 |

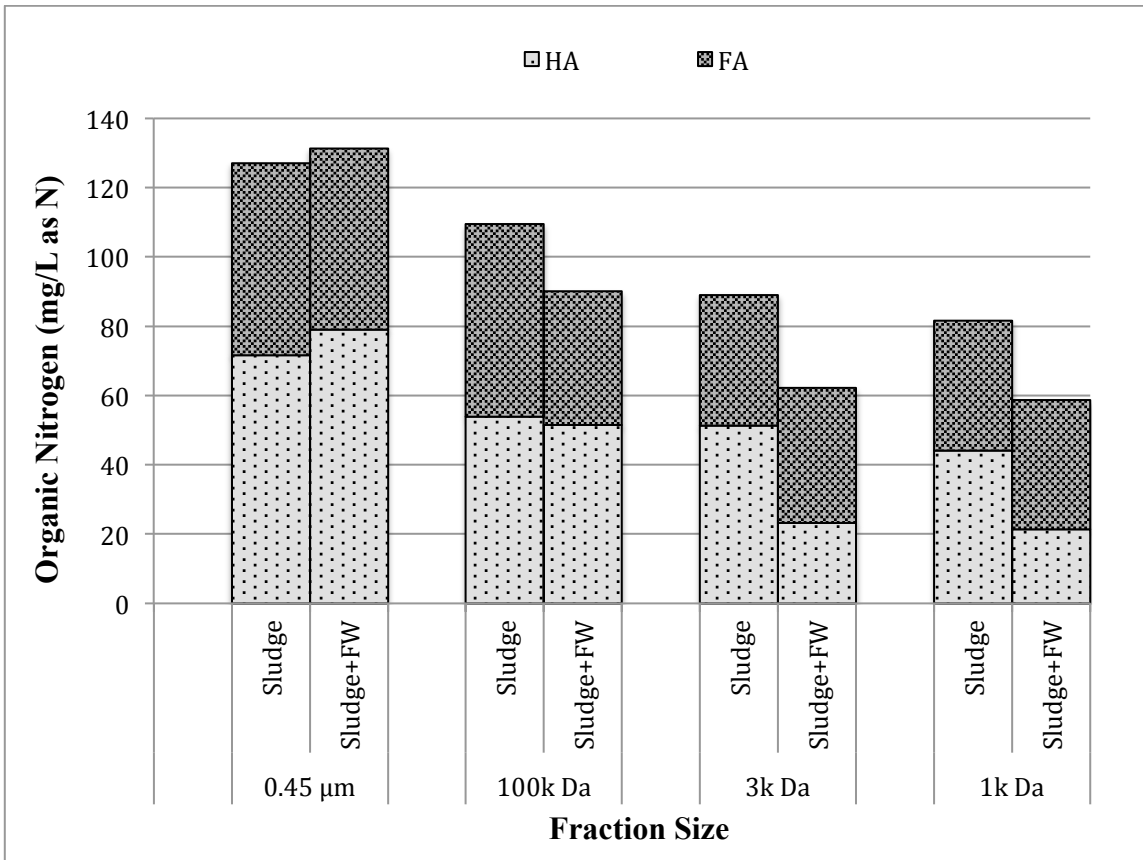


Figure 4-4: Molecular size based distribution of DON in HA and FA fraction for operating conditions without co-digestion (C-II) and with co-digestion (C-V) of sludge and food waste (FW)

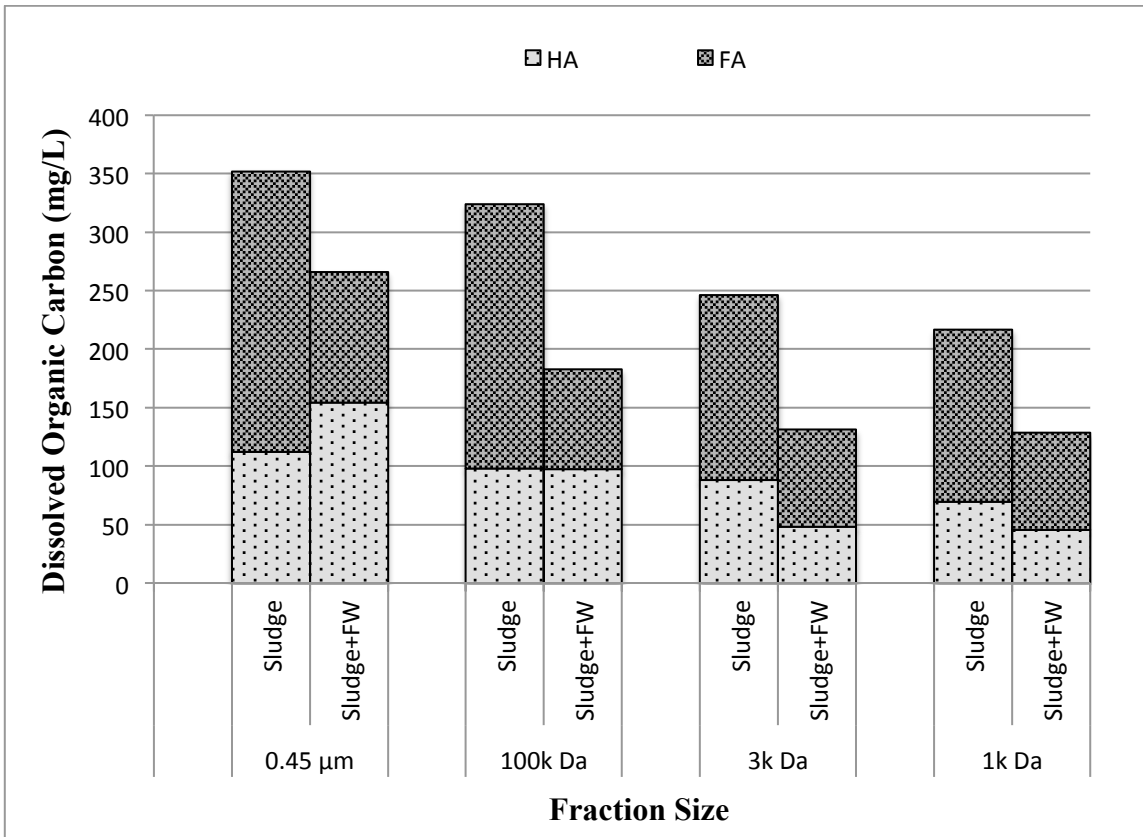


Figure 4-5: Molecular size based distribution of DOC in HA and FA fraction for operating conditions without co-digestion (C-II) and with co-digestion (C-V) of sludge and food waste (FW)

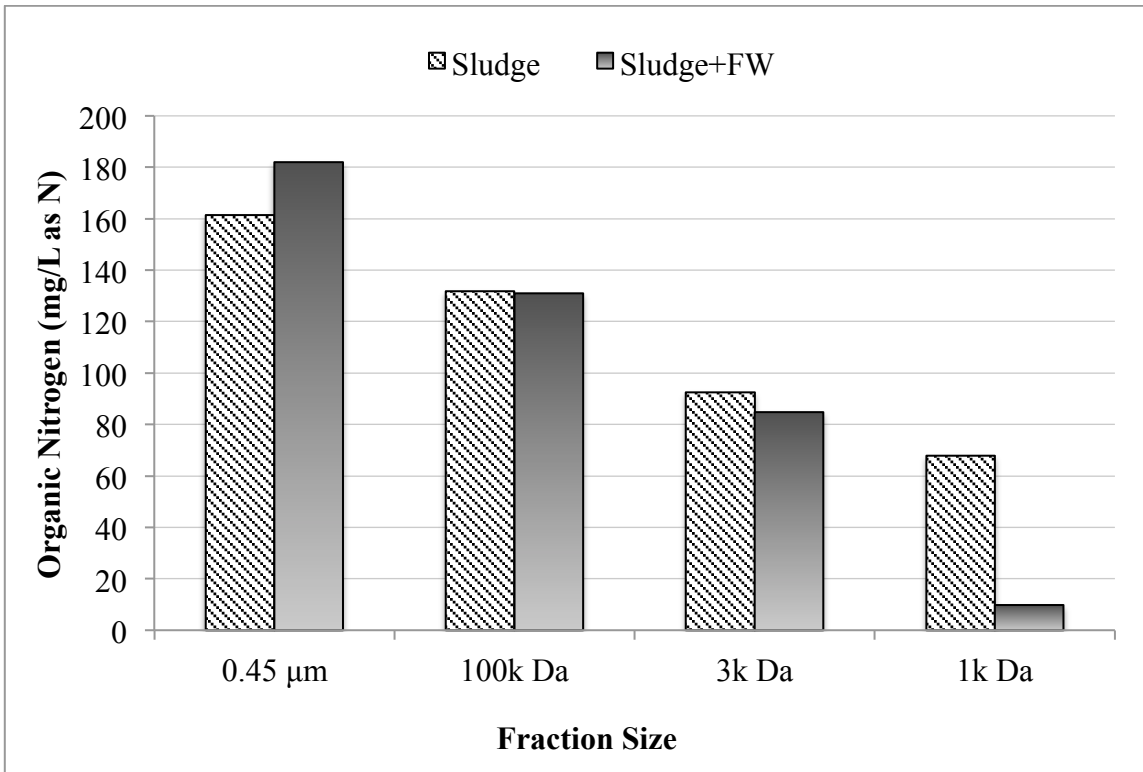


Figure 4-6: Molecular size based distribution of DON in Hpi fraction for operating conditions without co-digestion (C-II) and with co-digestion (C-V) of sludge and food waste (FW)

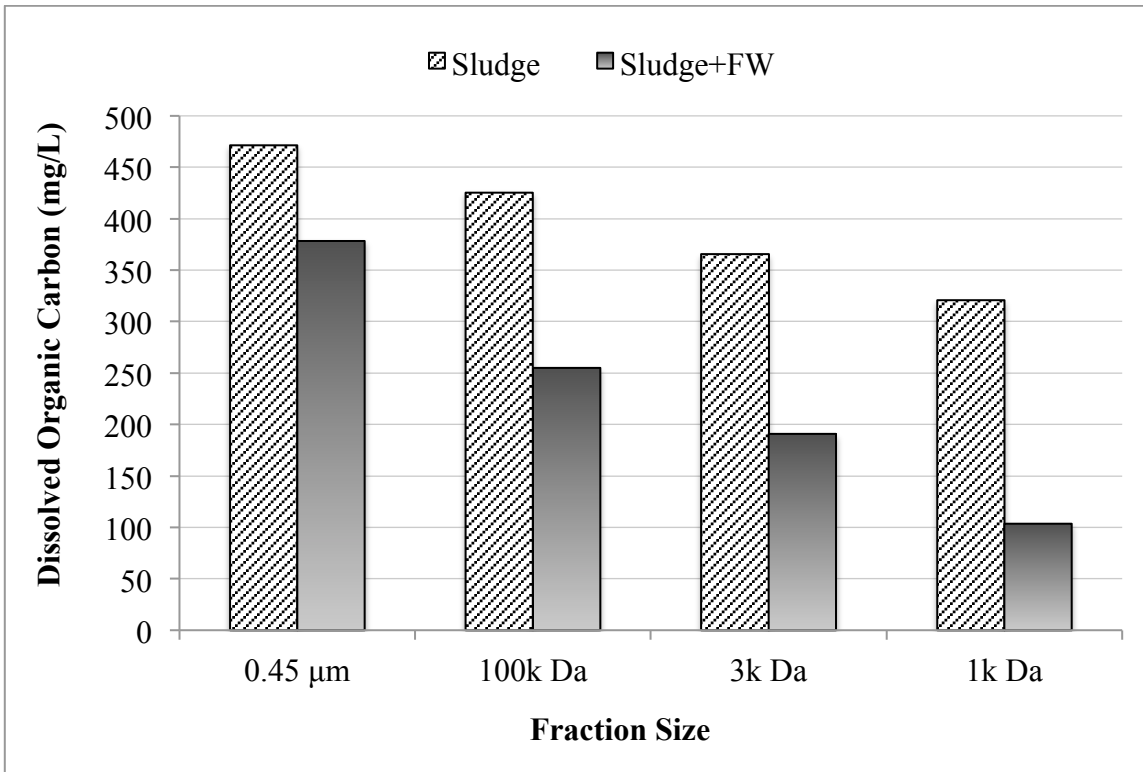


Figure 4-7: Molecular size based distribution of DON in Hpi fraction for operating conditions without co-digestion (C-II) and with co-digestion (C-V) of sludge and food waste (FW)

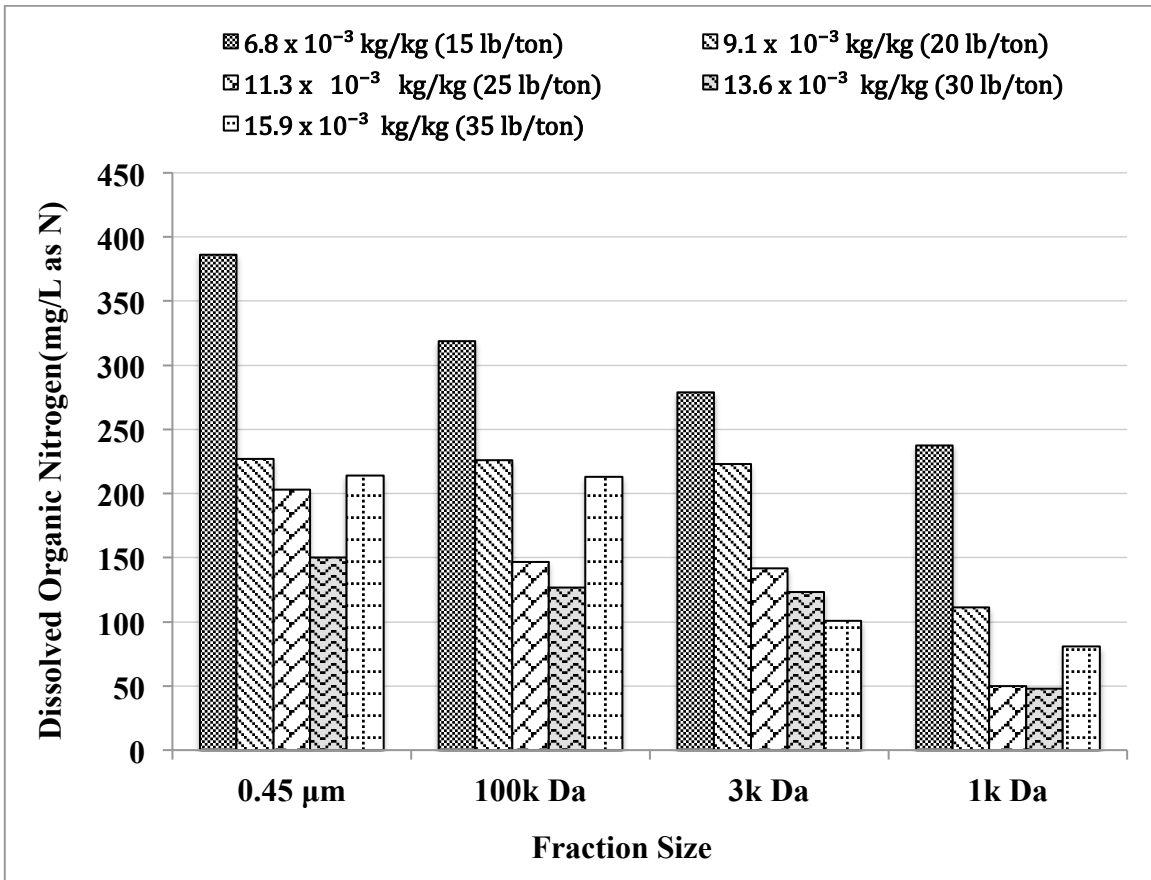


Figure 4-8: Molecular size based distribution of DON for varying polymer dose at operating temperature of 150°C (C-VI)

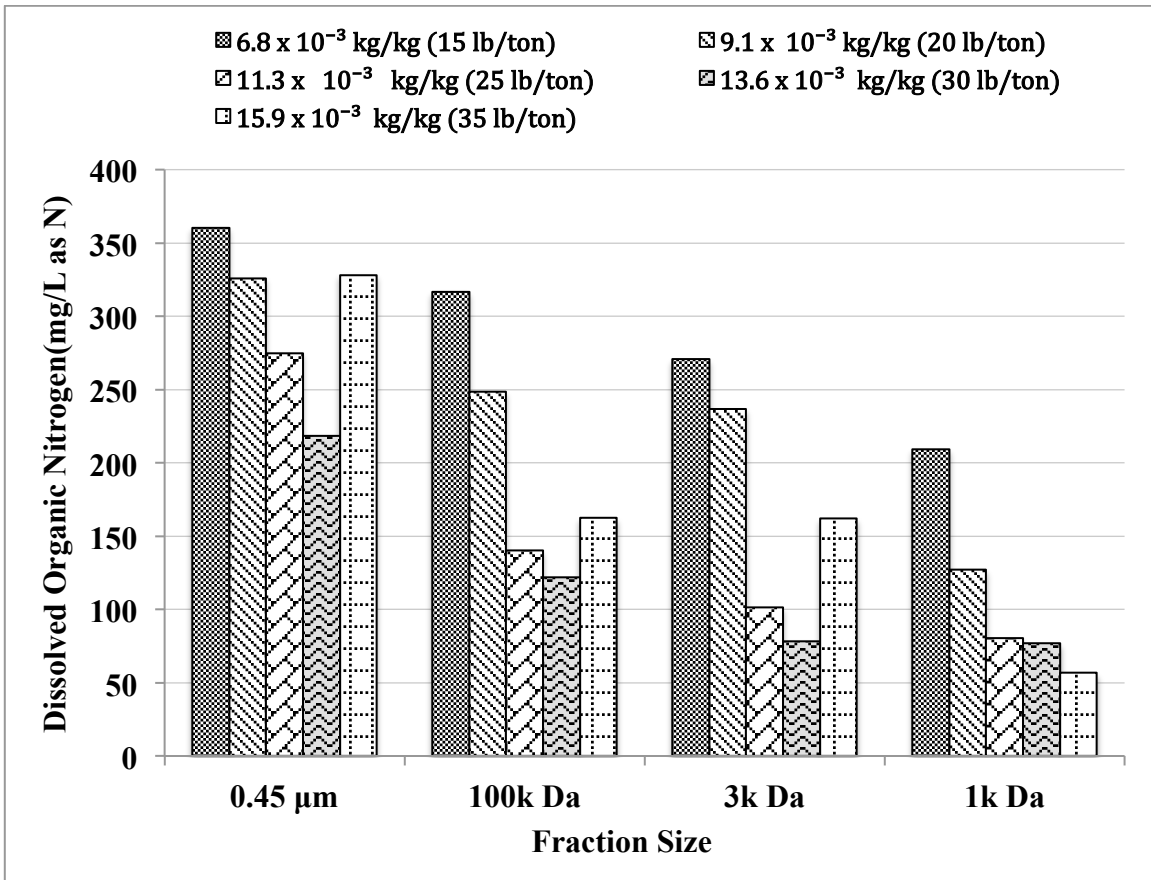


Figure 4-9: Molecular size based distribution of DON for varying polymer dose at operating temperature of 170°C (C-VII)

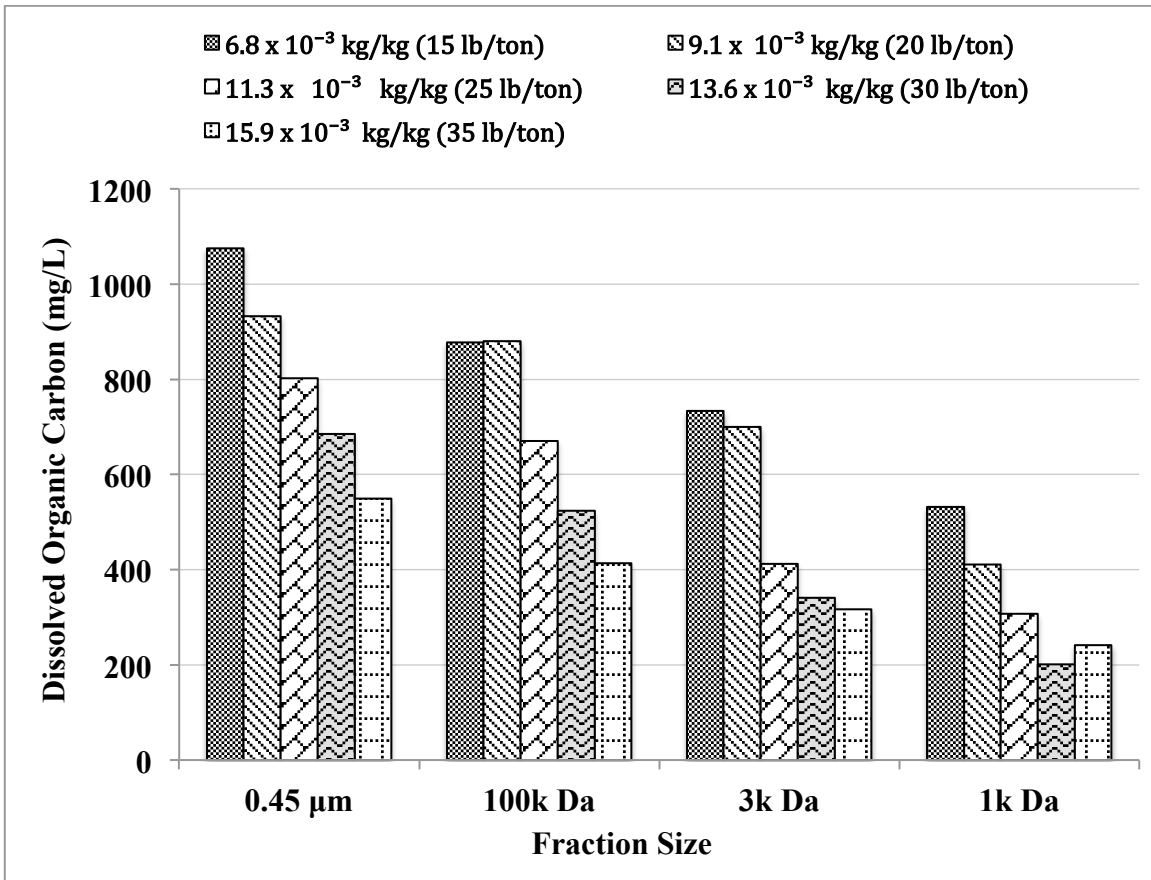


Figure 4-10: Molecular size based distribution of DOC for varying polymer dose at operating temperature of 150°C (C-VI)

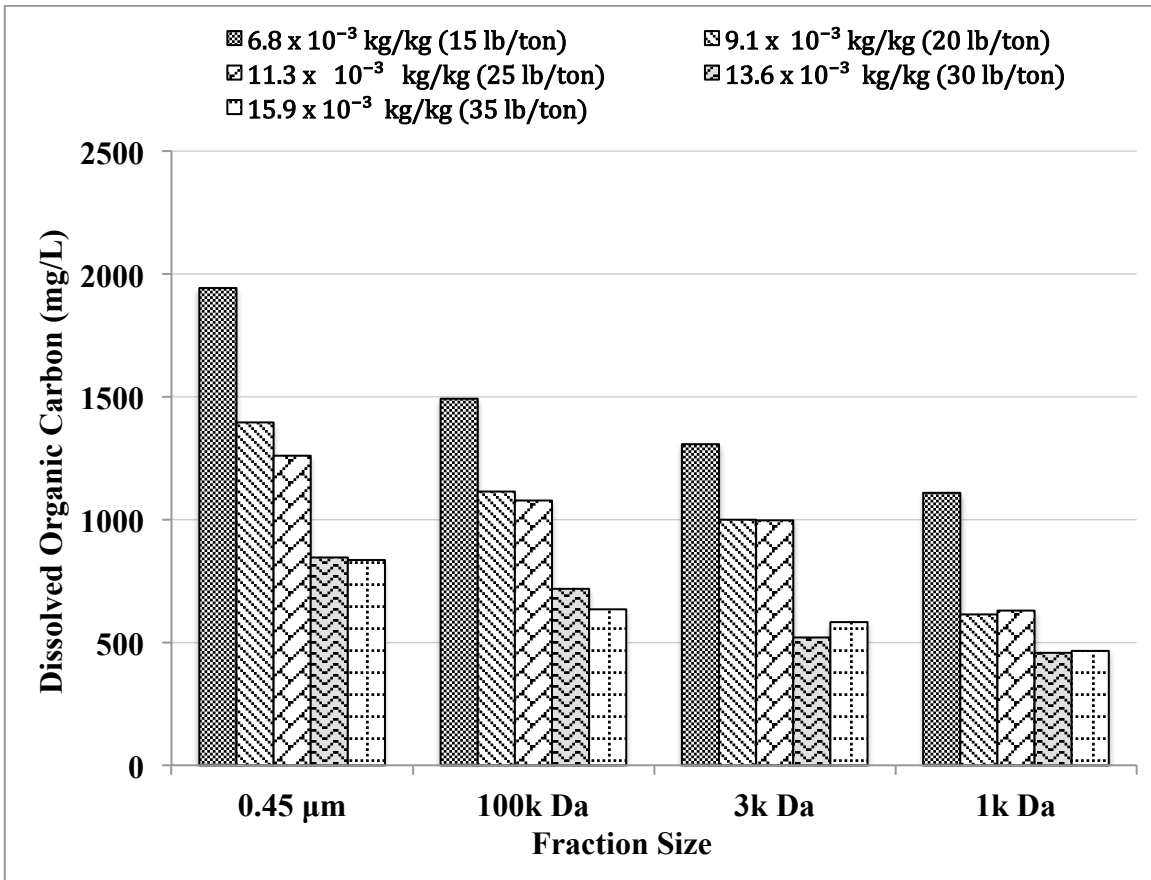


Figure 4-11: Molecular size based distribution of DOC for varying polymer dose at operating temperature of 170°C

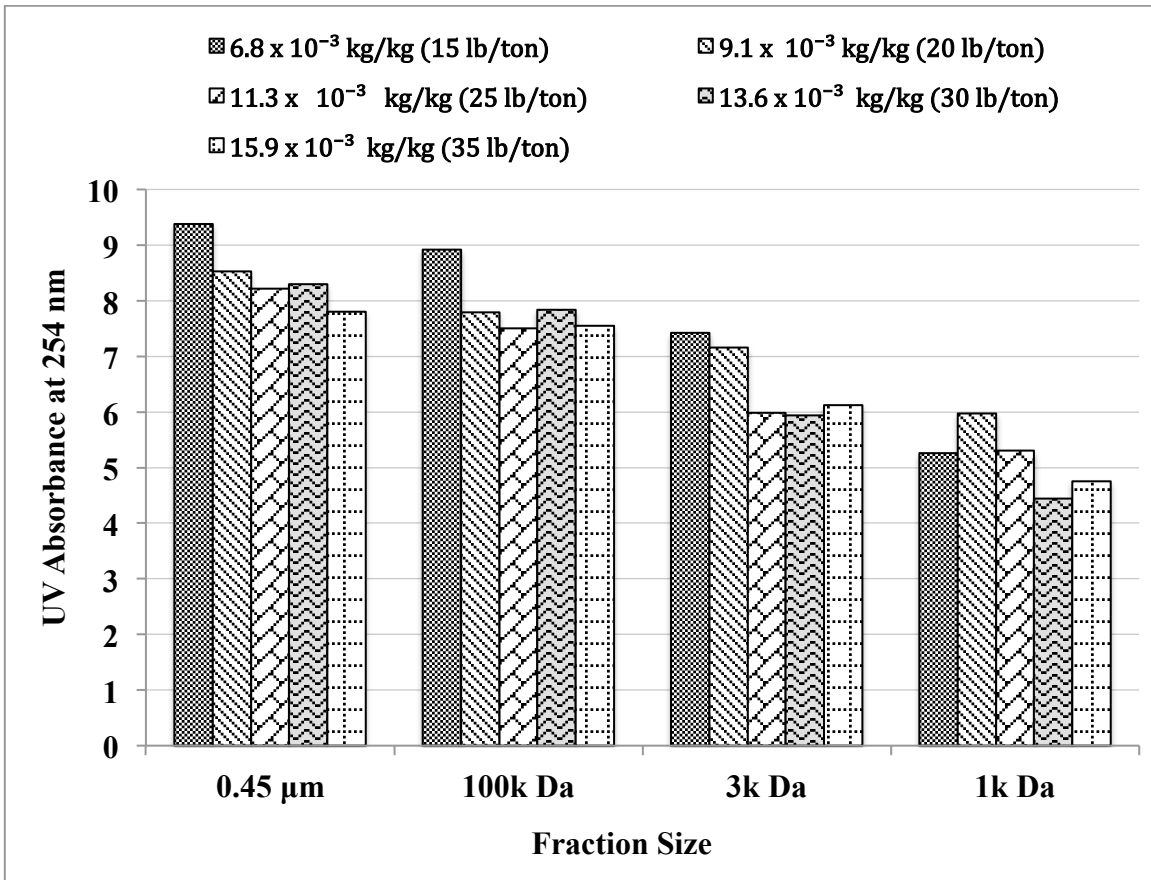


Figure 4-12: Molecular size based distribution of UV₂₅₄ abs for varying polymer dose at operating temperature of 150°C (C-VI)

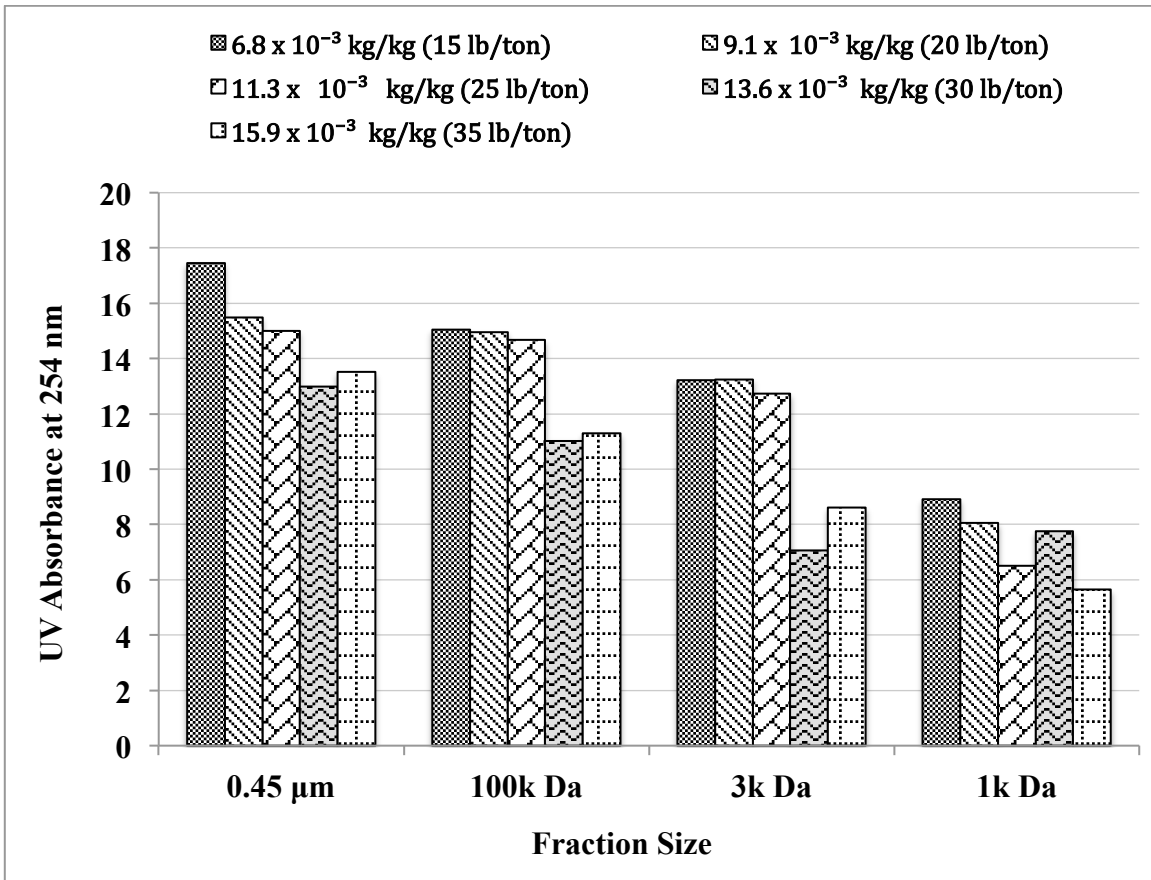


Figure 4-13: Molecular size based distribution of UV₂₅₄ abs for varying polymer dose at operating temperature of 170°C (C-VII)

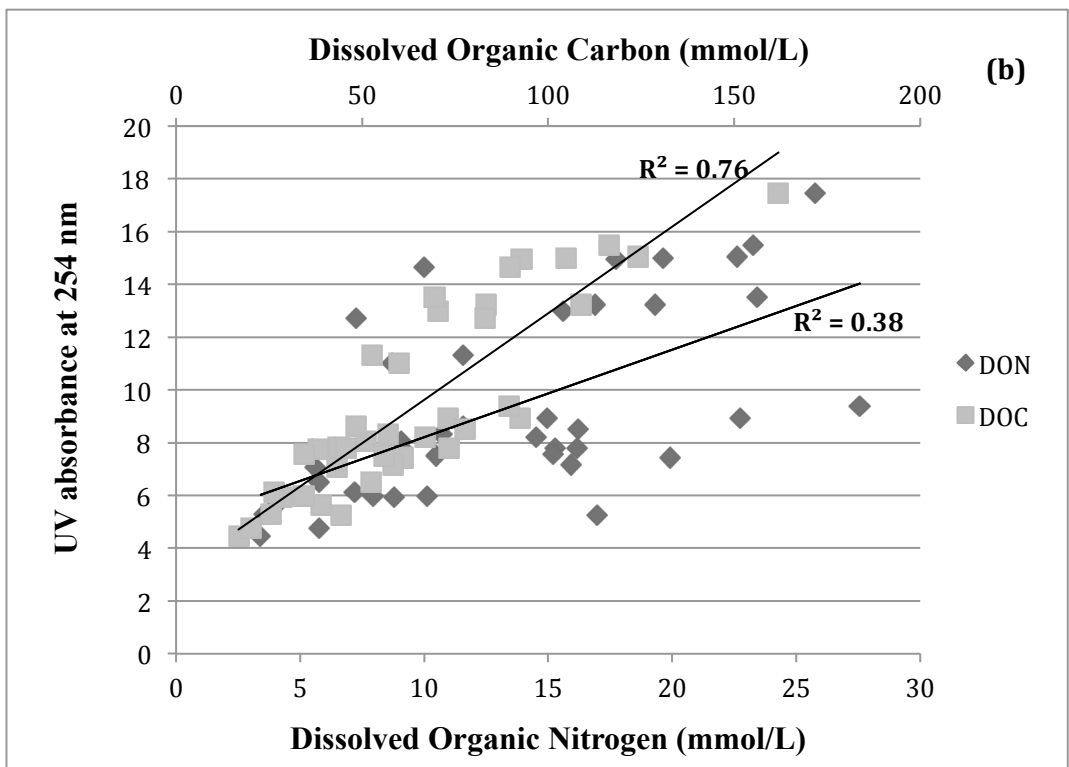
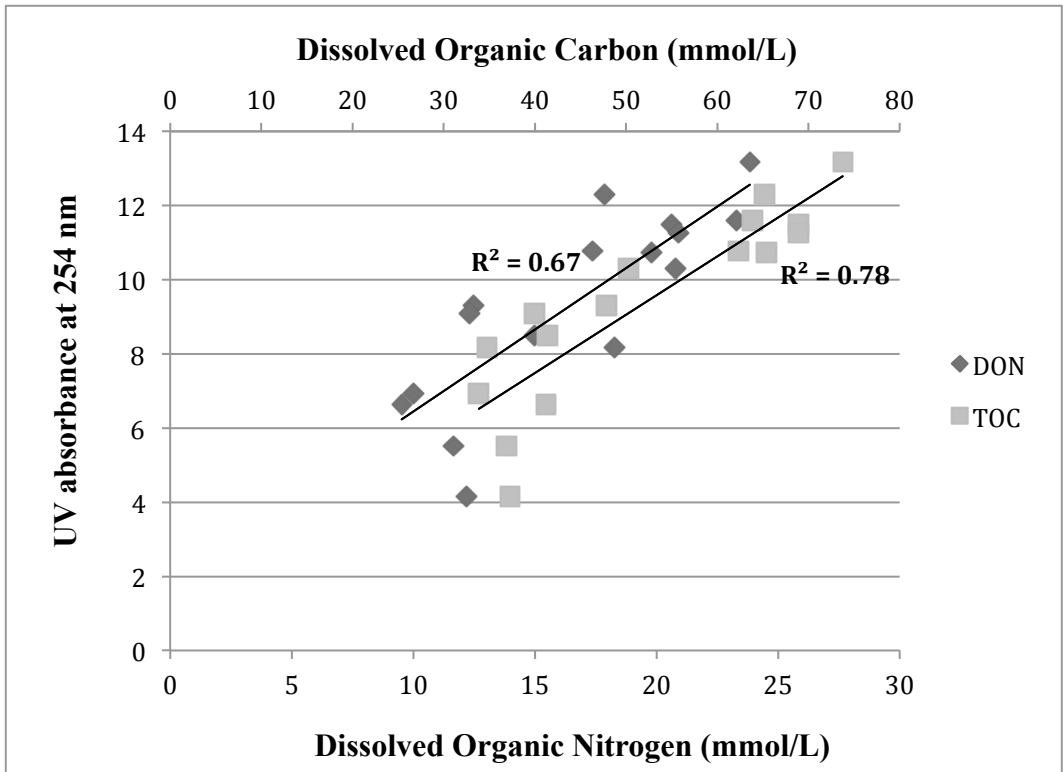


Figure 4-14: Correlation between DON, DOC and UV₂₅₄ abs for (a) C-I to C-IV (b) C-VI to C-VII

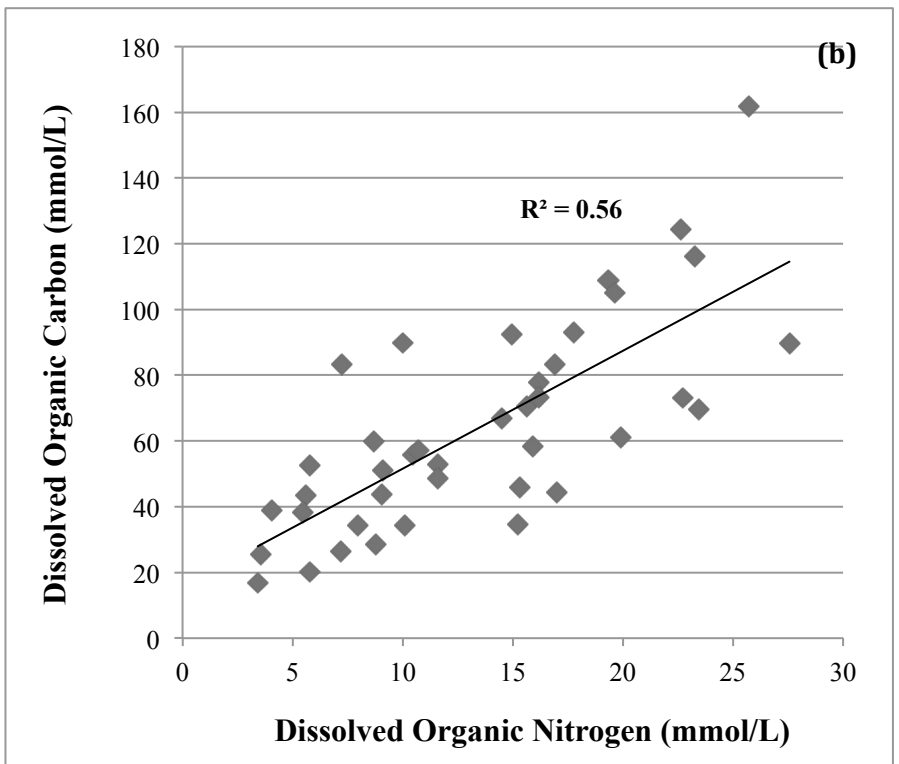
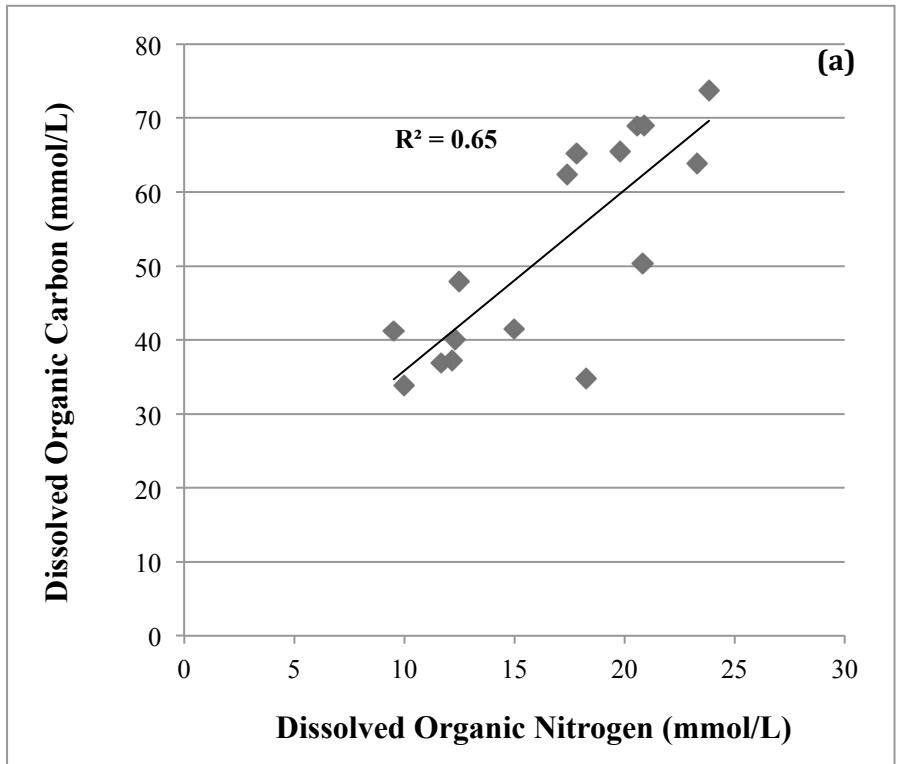


Figure 4-15: Correlation between DON, and DOC for (a) C-I to C-IV (b) C-VI to C-VII

Table 4-3: Expected DON contribution by the return liquor to the wastewater treatment units for varying operating conditions (for a recycle ratio of 0.33%)

| Operating Condition | DON observed in the return liquor | DON contributed by the return liquor to the WWTP |
|----------------------------|--|---|
| | <i>mg/L</i> | <i>mg/L</i> |
| C-I | 326 | 1.09 |
| C-II | 288 | 0.96 |
| C-III | 292 | 0.97 |
| C-IV | 334 | 1.11 |
| C-V | 305 | 1.02 |
| C-VI* | 150 | 0.50 |
| C-VII* | 219 | 0.73 |

*DON value reported for polymer dose of 13.6×10^{-3} kg/kg (30 lb/ton)

Appendix A: Challenges with accurate analysis of dissolved organic nitrogen (DON)

Introduction

Several researchers have attempted the characterization of compounds in dissolved organic nitrogen (DON) in wastewater but have not been able to account for a large fraction (Pehlivanoglu-Mantas and Sedlak 2008, Shouliang et al. 2013). This unidentified matrix of multiple organic compounds constituting DON in wastewater makes its direct analysis difficult. Traditional approaches to indirect measurements include bulk measurements combined with ammonia and ammonium using Total Kjeldahl Method (TKN). DON is then estimated by subtracting ammonia and ammonium concentration from TKN. These indirect measurements result in higher error margins especially when higher concentrations of dissolved inorganic nitrogen (DIN) species are present. The DIN could be distilled prior to the digestion step as an alternative to eliminate the interference by DIN (Pehlivanoglu-Mantas and Sedlak 2006). However, due to larger sample volumes required for analysis using TKN method, this approach may not be feasible. Due to the limitation of sample volumes available for the samples used in this study an attempt was made to understand the impact of varying DON/DIN ratios on the analysis accuracy of the traditional DON measurement approach. Any trends in the inaccuracy of DON analyses and, subsequently, a possibility of correcting them needed to be identified.

Materials and Methods

Sample Preparation

Synthetic solutions were prepared for varying DON/DIN ratios. Three amino acids: L-Phenylalanine ($C_9H_{11}NO_2$), L-Methionine ($HO_2CCHCH_2CH_2SCH_3$) and L-Serine (HO_2CCHCH_2OH) (Sigma-Aldrich, St. Louis, MO) were used as a DON source and ammonium chloride (NH_4Cl) (Sigma-Aldrich, St. Louis, MO) as the DIN source for preparation of these solutions. Stock solution of 1000 mg/L as N of individual amino acids and 10,000 mg/L as N of ammonium chloride was used for preparation of individual solutions with varying DON and DIN concentrations. The maximum concentration of DON and DIN used were approximately 140 mg/L and 2000 mg/L, respectively. This upper limit of DON and DIN concentrations was decided based on the approximate concentrations of DON and DIN in the thermal hydrolysis return liquor reported by Figdore et al. (2011). All glassware used for preparation of solutions was acid washed prior to use and nanopure water was used for preparation of all stock solutions and dilutions.

Analysis

Organic nitrogen in the samples was estimated by subtracting ammonium from Total Kjeldahl Nitrogen. Total Kjeldahl Nitrogen was measured by semi micro-Kjeldahl method per Standard Method 4500-C (APHA et al. 2012). Ammonium was determined by the salicylate method (Hach, Loveland, CO) and measured using a spectrophotometer (DR 2800, Hach, Loveland, CO).

Results and Discussion

DON observed for varying DON and DIN concentrations for the three amino acids are depicted in Figures 1 (a) (b) and (c). From Figure 1(a) it can be seen that the magnitude

of error is highest for DIN concentrations of 750 mg/L and 2000 mg/L across all DON concentrations when L-methionine is used as the DON source. The highest magnitude of error is observed for 1000 mg/L and 2000 mg/L of DIN for all DON concentrations with L-Phenylalanine as the DON source. With L-Serine as the DON source all except those solutions with DIN concentration of 2000 mg/L appear to have better accuracy than that observed in Figures 1 (a) and (b).

These observations indicate that there is no common trend of error when using the TKN method for analysis of DON with high DIN concentrations. Thus, it is impossible to develop a mathematical model to correct for its inaccuracy.

Figure 2 shows the DON concentrations measured against the expected DON value when all three amino acids were mixed in approximately equal proportions. The magnitude of error observed across all DIN concentrations is much less than that observed for individual amino acids. While the reason for the improved accuracy of DON measurement is not entirely understood, a probable explanation could be that upon mixing the amino acids the interference resulting in the inaccuracy of individual amino acid is being negated.

Conclusions

- Better accuracy of DON analysis at higher DON/DIN ratio.
- With increase in DIN concentration to 2000 mg/L, the error in measurement of DON increases substantially.
- No common trend of error observed with three amino acids used. Hence, it is

impossible to develop a mathematical model to correct for its inaccuracy.

- Better accuracy observed when mixture of three different amino acids used.

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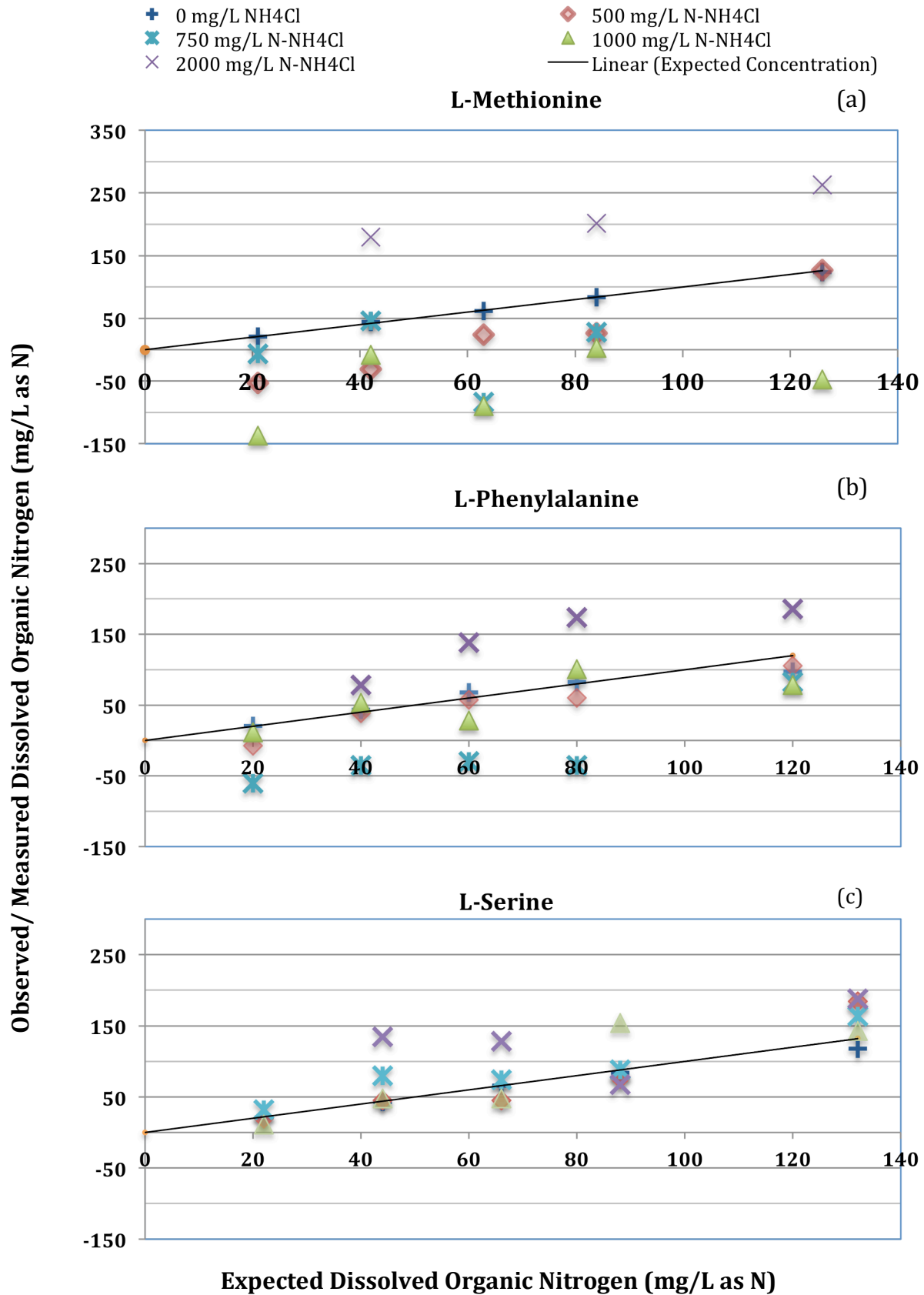


Figure A-1: Measured vs. Expected DON for varying DON/DIN ratios using individual amino acids

**L-Phenylalanine + L-Methionine + L-Serine
(equal proportions)**

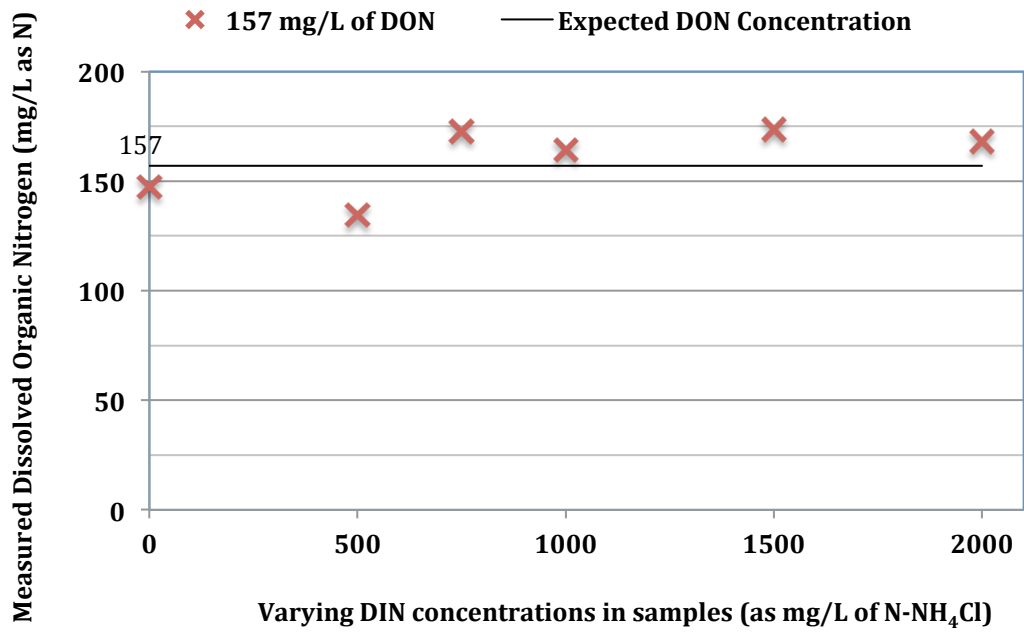


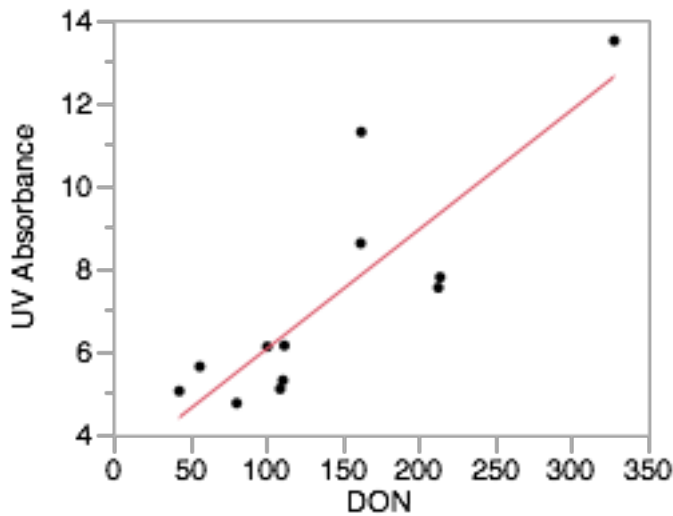
Figure A-2: Observed DON for varying DON/DIN ratios with mixture of amino acids as a DON source

Appendix B: Statistical Analysis

Chapter 3

1. Linear Regression analysis for correlation between DON and UV₂₅₄ abs for varying operating temperatures across all size fractions

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.719281 |
| RSquare Adj | 0.69121 |
| Root Mean Square Error | 1.521104 |
| Mean of Response | 7.24075 |
| Observations (or Sum Wgts) | 12 |

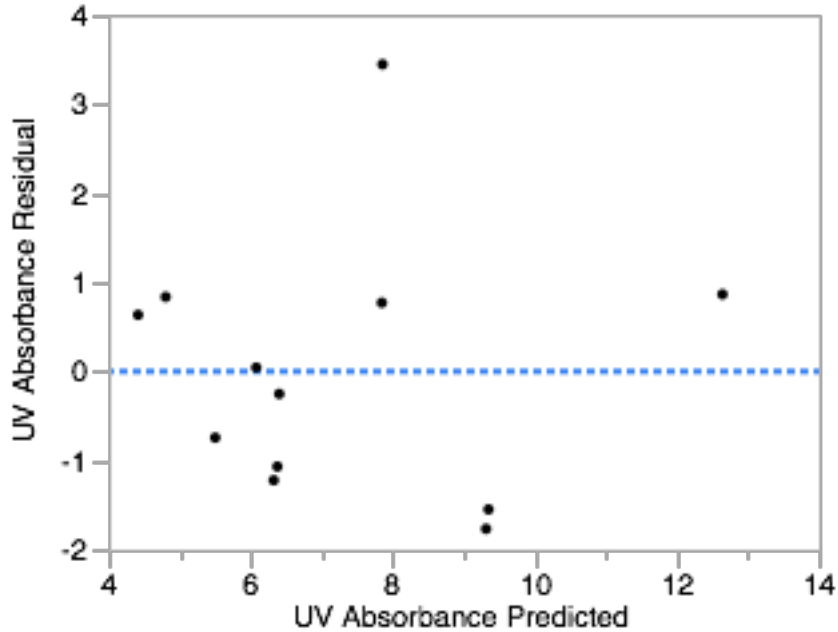
Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 1 | 59.285096 | 59.2851 | 25.6229 |
| Error | 10 | 23.137574 | 2.3138 | Prob > F |
| C. Total | 11 | 82.422670 | | 0.0005* |

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 3.1641269 | 0.917283 | 3.45 | 0.0062* |
| DON | 0.0288951 | 0.005708 | 5.06 | 0.0005* |

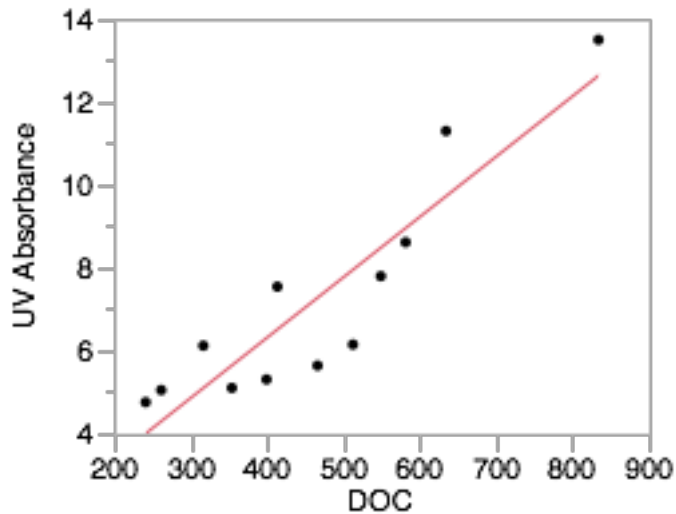
Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

2. Linear Regression analysis for correlation between DOC and UV254 abs for varying operating temperatures across all size fractions

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.826297 |
| RSquare Adj | 0.808927 |
| Root Mean Square Error | 1.19654 |
| Mean of Response | 7.24075 |
| Observations (or Sum Wgts) | 12 |

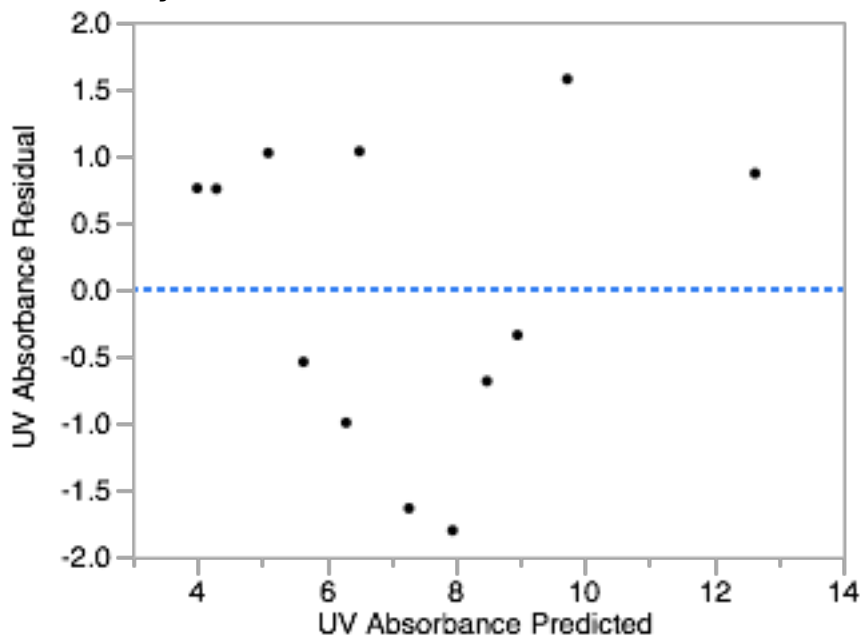
Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 1 | 68.105592 | 68.1056 | 47.5695 |
| Error | 10 | 14.317078 | 1.4317 | Prob > F |
| C. Total | 11 | 82.422670 | | <.0001* |

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 0.4827894 | 1.038932 | 0.46 | 0.6521 |
| DOC | 0.0145758 | 0.002113 | 6.90 | <.0001* |

Residual by Predicted Plot

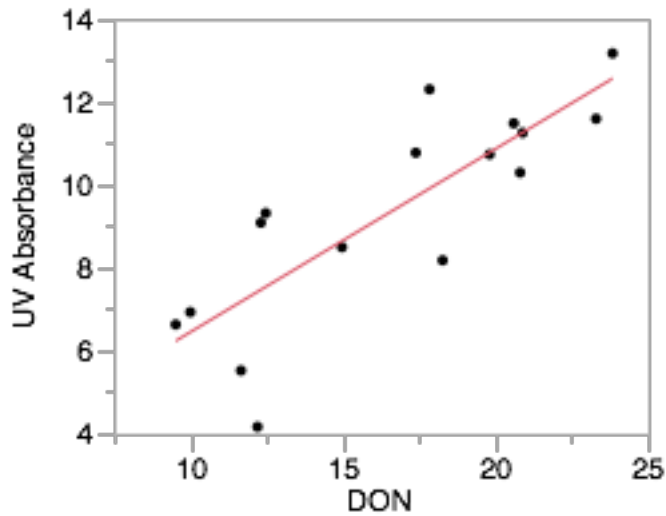


Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DOC and UV is significant.

Chapter 4

1. Linear Regression analysis for correlation between DON and UV254 abs for C-I to C-IV across all size fractions

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.674794 |
| RSquare Adj | 0.651566 |
| Root Mean Square Error | 1.513479 |
| Mean of Response | 9.374375 |
| Observations (or Sum Wgts) | 16 |

Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 2 | 66.541749 | 66.5417 | 29.0497 |
| Error | 14 | 32.068645 | 2.2906 | Prob > F |
| C. Total | 15 | 98.610394 | | <.0001* |

Mean of Response

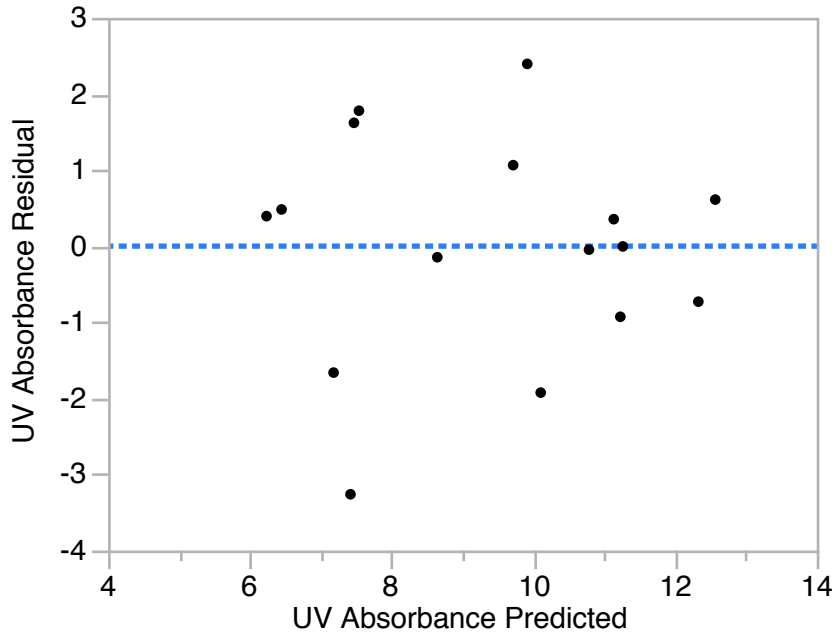
Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 2.0256585 | 1.414981 | 1.43 | 0.1742 |
| DON | 0.4422276 | 0.082049 | 5.39 | <.0001* |

Intercept

2.0256585
1.414981
1.43
0.1742

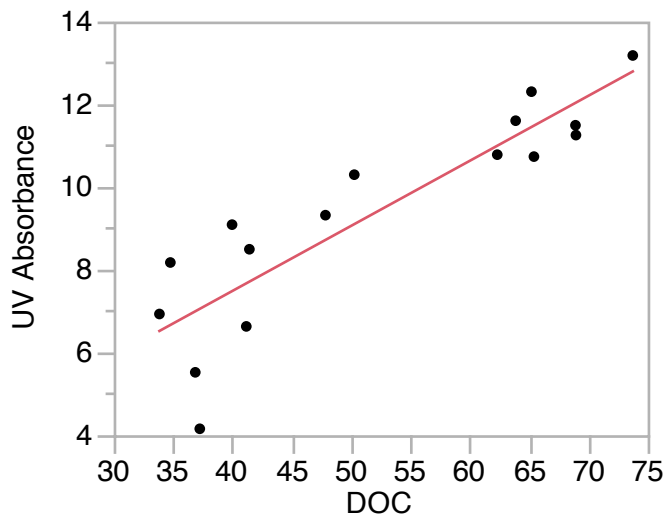
Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

2. Linear Regression analysis for correlation between DOC and UV₂₅₄ abs for C-I to C-IV across all size fraction

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.780755 |
| RSquare Adj | 0.765095 |
| Root Mean Square Error | 1.242935 |
| Mean of Response | 9.372813 |
| Observations (or Sum Wgts) | 16 |

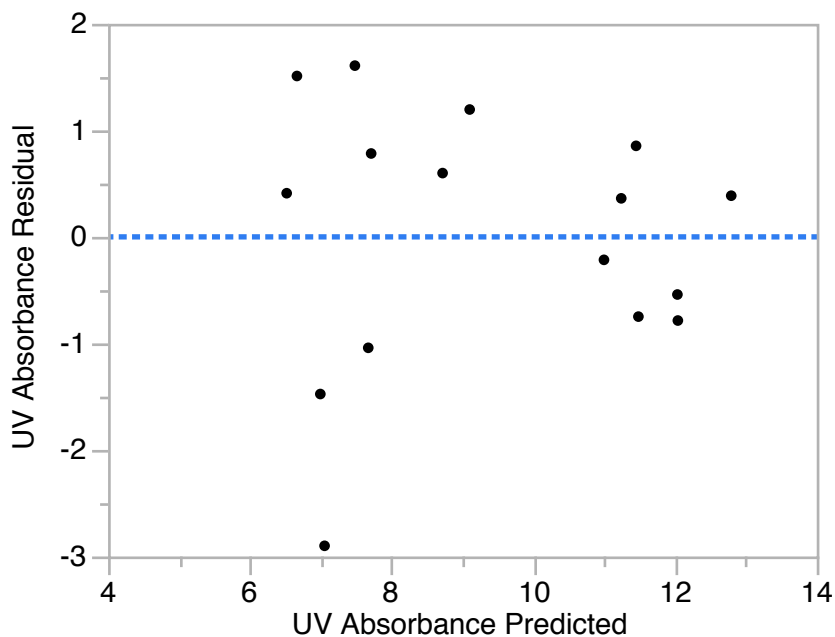
Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 1 | 77.021142 | 77.0211 | 49.8555 |
| Error | 14 | 21.628429 | 1.5449 | Prob > F |
| C. Total | 15 | 98.649570 | | <.0001* |

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 1.1951722 | 1.199128 | 1.00 | 0.3358 |
| DOC | 0.1572661 | 0.022273 | 7.06 | <.0001* |

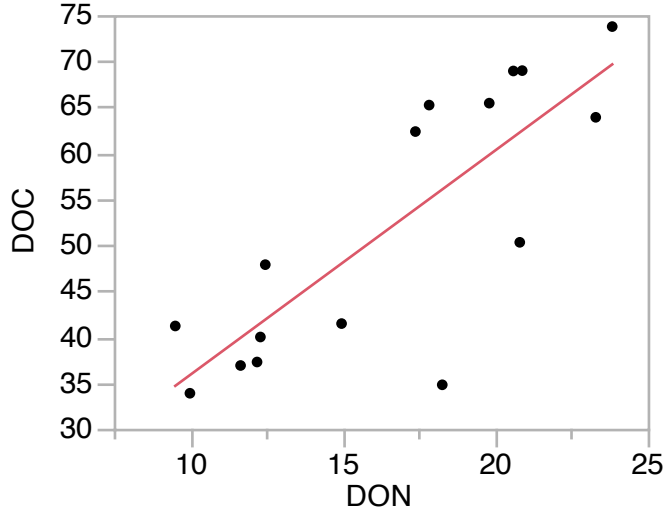
Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

3. Linear Regression analysis for correlation between DOC and DON for C-I to C-IV across all size fractions

Regression Plot



Summary of Fit

| | | |
|----------------------------|----------|----------|
| RSquare | 0.651596 | |
| RSquare Adj | 0.62671 | |
| Root Mean Square Error | 8.803345 | |
| Mean of Response | 51.99875 | 0.651596 |
| Observations (or Sum Wgts) | 16 | |

Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio | Prob > F |
|----------|----|----------------|-------------|---------|----------|
| Model | 1 | 2029.1673 | 2029.17 | 26.1832 | 0.0002* |
| Error | 14 | 1084.9842 | 77.50 | | |
| C. Total | 15 | 3114.1516 | | | |

Mean of Response

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 11.417696 | 8.230422 | 1.39 | 0.1871 |
| DON | 2.4420673 | 0.477251 | 5.12 | 0.0002* |

Error

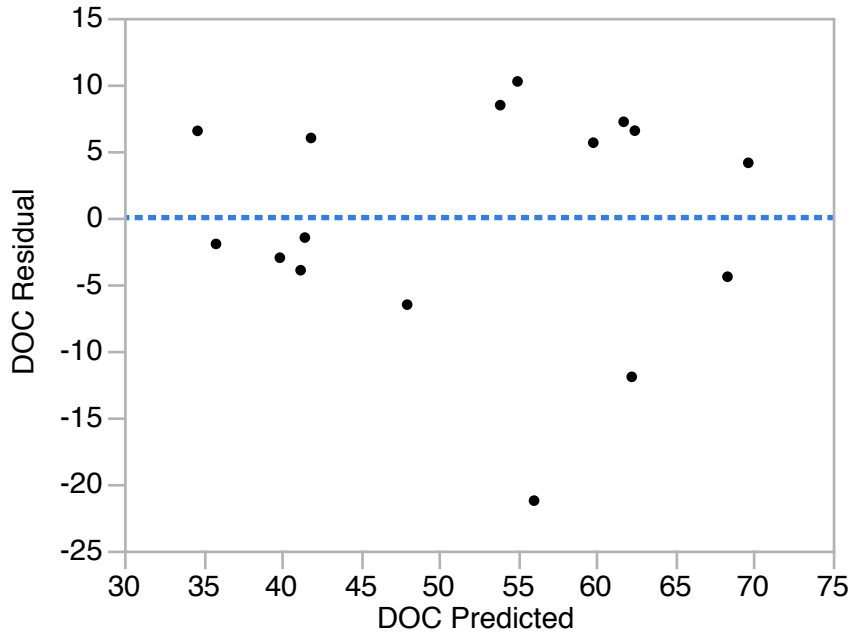
Intercept

C. Total

DON

51.99875
1
Estimate
2029.1673
Sum of Squares
1084.9842
14
77.50
Mean Square
26.1832
F Ratio
0.0002*
11.417696
8.230422
1.39
0.1871
14
1084.9842
77.50
8.230422
0.1871
15
3114.1516
2.4420673
0.477251
5.12
0.0002*

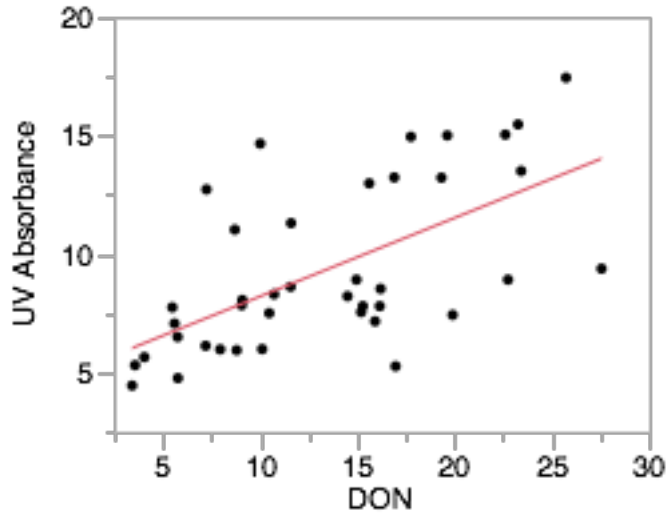
Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

4. Linear Regression analysis for correlation between DON and UV₂₅₄ abs for C-VI to C-VII across all size fraction for all polymer doses.

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.378228 |
| RSquare Adj | 0.361866 |
| Root Mean Square Error | 2.822653 |
| Mean of Response | 9.332259 |
| Observations (or Sum Wgts) | 40 |

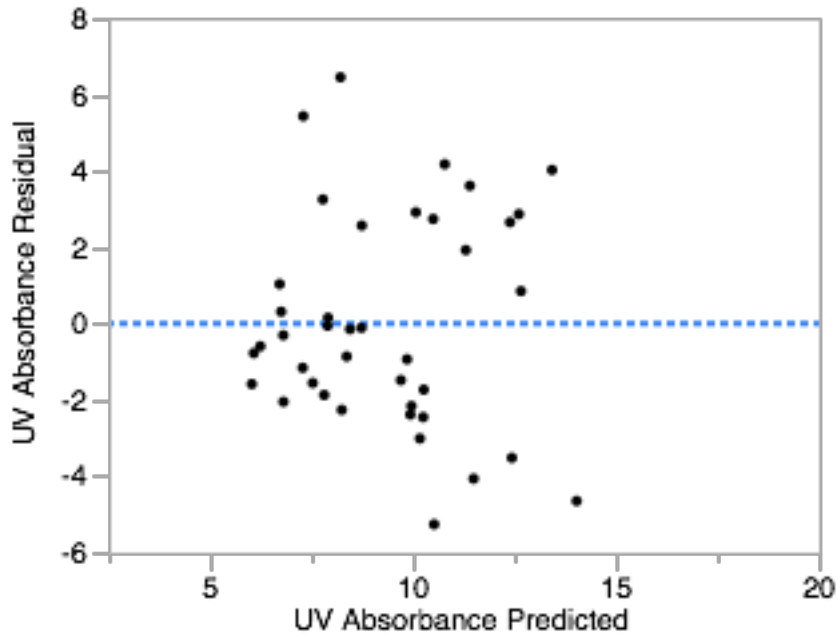
Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 1 | 184.17091 | 184.171 | 23.1157 |
| Error | 38 | 302.75999 | 7.967 | Prob > F |
| C. Total | 39 | 486.93090 | | <.0001* |

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 4.8917752 | 1.025766 | 4.77 | <.0001* |
| DON | 0.3314795 | 0.068945 | 4.81 | <.0001* |

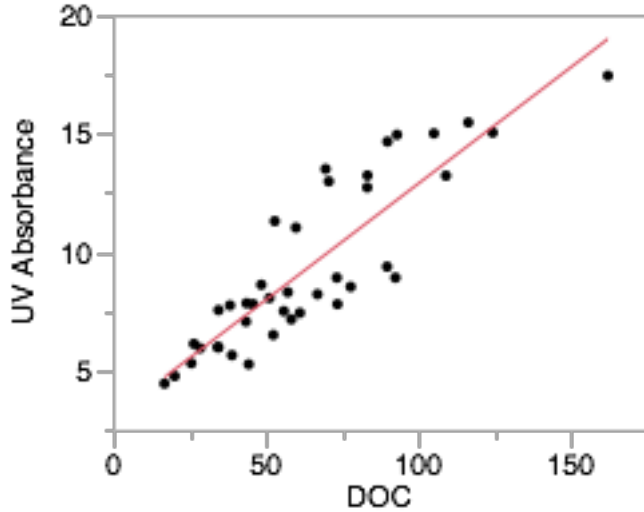
Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

5. Linear Regression analysis for correlation between DOC and UV₂₅₄ abs for C-VI to C-VII across all size fraction for all polymer doses.

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.764754 |
| RSquare Adj | 0.758563 |
| Root Mean Square Error | 1.736212 |
| Mean of Response | 9.332259 |
| Observations (or Sum Wgts) | 40 |

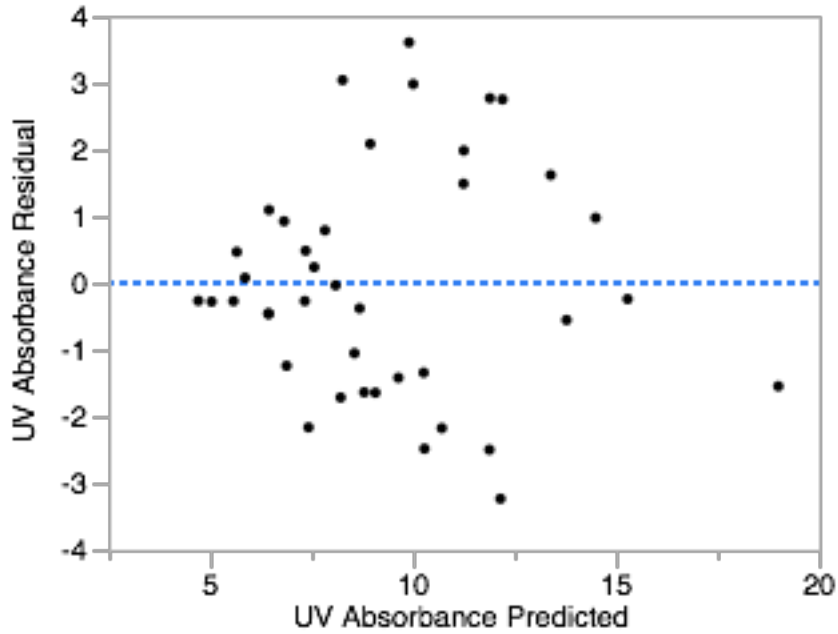
Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 1 | 372.38242 | 372.382 | 123.5331 |
| Error | 38 | 114.54848 | 3.014 | Prob > F |
| C. Total | 39 | 486.93090 | | <.0001* |

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 3.0557557 | 0.627901 | 4.87 | <.0001* |
| DOC | 0.0984633 | 0.008859 | 11.11 | <.0001* |

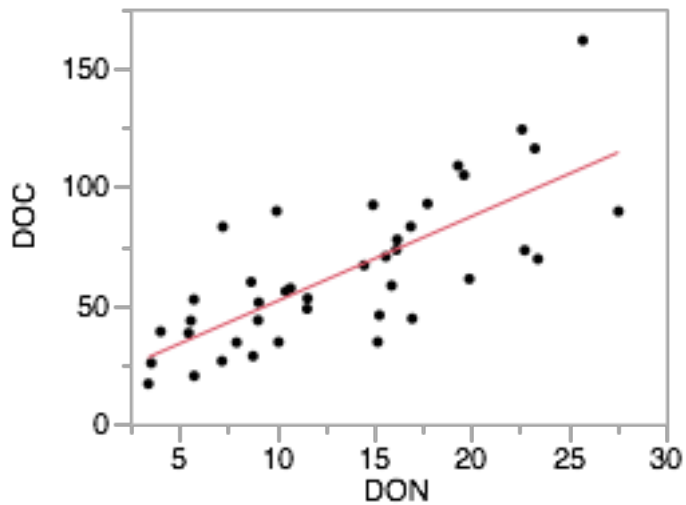
Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

6. Linear Regression analysis for correlation between DOC and DON abs for C-VI to C-VII across all size fraction for all polymer doses.

Regression Plot



Summary of Fit

| | |
|----------------------------|----------|
| RSquare | 0.561178 |
| RSquare Adj | 0.54963 |
| Root Mean Square Error | 21.06069 |
| Mean of Response | 63.74458 |
| Observations (or Sum Wgts) | 40 |

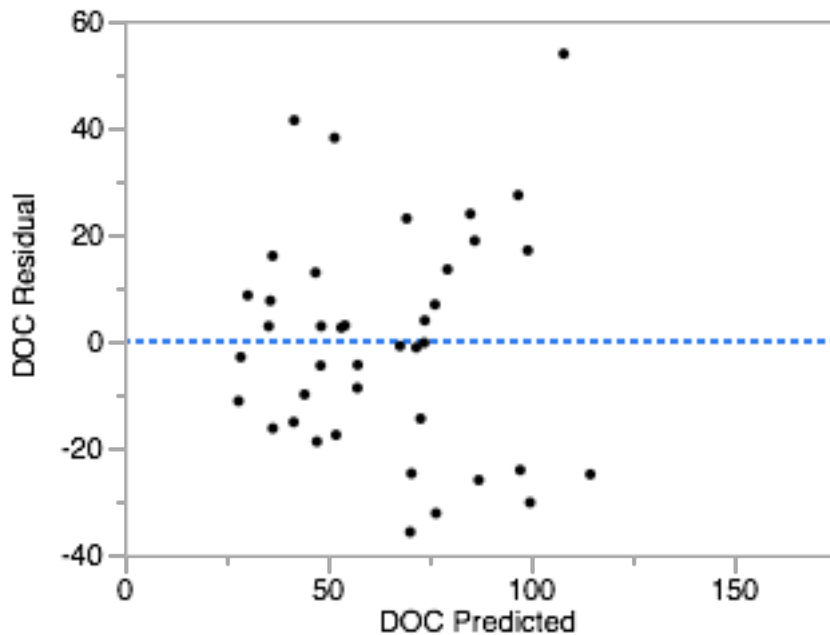
Analysis of Variance

| Source | DF | Sum of Squares | Mean Square | F Ratio |
|----------|----|----------------|-------------|--------------------|
| Model | 1 | 21554.629 | 21554.6 | 48.5954 |
| Error | 38 | 16855.004 | 443.6 | Prob > F |
| C. Total | 39 | 38409.634 | | <.0001* |

Parameter Estimates

| Term | Estimate | Std Error | t Ratio | Prob> t |
|-----------|-----------|-----------|---------|---------|
| Intercept | 15.706011 | 7.653557 | 2.05 | 0.0471* |
| DON | 3.5860513 | 0.514421 | 6.97 | <.0001* |

Residual by Predicted Plot



Since, the p-value is smaller than the significance level 0.05 and no trend is observed across residuals, we conclude that the relationship between DON and UV is significant.

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