

**Characterization and treatment of UV quenching substances and organic nitrogen in
landfill leachates and thermal hydrolysis/anaerobic digestion centrate**

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Abstract

Landfill leachates and thermal hydrolysis pretreated anaerobic digestion centrate can quench UV light at publically owned treatment works (POTWs). Increased eutrophication, has led to tightening of nutrient discharge limits in some regions of the country. Biologically recalcitrant organic nitrogen, adds to effluent nitrogen making it difficult to meet these requirements.

The study aimed at characterizing landfill leachate and centrate fractions to develop an understanding that might help design on-site treatment methods. Leachates varying in on-site treatment and ages were fractionated on basis of hydrophobic nature. Humic substances were the major UV light quenching fractions. Majority of the humic substances were > 1 kDa molecular weight cut off (MWCO) indicating that membrane treatment might be effective for UV quenching substances removal. UV absorbing substances were found to be more bio-refractory than organic carbon. Significant decrease in humic substances with long term landfilling indicated that age was important in determining the potential for leachates to impact the UV disinfection. Organic nitrogen was observed to be hydrophilic in nature (mostly < 1 kDa). Proteins which are easily biodegradable contributed around one-third of the organic nitrogen.

For thermal hydrolysis centrate, the optimum treatment depended on particle size and hydrophobic nature. Biological treatment was observed to be more effective for the removal of

organic matter and UV₂₅₄ quenching substances for fractions < 300 kDa. Biological treatment had little impact on organic nitrogen. Coagulation-flocculation is an effective treatment for higher molecular weight (MW) fractions whereas a membrane bioreactor would be more suitable for smaller MW fractions.

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Chapter 1. Introduction

Due to industrial and commercial development, the generation of municipal solid waste (MSW) is rapidly growing. In 2010, approximately 135.5 million tons out of 249.9 million tons of the municipal solid waste (MSW) generated in the USA was disposed to landfills (US EPA, 2011). Each ton of MSW has been estimated to generate 0.2 m³ of landfill leachate (Kurniawan et al., 2009). The costs involved in transportation and treatment makes leachate management a billion dollar industry.

Due to the complex composition of the solid waste accepted and diverse conditions of landfills, landfill leachate constituents vary significantly, but generally contain large amounts of organic matter (biodegradable and recalcitrant), ammonia-nitrogen, metals and chloride salts (Renou et al., 2008). Among all methods, including recycling, composting and incineration, sanitary landfilling is still the most common and widely accepted method of MSW disposal in the USA. New landfills are being constructed due to their economic advantages and practical convenience (Renou et al., 2008). Being a very cost effective approach for leachate disposal, landfill leachates are frequently discharged to publically owned treatment works (POTWs) (Zhao et al., 2012).

In the recent years, the presence of bio-refractory compounds in the landfill leachates has gained much attention (Vilar et al., 2011). It is widely accepted that humic substances are not readily biodegradable (Poblete et al., 2011), and can pass through the biological treatment processes in the POTWs and increase the organic matter in the effluent (Zhao et al., 2012). For disinfection in WWTPs, chlorination has been employed for about a century (Tchobanoglous et al., 2004). Over the last four decades, disinfection by-products (DBPs) produced during chlorination have been of

concern (Wu et al., 2003; Nikolaou et al., 2004; Zhang et al., 2005; Kim and Yu, 2007) due to their carcinogenicity.

Subsequently, ultra-violet (UV) disinfection has become quite popular in wastewater treatment because it can eliminate the formation of regulated disinfection by-products (DBPs) (NYSERDA, 1999). Though, $\lambda = 260$ nm is the most effective germicidal wavelength, in practice, POTWs utilize $\lambda = 254$ nm instead as it can be readily generated by mercury lamps (Tchobanoglous et al., 2004). The POTWs generally require that the UV_{254} transmittance in a wastewater stream be 60% - 65 % to insure that UV disinfection can work properly (Basu et al., 2007).

Recently, it was reported that humic substances can influence the UV disinfection in the surface water treatment plants by diminishing the effect of UV radiation on bacteria due to UV light absorption (Alkan et al., 2007). In practice, landfill leachates discharged to WWTPs are reported to interfere with their UV disinfection performance since landfill leachates from several landfills are found to strongly quench the UV light (Zhao et al., 2012). However, there have been limited investigations into the influence of bio-refractory organic matter, such as humic acids and fulvic acids on UV disinfection.

With the integration of nitrification and denitrification systems into most POTWs, the organic nitrogen fraction accounts for as high as 80 % of the total nitrogen in POTW effluents (Qasim, 1998). A major portion of the composition of organic nitrogen in wastewater effluents is still unknown with the sum of known specific components accounting for less than 10 % of the DON

([Pehlivanoglu-Mantas and Sedlak, 2008](#)). Also, with organic nitrogen being identified as an issue of concern, stricter discharge limits have been imposed for total nitrogen ([Chesapeake Bay Program, 2004](#)). Chlorination can also generate carcinogenic nitrogenous disinfection by-products (NDBP), especially in leachates with high dissolved organic nitrogen ([Mitch and Sedlak, 2004](#)).

Thermal hydrolysis is a solids pretreatment technique that uses high temperature and pressure prior to mesophilic anaerobic digestion to improve digestion and dewatering. It can result in increased biogas production, doubling of digester loadings and can produce pathogen-free biosolids with an increased cake solids concentration ([Kopp and Ewert, 2009](#); [Elliot and Mahmood, 2007](#); [Zabranska et al., 2000](#)). Since 1995, 20 plants have been built or are in construction (mainly in Europe) ([Camacho et al., 2008](#)). This technique is being implemented in the US for the first time ([Figdore et al., 2010](#)).

The dewatering sidestream or centrate from the process contains higher ammonium-N than conventional anaerobic digestion processes ([Kepp et al., 2001](#)). Ammonia can contribute to eutrophication and can be toxic to sensitive aquatic biota. This reject water stream can also significantly impact the performance of secondary treatment systems for nitrification and nitrogen removal ([Constantine, 2006](#)). In wastewater treatment plants with sludge digestion, the return liquor typically comprises about one percent of the total plant flow volume, but 10-30% of the nitrogen load to the plant ([Mulder et al., 2006](#); [Constantine, 2006](#)). With the permitted annual load limit for plant effluent total nitrogen being lowered in many regions of the country, several treatment techniques for the removal of nitrogen in the recycle stream, such as the DEMON process, are being explored ([Figdore et al., 2011](#)). Also, similar to landfill leachates the presence

of UV₂₅₄ quenching substances in the centrate can lead to a significant decrease in the efficiency of the UV₂₅₄ disinfection systems at treatment plants.

This study aims at the identification and characterization of the fractions of the landfill leachates and thermal hydrolysis/anaerobic centrate which are responsible for UV₂₅₄ quenching and organic nitrogen loading in the POTWs. The particle size and hydrophobic nature based fractions of the raw and biologically treated landfill leachates and thermal hydrolysis centrate were analyzed mainly for total organic carbon (TOC), UV₂₅₄ absorbance, organic nitrogen (ON) and proteins. This characterization might help us design effective on-site treatment techniques for the removal of the problematic fractions in the landfill leachates and thermal hydrolysis centrate.

In [Chapter 3](#), landfill leachates of varying ages and types of on-site biological treatment were collected from three landfills (Pennsylvania (PA), New Hampshire (NH) and Kentucky (KY)). These leachates were fractionated on the basis of their hydrophobic nature into humic acids (HA), fulvic acids (FA) and a hydrophilic fraction (Hpi). The particle size distribution of the different hydrophobic-hydrophilic fractions in all the leachates was also examined. The effectiveness of the different treatments namely: conventional biological treatment – sequencing batch reactor having cycles of nitrification and denitrification for the PA leachate, powdered activated carbon addition to activated sludge system (PACT) for the NH leachate and continuous aeration treatment for the KY leachate was also examined for the removal of organic matter and UV quenching substances. Humic substances (HA and FA) were observed to be the major UV quenching substances which were mainly > 1 kDa. The Hpi fraction which contributed to majority of the organic matter was observed to be mainly < 1 kDa. It was observed that the

biologically treated landfill leachates when subjected to a 1 kDa molecular weight cut-off (MWCO) membrane treatment were able to meet the 60 % transmittance requirement of the POTWs.

In [Chapter 4](#), to study variation in UV₂₅₄ absorbing organic carbon and organic nitrogen, leachate samples ranging from cells with ages, 2 to 30 years from a large landfill in Kentucky were collected and fractionated on basis of their particle size and hydrophobic nature into humic acids, fulvic acids and a hydrophilic fraction. The effectiveness of long term landfilling, aerobic biological treatment and membrane treatment for organic matter and organic nitrogen removal was examined. Humic materials which were the major UV₂₅₄ absorbing substances degraded significantly with landfill age. A significant decrease in humic substances with long term landfilling indicated that age is important in determining potential for leachates to impact UV disinfection in POTWs. Microorganisms capable of degrading UV₂₅₄ absorbing substances were found to require a longer detention time which cannot be provided by on-site aerobic biological treatment. The Hpi fraction which was the major contributor to organic nitrogen and proteins became increasingly recalcitrant with age. Proteins contributed around one-third of the organic nitrogen for all landfill ages.

In [Chapter 5](#), a particle size and hydrophobic nature based characterization of the raw and biologically treated thermal hydrolysis centrate is presented. It compares the different physico-chemical and biological treatment processes which can be implemented and what impact the treatment has on the particle size and hydrophobic distribution. Chapter 5 also tries to identify the hydrophobic fractions of the centrate which were the main contributors of UV₂₅₄ absorbance

and the organic nitrogen. The HA's and the Hpi's were the major contributors to the organic matter, but the humic substances were mainly responsible for the UV₂₅₄ quenching. Biological treatment was observed to be more effective for the removal of organic matter and UV₂₅₄ quenching substances for fractions < 300 kDa but had little impact on organic nitrogen for any of the MWCs. Coagulation-flocculation was observed to be a better treatment process for fractions > 300 kDa, exhibiting better UV₂₅₄ quenching substances and organic removal rates than biological treatment. Thus, coagulation-flocculation was observed to be better for the higher molecular weight (MW) fractions whereas a membrane bioreactor would be more suitable for the smaller MW fractions.

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Chapter 2. Literature review

2.1 Landfill leachate

2.1.1 Leachate formation and composition

A landfill is a system designed and constructed to dispose of discarded waste by land burial to minimize the release of contaminants to the environment. It is one of the oldest means of solid waste disposal. Landfill bacteria produce gas and soluble chemicals when biodegradable waste, such as paper, cardboard and waste food, is disposed of to the anaerobic conditions of a landfill. The soluble chemicals combine with liquids in the waste in addition to the precipitation falling over the landfill to form landfill leachate (Kostova, 2006). A composition of physical, chemical and microbial processes transfer pollutants from the landfilled waste to the percolating water (Christensen and Kjeldsen, 1989). The leachate is composed of water, and organic and inorganic chemicals from the decomposition of waste.

Leachate generation rates are primarily dependent on the amount of liquid which the waste originally contained, the quantity of precipitation that enters the landfill through the cover or falls directly on the waste and the seasonal variation in the precipitation. Chemical character will be affected by the biological decomposition of biodegradable organic materials, chemical oxidation processes, and dissolving of organic and inorganic materials in the waste. The leachate's chemical composition will change as the landfill goes through the various phases of decomposition (Farquhar, 1989). Thus, the stabilization state, which is related to the age of a landfill, is considered one of the important factors on which the chemical composition of a landfill leachate depends (Kjeldsen et al., 2002).

Landfill leachates contain a number of contaminants which can be broadly categorized into dissolved organic matter, inorganic macrocomponents, heavy metals, and xenobiotic compounds (Christensen et al., 1994). The concentrations of all these groups are pretty high during the initial phases of the landfilling process when the leachate is still young. During the initial phases, the leachate is generally characterized by extremely high concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total and ammoniacal nitrogen, anions (e.g. Cl^- and SO_4^{2-}), cations (e.g. Na^+ and K^+) and heavy metals (e.g. Cd, Cu and Zn). It also contains a variety of trace organics and xenobiotic compounds. Toxic organics such as halogenated aliphatic (e.g. chloroform and dichloromethane), aromatic hydrocarbons (e.g. benzene, toluene, ethyl benzene and xylene), phenolic and many others have been found in a number of different studies (Andreottola and Cannas, 1992; Krug and Ham, 1997; Oman, 1999).

As the leachate reaches a more stabilized state, lower concentrations and BOD/COD ratios are observed. Along with the decrease in the volatile fatty acids and organic matter, the BOD/COD ratio also decreased due to increased stabilization. With ageing, the leachate organic matter contains a greater portion of higher molecular weight humic and fulvic-like material (Milot, 1986). During this aging process, however, ammonia does not decrease; in fact at times it increases (Timur et al., 2000), and thus tends to remain as a consistent pollutant. Leachate from mature landfills is characterized by high N/COD ratio (> 0.5) (Klimiuk and Kulikowska, 2004). Due to complex composition and high concentration of hazardous compounds, pollution of groundwater and surface water are the major potential environmental impacts related to landfill leachates (Kjeldsen et al., 2002).

2.1.2 Characterization

Landfill leachate is a kind of wastewater with high dissolved organic matter (DOM) content (He et al., 2006 and Seo et al., 2007). The high DOM content is the main component of the wastewater rejected by nanofiltration. The DOM exhibits highly stable and microbially refractory properties. It is widely accepted that humic substances are not readily biodegradable (Poblete et al., 2011) and can pass through the biological treatment processes in the POTWs elevating the organic matter level in the effluent in addition to the formation of harmful disinfection by-products (Zhao et al., 2012).

Many investigations have focused on characterizing the chemical structure, molecular size and formation source of DOM in aquatic environments. The fractionation and characterization method recommended by the International Humic Substances Society is an effective method for characterizing the DOM (Alberts and Takács, 2004, Imai et al., 2002 and McDonald et al., 2004). After fractionation, DOM can be isolated into much purer humic acid (HA), fulvic acid (FA) and hydrophilic (Hpi) fractions for further analysis. Landfill leachate can be fractionated into humic acids (HA), fulvic acids (FA) and hydrophilic (Hpi) fractions based on their hydrophobic nature and solubility characteristics. Methods developed by Thurman and Malcolm, 1981; Leenheer, 1981 and Christensen et al., 1998 have long been as standard methods for the isolation and separation of humic substances from aquatic samples. This method uses chemical precipitation to remove humic acids followed by the XAD resin which is a non-ionic polystyrene resin to sorb fulvic acids. The remaining organic matter is considered to be the Hpi fraction.

The HA's and FA's together constitute what is called humic substances and are hydrophobic in nature. The fulvic acids are generally considered the lower molecular weight humic substances (Tan, 2003). Elemental analysis, spectroscopic characterizations, molecular distribution and titration are commonly used to describe the properties of the fractions (Kang et al., 2002, Ma et al., 2001 and Nanny and Ratasuk, 2002). The structural characteristics of HA and FA consists of an aromatic core surrounded by hydrolysable units of aromatic acids and phenols linked by ester and ether bonds (Göbbels and Püttmann, 1997).

In recent years, organic nitrogen has been recognized as a new emerging issue for the water environment. The discharge surface water total nitrogen limits are being lowered in many regions of the country. Most of the focus is with the removal of the inorganic nitrogen from the wastewater. However, the organic nitrogen can be a major contributor to the plant's effluent nitrogen (Johnson et al., 2010). With the wider use of nitrification/denitrification, organic nitrogen can account for up to 80% of dissolved nitrogen in the municipal WWTP nitrification-denitrification effluents (Qasim et al., 1999), impacting adversely many coastal and estuarine ecosystems as well as certain freshwater ecosystems by eutrophication (Pehlivanoglu-Mantas and Sedlak, 2004). On the other hand, dissolved organic nitrogen (DON) can be a potential source of nitrogenous disinfection by-products (NDBP) (Mitch and Sedlak, 2004).

There is not much information available on the identification of the chemical organic nitrogen species in wastewater treatment plant (WWTP) effluents. According to Pehlivanoglu-Mantas and Sedlak (2008), the sum of the specific compounds normally accounts for less than 10% of the organic nitrogen, leaving most of the organic nitrogen unidentified. A study by Westgate and

Park (2010) showed that, proteinaceous substances are significantly correlated with organic nitrogen and could comprise up to 60% of the organic nitrogen in the WWTP effluent.

Particle size fractionation of the DOM has been used to characterize organics in water (Xu et al., 2011), wastewater (Leiviska et al., 2009) and landfill leachate, in conjunction with measurements of general constituents such as TOC, BOD and COD and other specific compounds. To characterize landfill leachates, size fractionation has widely been conducted by means of microfiltration (0.1 to 10 µm) and ultrafiltration (0.001 to 0.1 µm) (Slater et al., 1985; Calace et al., 2001; Lou and Zhao, 2007; Li et al., 2009) to explore the particle size distribution of the organics. Studies have shown that 47-92% (in terms of TOC) and up to 50% (in terms of COD) of organic substances are from the < 1 kDa fraction, which has significant implications for landfill leachate treatment as these small molecular weight organics are difficult to physically or chemically remove.

2.1.3 Treatment

Some of the conventional methods for the treatment of landfill leachates include leachate transfer which includes the co-treatment of the landfill leachate with the municipal sewage in the POTWs. Biodegradation processes can be aerobic or anaerobic and physico-chemical processes may include chemical oxidation, adsorption, ion exchange, chemical precipitation, coagulation-flocculation, sedimentation/floatation and air stripping (Renou et al., 2008). The type of technique which is needed for the treatment of the leachate depends on the relationship between the age of the landfill and the amount of organics. The performance or efficiency of a treatment technique is usually evaluated in terms of removal of parameters like COD, TOC, ammonia and

heavy metals against the selected information on pH, dose required and other conditions required for the treatment.

The leachate transfer and co-treatment option has been a very popular option for the treatment of the landfill leachates due to its simplicity, easy maintenance and low operational costs (Ahn et al., 2002), but the presence of low biodegradability organic compounds like humic substances has led to decrease in the treatment efficiency of the combined waste in the WWTPs (Cecen and Aktas, 2004). In this co-treatment, the ratio of the landfill leachate to the domestic wastewater is of great importance as with increase in the amount of landfill leachate, especially greater than 10 % of the total flow, the COD and ammonia reduction considerably decreases.

Biodegradation results in the conversion of the organic matter in the leachates into carbon dioxide and sludge under aerobic conditions and into biogas under anaerobic conditions (Lema et al., 1988). Biological treatment has proven especially important for the degradation of the organic carbon and nitrogen species in young leachates with a relatively high BOD/COD ratio (>0.5). Aerobic biological processes based on suspended-growth of the biomass, such as aerated lagoons, conventional activated sludge processes and sequencing batch reactors (SBR), have been widely applied and extensively studied (Li and Zhao, 2001; Bae et al., 1999; Hosomi et al., 1989). As high as 96 % COD and 99 % ammonia removal efficiency have been reported for activated sludge and SBR systems (Lo, 1996). Anaerobic treatment techniques are more suitable for the treatment of highly concentrated leachate streams, and offer lower operating costs as well as production of usable biogas and a pathogen free residual that can be used as a cover material (Im et al., 2001). Among the various anaerobic biological treatment techniques, the use of

anaerobic bioreactors with cross flow membranes is a very attractive option for the removal of chemical oxygen demand (COD) and ammonia especially for landfill leachates (Chen et al., 2008). As high as 95 % COD removal has been observed to be achieved with a 10-20 % (v/v) leachate and a HRT of 1-7 days, organic loading rate (OLR) of 0.7–4.9 kg COD/m³ d with excellent biogas production (Bohdziewicz et al., 2008).

The physical/chemical techniques are usually used either as a pretreatment technique, a polishing step or a supplement to the biological treatment of the landfill leachate (Renou et al., 2008). Coagulation-flocculation is a popular technique which has been noted to be quite successful especially for the aged and stabilized leachates for whom biological treatment is not much effective (Kang and Hwang, 2000; Ramirez and Velasquez, 2004). It is also quite effective for the removal for the bigger molecular size organic species and can remove upto 85 % of the humic substances. The selective chemical precipitation of the ammonium ions has shown to have increased the efficiency of many biological treatment systems, as at times the high ammonium concentrations can be inhibitory to biological treatment (Li and Zhao, 2001). The adsorption of pollutants onto activated carbon in columns or in powder form provides better reduction in COD levels than the chemicals methods, whatever the leachate age and stabilization state (Fettig et al., 1996; Morawe et al., 1995). Adsorption by activated carbon has been used along with biological treatment for effective treatment of landfill leachate (Morawe et al., 1995, Cecen et al., 2003). The main drawback is the need for frequent regeneration of columns or an equivalently high consumption of powdered activated carbon (PAC).

Advanced oxidation processes (AOPs) generate and utilize hydroxyl radicals ($\bullet\text{OH}$), which can breakdown organic compounds that cannot be destroyed by biological processes or other conventional oxidation methods. AOPs improve the biodegradability of recalcitrant organic pollutants to a range compatible with subsequent economical biological treatment (Wang et al., 2003). These processes usually involve a combination of strong oxidants, e.g. O_3 , H_2O_2 and UV irradiation (Renou et al., 2008). The application of Fenton's reagent is widely reported for the treatment of landfill leachates. In terms of biodegradability improvement, BOD/COD ratios close to 0.5 have been reported especially for mature leachates (Morais et al., 2005). The reported COD removal efficiencies range from 45% (Kim et al., 2001) to 85% (Roddy and Choi, 1999). AOPs have been used in the past for the biologically treated landfill leachates because of their operational simplicity and effectiveness (Lopez et al., 2004). Ion Exchange is capable of effectively removing organic compounds, ammonia nitrogen and traces of metal impurities to meet the increasingly strict discharge standards in developed countries. Ion exchange has been found to be an effective refining step for biologically treated leachates (Kurniawan et al., 2006). Recent studies have indicated that ion exchange treatment using an anionic resin can be very effective for controlling the color, COD, suspended solids and turbidity problems in stabilized leachates (Bashir et al., 2010). They have also been observed to be effective for the removal of humic substances (Fettig, 1999).

The conventional treatment techniques even when applied in different combinations are not sufficient to meet the tightening leachate discharge regulations in many of the countries, especially, for the ageing and stabilized landfill sites. Membrane treatment processes like microfiltration, ultrafiltration, nanofiltration and reverse osmosis systems are the newest leachate treatment techniques which have been gaining a lot of popularity in the recent years.

Ultrafiltration has not just been used for the removal of the higher molecular weight substances like humic substances in the leachates but also may be used as a tool to fractionate organic matter and so to evaluate the preponderant molecular mass of organic pollutants in a given leachate. It can be used to remove the components which can foul reverse osmosis process and can also be applied as a post-biological treatment technique (Bohdziewicz et al., 2001). Studies have demonstrated that upto 50 % of the organic matter can be removed using the ultrafiltration alone and this can also be used as the separation medium in membrane bioreactors. Membrane bioreactor process efficiencies have been found to be in the range of 95–98% in terms of TOC reduction, and have exceeded 97% for specific organic pollutants (Renou et al., 2008).

Nano filtration membranes have a typical pore size from 200 to 2000 kDa. They have a high rejection rate for sulfate ions and for dissolved organic matter in addition to very low rejection for chloride and sodium which greatly reduces the volume of concentrate (Peters, 1998). Physical methods in combination with nanofiltration have been found to be able to achieve COD removal rates of upto 80% (Trebouet, 2001). Reverse osmosis systems not only have a very high installation cost but also involve high recurring maintenance costs. Also, it's extremely difficult to handle and post-treat the RO system's concentrate (Mickley and Jordahl, 2012). The treatment of the concentrate accounts for a major portion of the total cost of the entire RO process (Yamada, 2005). Reverse osmosis though has a high energy requirement but have can result in up to 98-99 % removal of the COD.

2.2 Thermal hydrolysis pretreated anaerobic digestion centrate

Thermal hydrolysis process is a high-pressure steam and high temperature (165-180 °C) pretreatment for anaerobic digestion of municipal, industrial sludge, and bio-waste. This process has been under operation in different parts of the world, especially Europe since 1995 and presently has more than 20 operational plants around the world. It can help reduce disposal quantities and the cost of building and operating digesters. It can result in doubling digester loadings when compared with conventional mesophilic digesters through lower retention times and higher dry-solids content in digesters, increased biogas production (50-65 % of the volatile solids in the sludge are converted to biogas which is rich in methane and low in hydrogen sulfide) and can produce pathogen-free and stabilized biosolids product with increased cake dewaterability (50-100 % increase in cake dewaterability). It is a highly energy efficient process with low operating costs. The production and quality of the resultant biosolids save transport and energy costs as well. The end product can be classified as a class A solid and can thus be applied directly to agricultural processes or composted or dried for use as fertilizer or bio-fuel. In addition to optimizing energy-efficiency and lowering operating costs, it also eliminates odor problems associated with the treatment of organic materials. Thus, this process maximizes both flexibility and profitability (Cambi, 2013).

The reject sidestream/filtrate/centrate is which produced due to the dewatering of the thermal hydrolysis sludge contains higher ammonium-N and VFA concentrations than conventional anaerobic digestion processes (Figdore et al., 2011). High levels of ammonia can contribute to eutrophication and can be toxic to sensitive aquatic biota. This reject water stream can also significantly impact the performance of secondary treatment systems for nitrification and

nitrogen removal ([Constantine, 2006](#)). In wastewater treatment plants with sludge digestion, the return liquor typically comprises about one percent of the total plant flow volume, but 10-30% of the nitrogen load to the plant ([Mulder et al., 2006](#); [Constantine, 2006](#)). With the permitted annual load limit for plant effluent total nitrogen being lowered in many regions of the country, several treatment techniques for the removal of nitrogen in the recycle stream are being explored ([Figdore et al., 2011](#)).

Usually, in order to effectively manage the centrate and treat it, it is subject to separate treatment. A number of physico-chemical processes like hot air/steam stripping, ammonia recovery process, ion exchange, breakpoint chlorination and struvite precipitation are considered for removing the excess ammonia in the centrate. The biological process being practised for this purpose include suspended growth activated sludge, fixed film, bioaugmentation, nitrification and deammonification with the energy demand being least for the deammonification process ([Law, 2012](#); [Constantine, 2006](#)). During biological centrate treatment, completely mixed activated sludge basins are used, each with its own final clarifier. A completely mixed regime in the bioreactors is desirable in this application so that the high ammonia concentration in the centrate stream does not cause an inhibitory effect on the biological process ([City of Winnipeg, 2000](#)). Most of the focus in centrate treatment is on the removal of the inorganic nitrogen. However, the organic nitrogen from the centrate can be a major contributor to the plant's effluent nitrogen ([Johnson et al., 2010](#)).

There is not much literature available on the characterization or removal of the organic matter from the centrate. Ultra-violet (UV) disinfection has become quite popular in wastewater

treatment because it can eliminate the formation of regulated disinfection by-products (DBPs) (NYSERDA, 1999). The POTWs generally require that the UV_{254} transmittance in a wastewater stream be 60% - 65 % to ensure that UV_{254} disinfection can work properly (Basu et al., 2007). Thus, the organic matter which is present in the centrate is of particular important as it can quench UV light reducing its efficiency in a manner similar to landfill leachates.

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Chapter 3. Characterization and treatment of organic constituents in landfill leachates that influence the UV disinfection in the publicly owned treatment works (POTWs)

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3.0 Abstract

Landfill leachates strongly quench UV light. When discharged to POTWs, leachates can interfere with UV disinfection. To investigate the UV quenching problem of landfill leachates, a variety of landfill leachates with a range of conditions were collected and characterized. The UV blocking component was found to be resistant to biological degradation so they pass through wastewater treatment plants and impact the subsequent UV disinfection system. Leachate samples were fractionated into humic acids (HA), fulvic Acids (FA) and hydrophilic (Hpi) fractions to investigate the source of UV absorbing materials. Results show that for all leachates examined, the specific UV₂₅₄ absorbance (SUVA₂₅₄) of the three fractions follows: HA > FA > Hpi. However, the overall UV₂₅₄ absorbance of the Hpi fraction was important because there was more hydrophilic organic matter than humic or fulvic acids. The size distribution was also investigated to provide information about the potential for membrane treatment. It was found that the size distribution of the three fractions follows: HA > FA > Hpi. This indicates that membrane separation following biological treatment is a promising technology for removal of humic substances from landfill leachates. Leachate samples treated in this manner could meet the UV transmittance requirement of the POTWs.

Keywords: humic substance, size distribution, nanofiltration, biodegradability, XAD resin.

3.1 Introduction

In 2010, about 135.5 million tons out of 249.9 million tons of municipal solid waste (MSW) generated in the USA were disposed to landfills [1]. The landfilled MSW decomposes through a series of biological and physical-chemical processes [2]. Soluble waste fractions and

decomposition products are carried away by rainwater percolation and infiltration, generating a highly contaminated landfill leachate which threatens the surrounding surface and ground water. In modern sanitary landfills, impermeable liners and collection systems are installed to prevent the escape of leachate. It is estimated that 1 ton of landfilled MSW will produce 0.2 m³ of leachate [2]. Hence, a large amount of collected landfill leachate must be treated before being discharged. Accordingly, governments of many countries and regions apply strict regulation for the discharge of landfill leachate.

Generally, the collected landfill leachate is either treated on-site, and then discharged directly to water bodies, discharged or transported to an off-site waste water treatment facility, or pretreated on-site, then discharged or transported to a publicly owned treatment works (POTW) or other waste water treatment facilities. A variety of treatment technologies have been applied to landfill leachate. Among those treatment processes, biological treatment (on-site and off-site) is commonly used for the removal of bulk organic compounds, based on its reliability, simplicity and cost effectiveness [3]. Usually leachates are pretreated to avoid an impact on the downstream biological treatment process. Hence, transporting to local municipal sewer systems with appropriate pretreatment or co-treatment of leachate and wastewater in the wastewater treatment plants (WWTPs) is a favored option for landfill leachate disposal.

However, the unique characteristics of landfill leachate create some challenges for co-treatment of leachate and wastewater, such as the high concentration of ammonia [4] and low biodegradability [5]. In recent years, the presence of bio-refractory compounds in landfill leachate has gained attention [6-8]. Humic substances (humic acids and fulvic acids) are believed

to be the main components that show recalcitrant properties [9]. Vegetation derivatives (paper and paperboard, yard trimmings and wood) are believed to be one of the sources of the lignin that act as the primary source for humic substances [10]. Food scraps in MSW can provide proteins, polysaccharides, lipids and nucleic acids for humification. In 2010, vegetation and its derivatives in MSW accounted for 48.3% (28.5% from paper and paperboard, 13.4% from yard trimmings and 6.4% from wood) of total MSW generation by weight [1]. Hence, landfills can provide suitable conditions for the formation of humic substances.

Over the last four decades, disinfection by-products (DBPs) produced during chlorination has been of concern [11-14] due to their carcinogenicity [12, 15]. There has been a regulatory trend toward lower residual chlorine level, but with the same pathogen kill requirement, forcing WWTPs to turn to alternative disinfectants [16]. UV disinfection has become more popular for waste water treatment because it eliminates the formation of regulated DBPs, has small footprint and results in less risk for toxic/hazardous chemical leakage. Though $\lambda = 260$ nm is the most effective germicidal wavelength, in practice, WWTPs utilize $\lambda = 254$ nm instead as it is readily generated by mercury lamps [17].

Recently, it was reported that humic substances can influence the UV disinfection in surface water treatment plants by diminishing the effect of UV radiation on bacteria due to UV light absorption [18]. In practice, landfill leachates discharged to WWTPs are reported to interfere with their UV disinfection performance since landfill leachates have been found to strongly quench UV light [19]. However, there have been limited investigations into the influence of bio-refractory organic matter, such as humic acids and fulvic acids on UV disinfection.

In this study, a variety of landfill leachates were collected from 3 landfills to examine their biodegradability, physical-chemical treatability and UV quenching characteristics. UV absorbance and organic matter level in terms of total organic carbon (TOC) were examined for bulk leachates. Then, the dissolved organic matter (DOM) in each leachate sample was fractionated into humic acids (HAs), fulvic acids (FAs) and hydrophilic (Hpi) fractions. UV quenching characteristics were examined for each fraction. Thereafter, the size distribution of each fraction was characterized to provide information for membrane separation and filtration. This study provides insight into the short term biodegradation characteristics in the engineered biological treatment of different fractions of DOM in landfill leachate and their long term biodecomposition characteristics in landfilling.

3.2 Materials and Methods

3.2.1 Leachate sample locations and processes

Leachates samples investigated in this research were collected from landfills located in Pennsylvania (PA), New Hampshire (NH) and Kentucky (KY), USA. Leachates before and after the on-site biological treatment were collected from the PA and NH landfills. Details about the on-site biological treatment facilities, the technical specifications of PA and NH landfills and leachate characteristics have been described [Zhao et al. \[19\]](#).

The KY landfill is comprised of eight separate units, designated Units 1 through 8. Leachate samples collected for this study were from Units 3, 5, 7 and 8 (KY-3, KY-5, KY-7 and KY-8). Unit 3 is an inactive landfill unit that is not receiving waste. Unit 5 has had no input for over a decade, but was operated as a bioreactor landfill for a period of time. Unit 7 was closed in 2005

and was operated as a bioreactor landfill. Unit 8 is an active permitted landfill unit. The landfill has been used for solid waste disposal for 35 years. The average ages of Units 3, 5, 7 and 8 are 30, 16, 9 and 2.5 years, respectively. The landfill has a total property of approximately 782 acres. Characteristics of the KY leachates are shown in [Table 3-1](#).

The leachate samples were shipped directly from the landfills in 20-liter polyethylene buckets and stored in a refrigerator at 4 °C to reduce microbial activity. Leachate buckets were shaken well to resuspend settled particles before sampling.

Biological treatment of the KY leachates was conducted by continuous aeration in the lab. Since leachates contain microorganisms from the waste layer of the landfill, no external seed was added. Biological flocs similar to activated sludge flocs were observed during the aeration process. Each leachate was aerated using a porous ceramic air diffuser and distilled water was added to compensate the water lost by evaporation. KY-8 and KY-7 leachate samples were aerated for 53 days and aerated leachates were sampled on the 21st, 38th and 53rd days for fractionation and analysis. KY-5 and KY-3 leachate samples were aerated for 21 days, then sampled for fractionation and analysis.

3.2.2 Fractionation

Landfill leachate samples were fractionated into humic acids (HA), fulvic acids (FA) and hydrophilic (Hpi) fractions based on their hydrophobic nature and solubility characteristics. Methods developed by [Thurman and Malcolm \[20\]](#), [Leenheer \[21\]](#) and [Christensen et al. \[22\]](#) were used in this study since they have long been a standard method for the isolation and

separation of humic substances from aquatic samples. This method uses chemical precipitation to remove humic acids followed by the XAD resin to sorb fulvic acids. The remaining organic matter is considered to be the hydrophilic fraction.

The XAD-8 resin (currently Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO) was cleaned following the method described by [Leenheer \[21\]](#). Approximately 3.5-4.5 mL bed volume of cleaned XAD-8 resin slurry was packed in a borosilicate glass column (1.0 cm×10 cm, Thomas Scientific, Swedesboro, NJ).

Ultrafiltration of leachate samples was conducted using a dead end batch ultrafiltration apparatus (Model 8200, Amicon, Belford, MA) and membrane discs with the molecular weight cut offs of 0.5 kDa, 1 kDa, 3 kDa and 100 kDa (YC05, YM1, PLBC, and PLHK, Millipore, Billerica, MA). Details can be found in [Zhao et al. \[19\]](#).

3.2.3 Analysis

All the glassware was washed with soapy water, rinsed with tap water, soaked in a 10% nitric acid solution, thoroughly rinsed with deionized water then baked at 450°C for four hours. All the chemicals used were analytical grade. Total organic carbon (TOC) was analyzed using high temperature combustion method with a TOC analyzer (TOC-5000A, Shimadzu, Japan). The chemical oxygen demand (COD) analysis was executed by the closed reflux, titrimetric method per Standard Method 5220-D [\[23\]](#). The ultraviolet absorbance at 254 nm (UV₂₅₄ absorbance) was measured with a spectrophotometer (DU 640, Beckman Coulter, Brea, California). Leachate samples and fractions were diluted in order to yield a reading within the detection range. UV readings were multiplied by the corresponding dilution factor to give the final UV absorbance

values. Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was calculated as UV_{254} divided by TOC. Total nitrogen concentrations for the samples were determined by the persulfate digestion method (Hach Company, Loveland, CO) with the measurements being made by a spectrophotometer (DR 2800, Hach Company, Loveland, CO). For FT/IR analysis, leachate samples were lyophilized under $-75\text{ }^{\circ}\text{C}$, 3 kPa, pressed with KBr pellets for the FT/IR spectroscopy (Equinox 55, Bruker, Billerica, MA) analysis. Metal analysis was conducted using a Thermo Electron X-Series inductively coupled plasma with mass spectrometer (ICP-MS) per Standard Method 3125-B [23]. Anion analysis was conducted with an Ion chromatograph (DX120, Dionex, Sunnyvale, CA) equipped with an AS9-HS column (Model No. 051786, Dionex, Sunnyvale, CA). For details please refer to Zhao et al. [19].

3.2.4 Statistics

Data were graphed using Microsoft Office Excel 2010 (Microsoft Corporation, Redmond, WA). Linear regression, hypothesis testing and other statistical analysis were performed using R version 2.14.1.3.

3.3 Results and discussion

3.3.1 Biodegradation of TOC and UV

In the first phase of this study, a comparison of biodegradability was made between the UV_{254} absorbing compounds and TOC. Leachate samples were examined for the treatment performance by various biological processes (Table 3-2). Figure 3-1 (A) shows the organic matter concentration (in terms of TOC) and Figure 3-1 (B) shows the UV_{254} absorbance data for various landfill leachates before and after biological treatment.

As shown in [Figure 3-1](#), a significant removal of organic matter (TOC) was achieved in each biological treatment process, while UV_{254} absorbance removal by biological degradation was much less than TOC removal for all leachates. Almost no biological removal of UV_{254} absorbance was found for the KY-5, KY-3 and PA leachate samples. The data in [Table 3-2](#) illustrates quantitatively the treatment efficiency of TOC and UV_{254} absorbance for various landfill leachates in the corresponding biological treatment processes. TOC removal efficiency ranged from 35% to 56%, while that of UV_{254} absorbance was no more than 29%. The data in [Table 3-2](#) shows that more TOC than UV_{254} absorbance was reduced by biological treatment, regardless of the type of treatment process and the leachate source ($p=5.611e-05$, refer to Appendix for details).

FT/IR analysis was conducted for all KY leachate samples at various ages to provide insight into the change of organic matter chemical structure associated with long term landfilling. As shown in [Figure 3-2](#), all 4 KY leachate samples show absorbance bands at the wavenumber of 1400-1310 cm^{-1} , which may be attributed to COO- groups in carboxylic organic matter [\[24\]](#). KY-8 and KY-7 spectra show absorbance bands around 1690-1630 cm^{-1} and 1570-1540 cm^{-1} , which may be attributed to the C=O stretching of amide groups (amide 1) and N-H bending of amide groups (amide 2) respectively [\[25-27\]](#). KY-5 and KY-3 did not show obvious absorbance around these ranges. This indicates decomposition of amide containing compounds, such as proteins, peptides and combined amino acids during the long term landfilling process. In addition, both KY-8 and KY-7 samples have absorbance around 1120-1000 cm^{-1} , which may be assigned to the C-O stretching of aliphatic ethers. Both KY-5 and KY-3 samples show peaks at 1030-950 cm^{-1} , which may result from the carbon rings in cyclic compounds [\[26, 27\]](#). The increasing trend of

aromaticity with landfill age may result from the bio-refractory characteristics of the aromatic compounds during decomposition in landfills. Complex absorbance bands around 700-650 cm^{-1} are related to halogenated compounds [28].

3.3.2 Hydrophobic nature based distribution of TOC and UV absorbance and their correlation

Previous studies [29-31] revealed a correlation between the UV absorbance of aqueous organic matter and the aromaticity. The study by Chin et al. [29] showed that π - π^* electron transitions occur in the UV wavelength range for phenolic substances, lignin derivatives, benzoic acids, polyenes and polycyclic aromatic hydrocarbons, many of which are precursors or components of certain types of humic substances. Also, a strong correlation was indicated in the Weishaar et al. [31] study between the specific UV absorbance (SUVA) and the aromaticity extent determined by ^{13}C NMR for various aquatic environmental organic matter samples. Proportional correlation of the SUVA₂₅₄ and the aromatic content of organic matter was also reported by Dong et al. [30]. This correlation between the aromaticity and the UV spectroscopic properties of organic matter has been used to characterize and predict the removal of NOM (natural organic matter) by ozone [32] and chlorine [33].

In this study, based on the chemical structure and composition of their origin (lignin and its derivatives), the aromaticity of humic substances (humic acids and fulvic acids) are expected to be higher than other substances in landfill leachates. Therefore, humic substances are thought to be an important contributor of the UV quenching phenomenon in landfill leachates among all categories of organic matter. To verify this hypothesis, landfill leachate samples from several sources were separated into HA, FA and Hpi fractions. UV and TOC were measured for each

fraction to provide a profile of the distribution of organic matter and the UV₂₅₄ absorbance among these hydrophobic nature based fractions.

Figure 3-3 shows the hydrophobic nature based distribution of organic matter (in terms of TOC) for the various leachates. Figure 3-3 (A) shows the data for the PA leachate samples before and after on-site sequencing batch reactor (SBR) activated sludge treatment. Figure 3-3 (B) shows the data for the NH leachate samples before and after the on-site biological treatment which was a combination of activated sludge and powdered activated carbon (PACT). Figure 3-3 (C) shows the data for the untreated KY leachate samples with different landfill ages. As shown in Figure 3-3, the TOC concentration of the Hpi fraction was the highest among all three categories and even higher than the sum of HA and FA fractions in all leachates examined.

By investigating the PA and NH leachate before and after aerobic biological treatment, it can be seen that each fraction was partially removed by biological treatment. For the PA leachate, the HA, FA and Hpi fractions were removed 41%, 40 % and 27 %, respectively in the on-site biological treatment process (SBR). For the NH leachate, the HA, FA and Hpi fractions were removed 59.8 %, 44.2 % and 53.1 %, respectively by the on-site PACT system. No significant change of the HA, FA and Hpi fractions distribution was observed for either the PA or the NH leachates after biological treatment.

By comparing the KY samples with different landfill ages (Figure 3-3 (C)), it can be seen that each fraction declined, as TOC, with increasing landfill age. The distribution of TOC also changed over time, with the HA fraction undergoing the greatest percentage decrease. The

percentage of FA was greatest in the oldest leachate (KY-3); however, the major organic fraction for all the leachates was still the Hpi fraction.

Figure 3-4 shows the hydrophobic nature based distribution of UV₂₅₄ absorbance among the HA, FA and Hpi fractions. Figure 3-4 (A) shows the UV₂₅₄ absorbance data for the PA leachate samples and Figure 3-4 (B) shows the UV₂₅₄ absorbance data for NH leachate samples, before and after on-site biological treatment. Figure 3-4 (C) shows the UV₂₅₄ absorbance data for untreated KY leachate samples at different landfill ages. As shown in Figure 3-4, UV₂₅₄ absorbance by the Hpi fraction was the highest among all three categories of fractions in all leachates studied. However, the UV absorbance by the combined HA and FA exceeded that of the Hpi fraction.

By comparing the untreated and biologically treated sample data for the PA and NH leachates, it can be seen that there was considerable difference between the impact of biological treatment between the PA and NH leachates. Almost no UV₂₅₄ absorbance was removed by biological treatment for the PA leachate. For the NH leachate, the UV₂₅₄ absorbance removal for the HA fraction was 27%, but the FA and Hpi fractions were degraded less than 10%. The removal of UV₂₅₄ absorbing compounds is much lower than overall organic matter removal (in terms of TOC), indicating the bio-refractory characteristics of the UV absorbing material. The distribution of the Hpi, HA and FA fractions in terms of UV₂₅₄ absorbance changed little for the PA leachate and NH leachates as a result of biological treatment.

To better understand the spectroscopic characteristics of the hydrophobic fractions of leachates, in a specific organic matter amount basis, UV_{254} absorbance and the corresponding TOC of all leachates examined in this study were plotted in [Figure 3-5](#). Regression plots were generated for HA, FA and Hpi fractions respectively. As shown in [Figure 3-5](#), UV_{254} absorbance is directly proportional to the concentration of organic matter (in terms of TOC) in all three organic fractions (p values were $1.17e-06$, $2.97e-05$ and $2.38e-06$ for the HA, FA and Hpi fractions respectively, refer to Appendix for details), R^2 values were 0.97, 0.93 and 0.97 for HA, FA and Hpi fractions respectively.

It should be noted in [Figure 3-5](#) that, slopes of the three regression lines are clearly different from each other. The slope of HA regression curve (0.0334) is higher than that of FA (0.0234), while the slope of FA regression curve is higher than that of Hpi (0.0130). The differences between slopes indicate that, in a specific organic matter amount basis, the HA fraction in the landfill leachate is the strongest absorber of UV light, while the Hpi fraction is the weakest UV absorber.

[Table 3-3](#) shows the $SUVA_{254}$ data of HA, FA and Hpi fractions for the leachates examined. Statistical analysis shows that the $SUVA_{254}$ for the leachate fractions follows: HA>FA>Hpi (refer to Appendix for details).

By comparing the $SUVA_{254}$ of untreated and treated leachate samples for the PA and NH landfills, it was found that the $SUVA_{254}$ of HA, FA and Hpi fractions in PA leachate increased from 2.77 L/mg·m, 1.92 L/mg·m and 1.55 L/mg·m to 4.70 L/mg·m, 3.25 L/mg·m and 2.05

L/mg·m, respectively. The increasing trend of $SUVA_{254}$ indicates that the organic matter that was biodegraded in the treatment facilities (SBR and PACT in PA and NH respectively) is not the same as the organic matter that absorbs UV light.

Different from the PA and NH leachate samples, the $SUVA_{254}$ of HA, FA and Hpi fractions in KY leachates at a variety of ages were comparable to each other, indicating that the organic matter that absorbs UV light was degraded along with the other organic matter during the long-term landfilling process.

3.3.3 Particle size distribution of HA/FA/Hpi fractions in terms of TOC and UV

The detailed particle size distribution data shown in [Figure 3-6](#) is in the pore size range of microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF). This can be a useful reference when considering the selection of membrane technologies for treatment of landfill leachates and other wastewaters.

[Figures 3-6 \(A\) and \(B\)](#) show the particle size distribution (in terms of TOC) for the HA fraction of PA and NH leachates. It can be seen that the molecular weight cut-off (MWCO) (in terms of TOC) for the HA fractions are mainly greater than 3 kDa. The > 3kDa material accounts for 78 % and 53 % TOC of the HA fractions of PA untreated and treated leachates respectively. For the NH leachates, the > 3 kDa part accounts for 50 % of the TOC of the HA fractions for both the treated and untreated leachate. It should be noted that, the > 100 kDa portion of the HA fractions of the PA and NH leachates were removed in the biological treatment processes. The removal of some of the HA fraction in the activated sludge processes might be caused by partial degradation or bio-flocculation.

Figures 3-6 (C) and (D) show the particle size distribution for the FA fraction of PA and NH leachates. Different from HA fractions, the size distribution of FA fractions is relatively evenly distributed among the size fractions. No single size fraction exceeded 50%. Except for the PA leachate, the largest fraction of FA was in the size fraction less than 500 Da.

Figures 3-6 (E) and (F) show the size distribution of Hpi fraction of PA and NH leachates. It can be seen that organic matter with MWCO < 1 kDa is the dominant in the Hpi fraction. For the Hpi fraction of PA untreated and treated leachates, the < 1 kDa part account for 68 % and 67 % of TOC respectively. For the Hpi fraction of NH untreated and treated leachates, the < 1 kDa part accounts for 73 % and 75 % of TOC respectively.

In addition, statistical analysis of the the percentage of < 1 kDa portion of HA, FA and Hpi fractions of leachates is shown in Table 3-4, it can be seen that the percentage of < 1 kDa portion in HA fractions of all leachates is smaller than that of FA fractions, while, the percentage of < 1 kDa portion in FA fractions is smaller than that of Hpi fraction (refer to Appendix for details). Therefore, generally speaking, the size of the HA fractions is bigger than the FA fraction, while the FA fraction is bigger than the Hpi fraction. The order of size is HA > FA > Hpi. This result indicates that membrane separation with a 1kDa MWCO can remove most of the HA and FA fractions, leaving predominantly the Hpi fraction which is primarily < 1kDa size.

3.3.4 Performance of combined biological treatment and membrane separation

The SUVA is greatest for HA and least for Hpi, so, the removal of the HA and FA fractions will be important for the reduction of UV absorbance in landfill leachates. The mean size of the HA and FA fractions is bigger than the Hpi fraction so membrane separation with an appropriate

pore size/MWCO is a practical technology that can remove much of the UV absorbing material by removing the HA and FA fractions.

On the other hand, based on the abundance of organic matter in Hpi fractions, the total amount of UV absorbance of the Hpi fraction is always higher than either the HA or FA fractions in all leachates samples examined. A previous study showed that biological treatment can degrade organic matter of low MW [34]. However as shown in [Figure 3-4 \(A\) and \(B\)](#), biological removal of UV absorbing organics using conventional activated sludge technology is poor for some leachates.

In this study, the treatment performance for the removal of UV absorbing material was evaluated for the combination of biological treatment and membrane separation. As shown in [Figure 3-7](#), biologically treated leachates samples (PA and NH leachates) were filtered by membranes with various MWCOs (500 Da, 1 kDa and 100 kDa). Then each filtrate was separated into HA, FA and Hpi fractions and the UV absorbance was measured for the fractions. Thus, the treatment efficiency and mechanism of UV absorbance in landfill leachates can be examined.

As shown in [Figure 3-7 \(A\)](#), the membrane with a MWCO of 100 kDa reduced the UV absorbance slightly (15%) for the PA treated leachate, while a significant removal was achieved by the 1 kDa membrane, which reduced the UV_{254} absorbance by 65%. By comparing the UV absorbance of 1 kDa and 100 kDa filtrates, it can be seen that the overall UV absorbance decrease was contributed mostly by the removal of the HA and FA fractions. From 100 kDa to 1 kDa, HA, FA and Hpi fractions decreased by 3.5 cm^{-1} , 2.1 cm^{-1} and 1.3 cm^{-1} respectively. Eighty

one percent of the UV absorbance reduction was contributed by removal of the HA and FA fractions.

By reducing the MWCO to 500 Da, the UV absorbance of the PA biologically treated leachate decreased from 4.88 cm^{-1} to 1.21 cm^{-1} . By comparing the UV absorbance of the 500 Da and 1 kDa filtrates, it can be seen that the overall UV absorbance decrease was mainly contributed by the Hpi fraction. From 1 kDa to 500 Da, the HA, FA and Hpi fractions decreased by 0.48 cm^{-1} , 0.85 cm^{-1} and 2.34 cm^{-1} , respectively. Sixty four percent of the UV absorbance reduction was contributed by the Hpi fraction. This result shows that the 500 Da membrane can remove most of the UV absorbing Hpi fraction.

[Figure 3-7 \(B\)](#) shows the data for the NH leachate. Similar to the PA leachate, the 100 kDa membrane reduced the overall UV absorbance slightly (19%), while the 1 kDa membrane reduces the overall UV absorbance by 54%. Most of the reduction in UV absorbance by the 1 kDa membrane is contributed by the removal of the HA and FA fractions. The 500 Da membrane can further remove the Hpi fraction and reduce the overall UV absorbance to a lower level (2.13 cm^{-1}).

In practice, the POTWs require UV transmittance of mixed wastewater stream to be 60% - 65 % to insure that the UV disinfection can work properly [35]. As little as 3-5% of leachate in the total flow of the POTWs may cause UV disinfection to fail [19]. As shown in [Figure 3-7 \(A\)](#), the UV transmittance of the 1 kDa filtrate for the PA biologically treated leachate is 57 % when diluted to 5%, which is close to the 60% UV transmittance requirement. Similarly, the UV

transmittance for the 1 kDa filtered NH biologically treated leachate sample (diluted to 5%) is 62 %, which meets the requirement. Hence, in this case, the combination of biological treatment and nanofiltration with a MWCO of 1 kDa is a practical treatment option to make most landfill leachates acceptable to the POTWs with regard to the UV quenching problem.

3.4 Conclusions

(1) Most of the UV absorbing substances are refractory in aerobic biological treatment processes. The microorganisms with the capability to degrade UV absorbing materials require very long retention times. Landfills under strict anaerobic conditions with a retention time greater than ten years are required to degrade UV absorbing substances.

(2) In all leachates examined, $SUVA_{254}$ follows: HA>FA>Hpi. The overall UV absorbance of the Hpi fraction is always higher than that of HA and FA fractions due to the high amount of Hpi organic material.

(3) The organic matter size distribution study showed that in all leachates examined, the particle size distribution follows: HA>FA>Hpi. Nanofiltration can be used to selectively remove HA and FA.

(4) For the PA and NH leachates, on-site biological treatment followed by membrane separation with a 1 kDa NF was successful in meeting the UV transmittance requirement of 60-65% transmission when the leachate made up 5% of the mixed flow at the POTWs.

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Table 3-1: Characteristics of KY leachates

Parameter	Unit	KY-8	KY-7	KY-5	KY-3
COD	mg/L	6602.1 – 6855.9	3660.0 – 3786.8	836.4 - 1047.8	712.3 - 902.7
TOC	mg/L	1649.5 - 1860.1	1024.2 – 1169.4	248.3 - 319.7	205.0 - 260.2
UV ₂₅₄ abs.	cm ⁻¹	30.1 - 39.5	20.2 – 23.0	5.8 - 8.2	4.2 - 5.3
pH	—	7.8	7.5	8.0	7.7
NO ₃	mg/L	3.6 - 5.0	1.4	n.d. ^a	n.d.
NH ₃	mg/L	1190.4 - 1372.2	1238.4 – 1418.0	513.1 - 573.5	461.6 - 613.4
Total nitrogen	mg/L	1407.0 - 1573.8	1474.7 - 1561.9	554.8 - 657.0	498.6 - 621.6
PO ₄	mg/L	3.4 - 4.6	3.9 - 5.9	n.d.	n.d.
SO ₄	mg/L	22.0 - 41.2	30.0 - 42.2	7.0 - 8.2	3.5 - 4.1
Cl	g/L	2.2 – 2.4	2.7	1.7 – 1.9	1.2
Na	g/L	2.5	1.4 - 2.0	1.1 - 1.3	0.7 - 0.9
Mg	mg/L	41.6 - 54.6	45.1	72.2 - 80.8	109.7 - 109.9

^a not detected

Table 3-2: Biological treatment efficiency of various landfill leachates in terms of TOC and UV absorbance

Sample	TOC (%)	UV absorbance (%)	Condition
KY-8	37.40	17.85	53-day aeration; 2.5 years old
KY-7	42.25	9.82	53-day aeration; 9 years old
KY-5	36.49	2.70	21-day aeration; 16 years old
KY-3	37.50	-2.30	21-day aeration; 30 years old
PA	34.82	2.51	SBR treatment ; active landfill
NH	55.78	29.09	PACT treatment; active landfill

Table 3-3: SUVA₂₅₄ of hydrophobic nature based fractions of various landfill leachates

Sample	SUVA ₂₅₄ (L/mg·m)		
	HA	FA	Hpi
PA untreated	2.77	1.92	1.55
PA treated	4.70	3.25	2.05
NH untreated	2.65	2.31	1.30
NH treated	3.68	3.29	2.28
KY-8	3.37	2.57	1.45
KY-7	3.72	2.29	1.49
KY-5	3.79	2.64	1.87
KY-3	3.13	2.33	1.54

Table 3-4: TOC size distribution of hydrophobic nature based fractions in various landfill leachates

Sample	HA %			FA %			Hpi %		
	< 1 kDa	1 kDa-100 kDa	> 100 kDa	< 1 kDa	1 kDa-100 kDa	> 100 kDa	< 1 kDa	1 kDa-100 kDa(10 kDa)	> 100 kDa (10 kDa)
PA untreated	17.78	39.59	42.63	29.54	33.29	37.17	67.93	10.16	21.91
PA treated	23.03	74.39	2.57	33.74	57.04	9.22	67.44	20.52	12.04
NH untreated	39.12	43.86	17.01	63.54	29.12	7.34	68.02	19.15 ^a	12.83 ^b
NH treated	37.43	48.55	14.02	48.28	34.51	17.21	73.66	16.91 ^a	9.43 ^b

^a 1 kDa -10 kDa

^b > 10 kDa

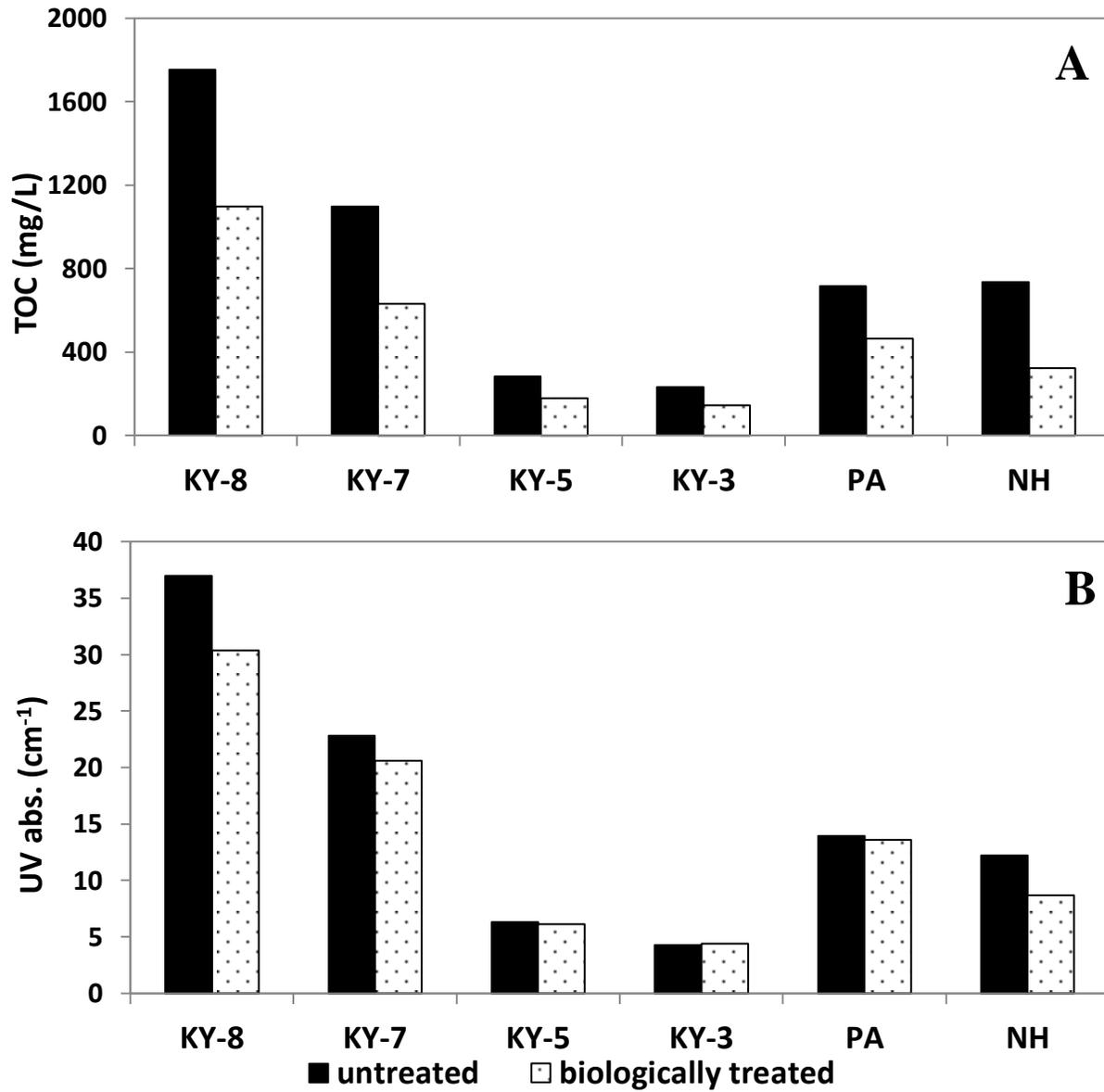


Figure 3-1: TOC (A) and UV₂₅₄ absorbance (B) before and after biological treatment of various landfill leachates

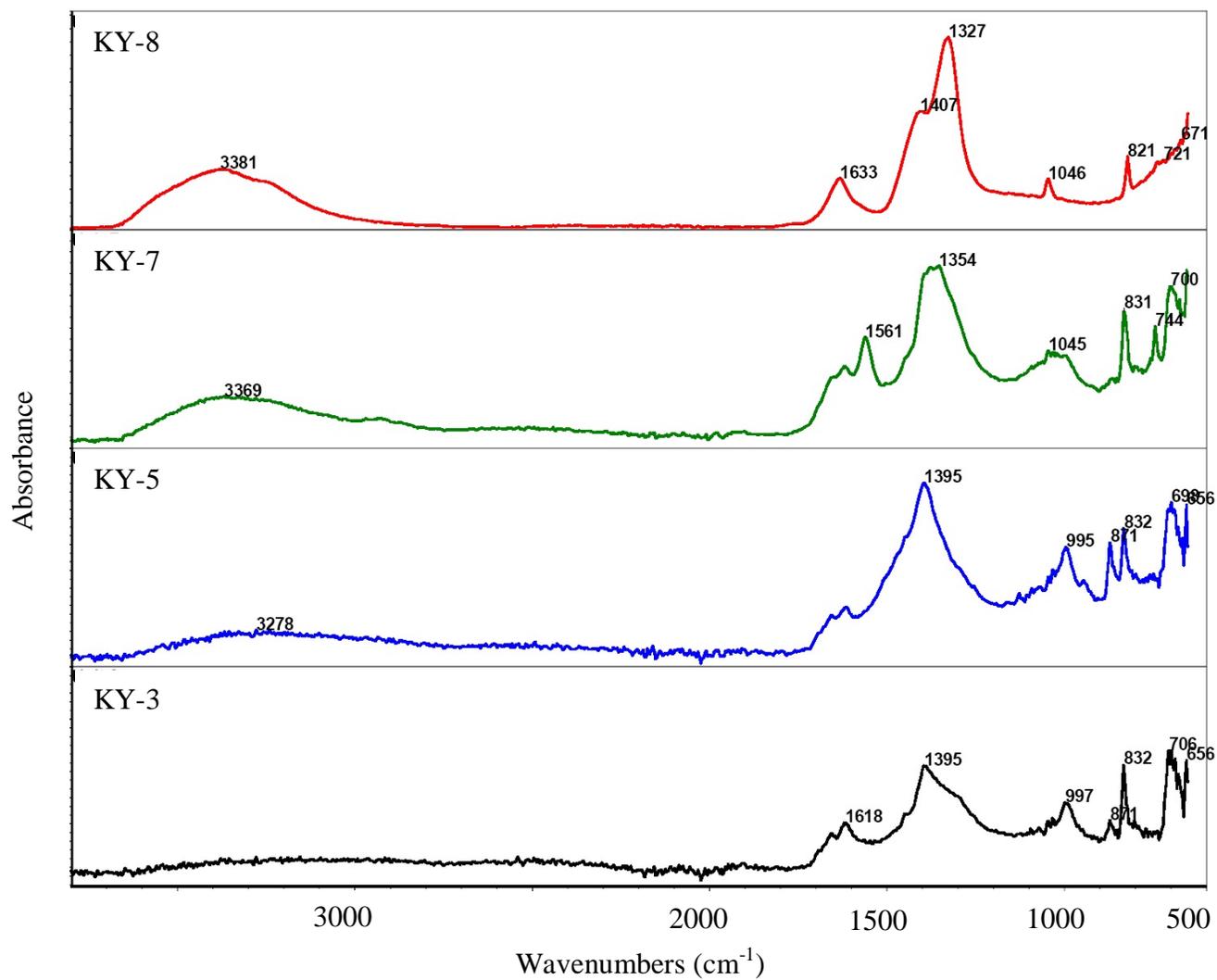


Figure 3-2: FT/IR spectra of KY leachates

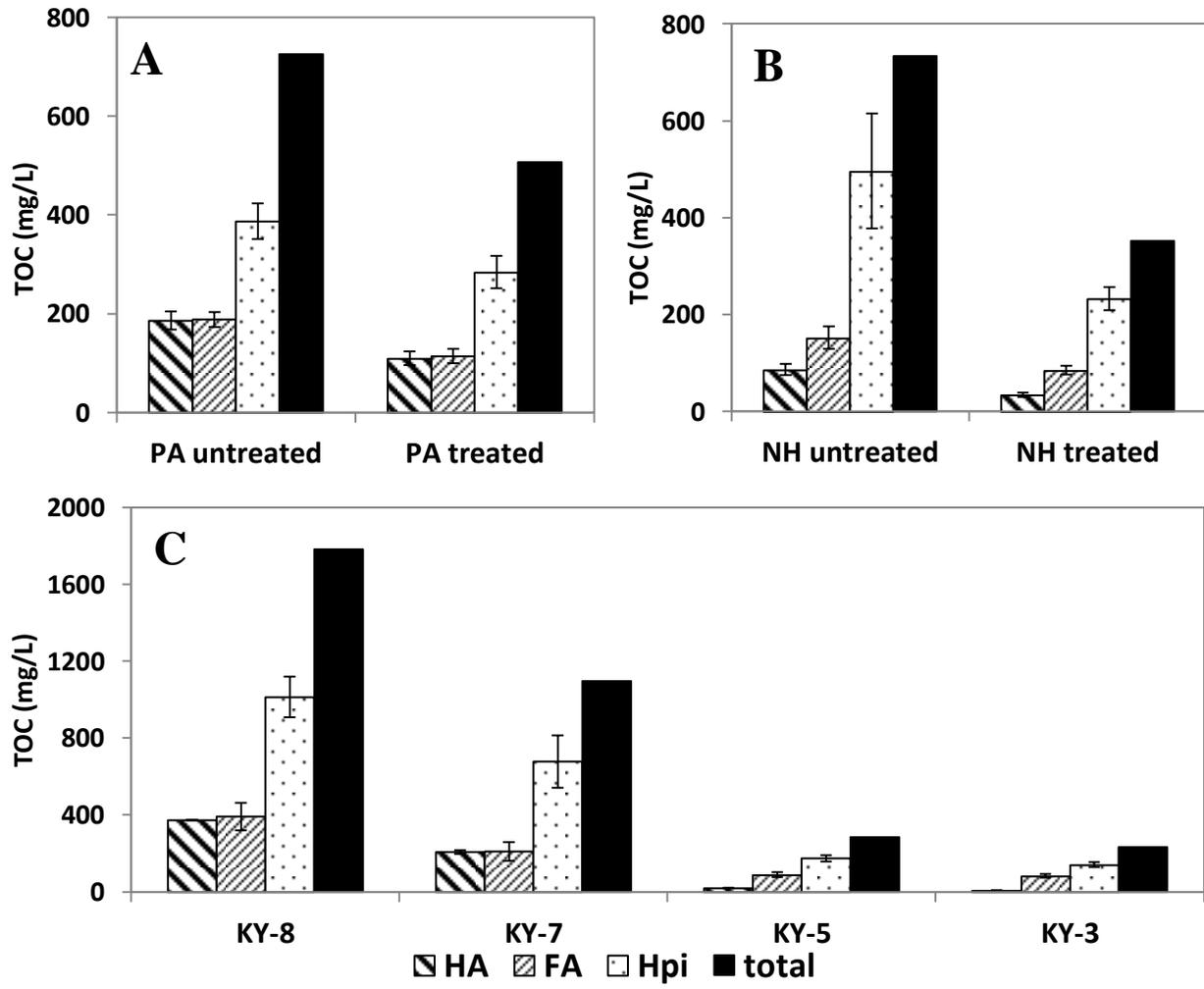


Figure 3-3: Hydrophobic nature based distribution of PA (A), NH (B) and KY (C) landfill leachates in terms of TOC

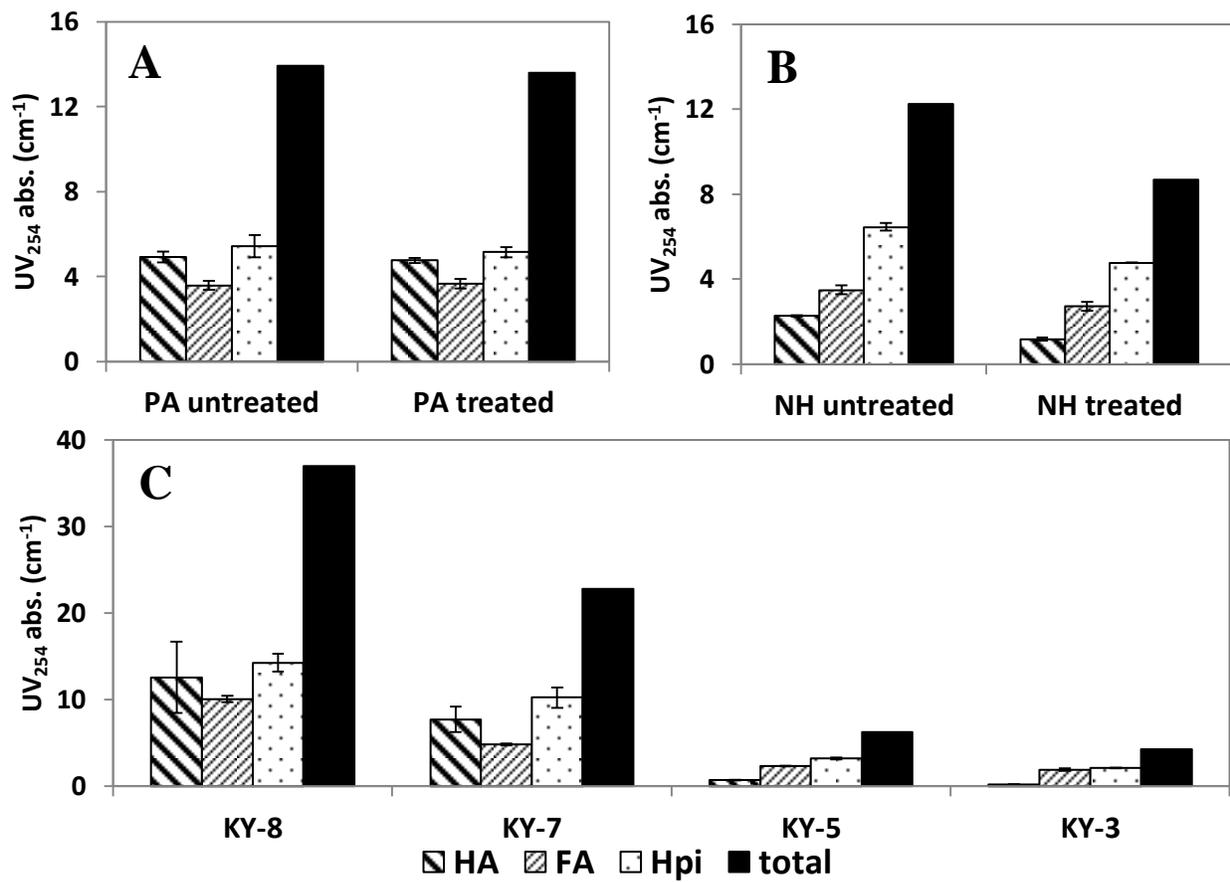


Figure 3-4: Hydrophobic nature based distribution of PA (A), NH (B) and KY (C) landfill leachates in terms of UV₂₅₄ absorbance

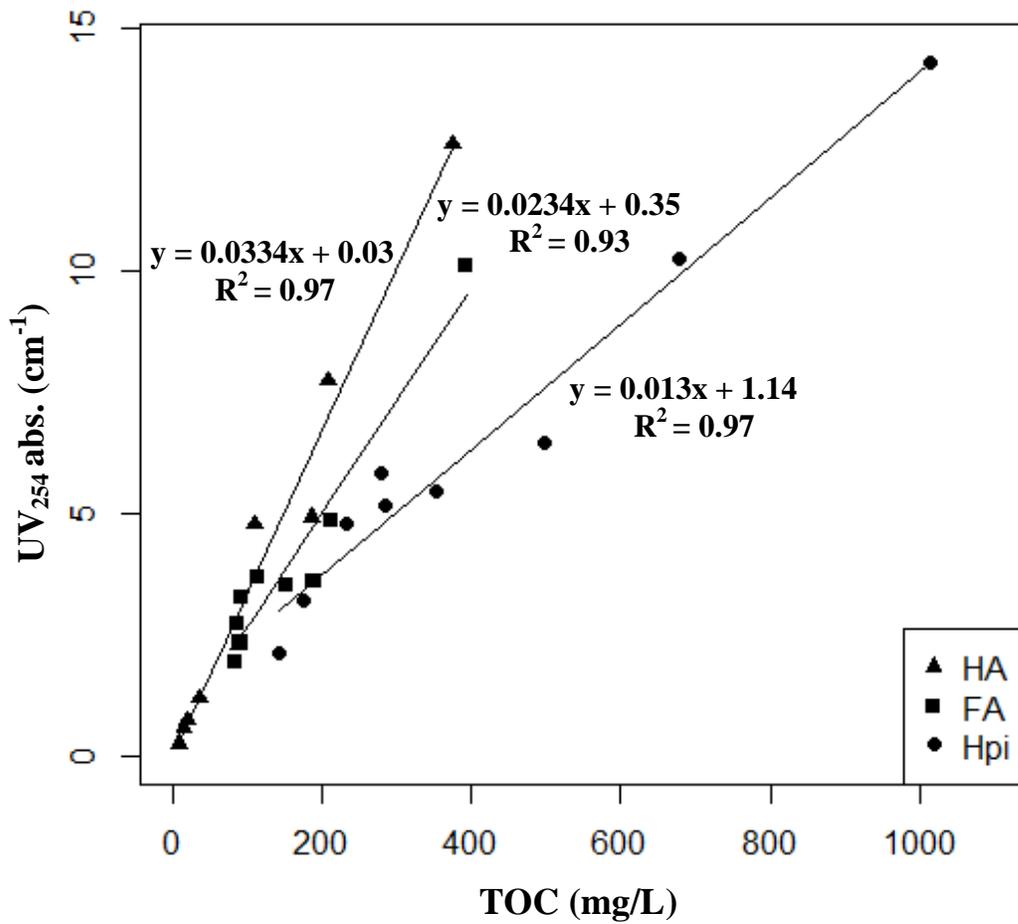
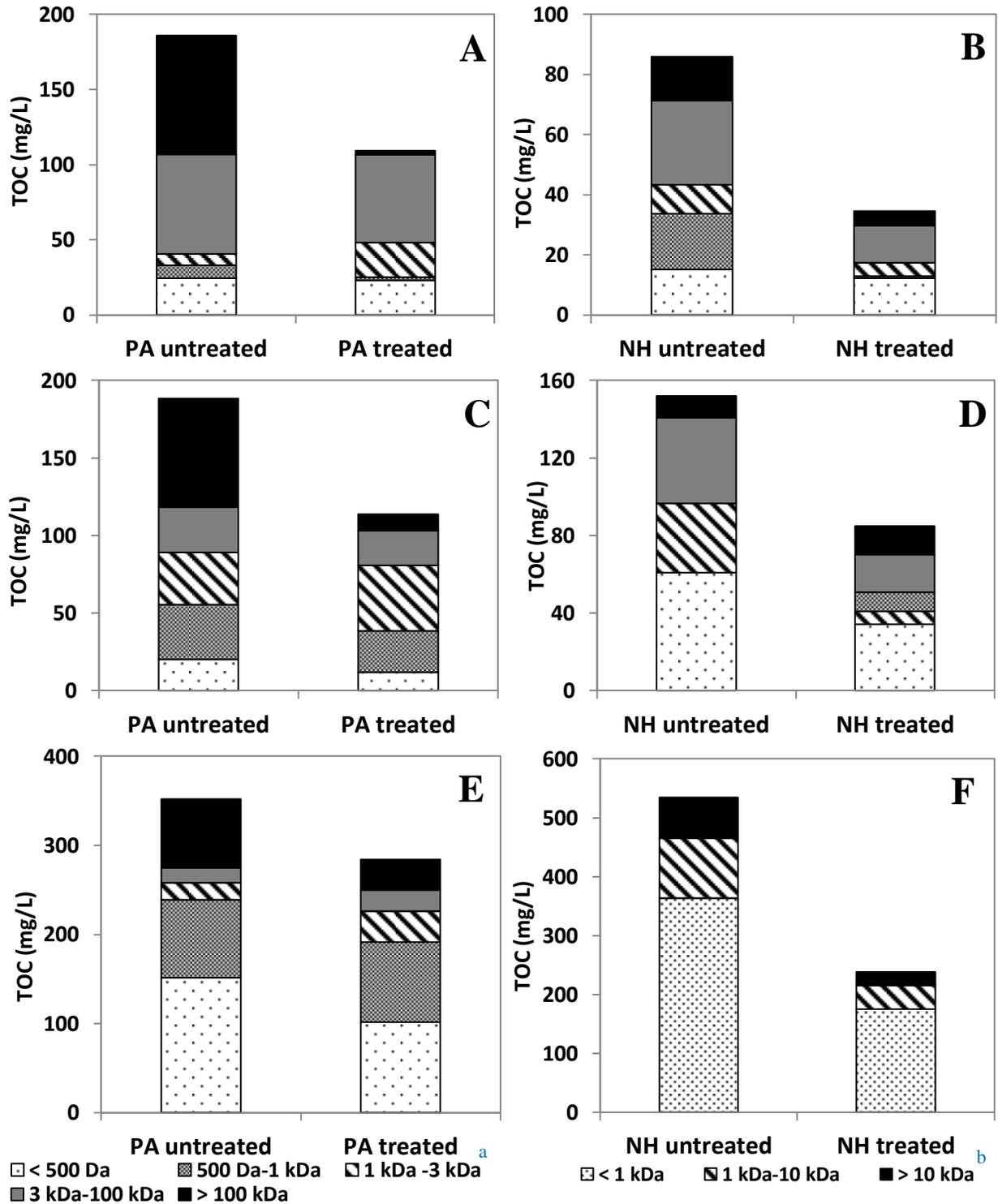


Figure 3-5: Linear Regression analysis of UV₂₅₄ absorbance and TOC for humic acids, fulvic acids and hydrophilic fractions in landfill leachates



^a Figure 3-6 A-E ^b Figure 3-6 F

Figure 3-6: Humic acids (A, B), Fulvic acids (C, D) and Hydrophilic fraction (E, F) size distribution of various landfill leachates

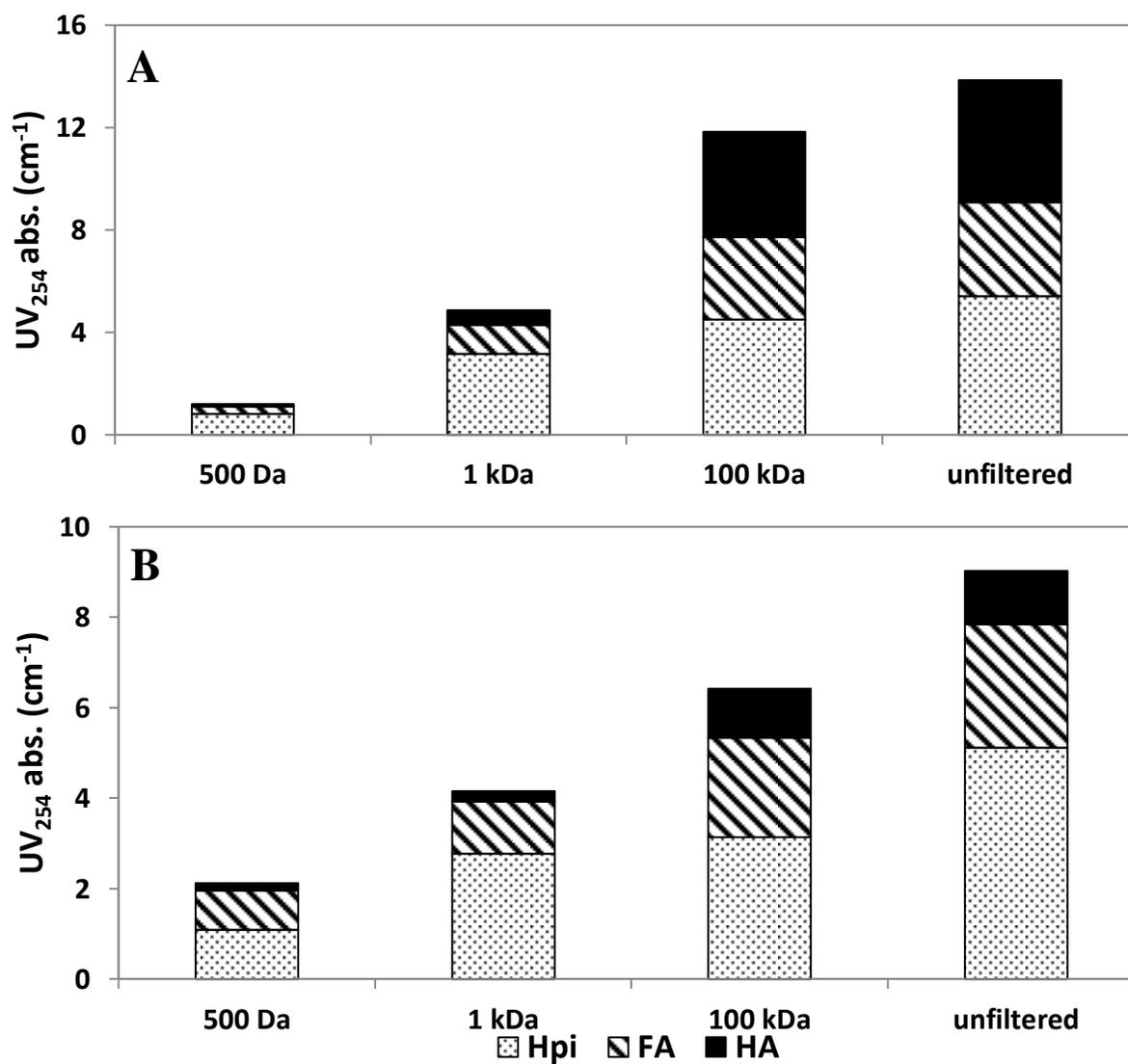


Figure 3-7: UV₂₅₄ absorbance distribution of biologically treated PA leachate (A) and NH leachate (B) size fractions

Chapter 4. Variation in organic matter and organic nitrogen in landfill leachates with landfilling age

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4.0 Abstract

The discharge of landfill leachates to publically owned treatment works (POTWs) can cause interference with UV₂₅₄ disinfection. In addition, biorefractory organic nitrogen in leachates can contribute to effluent nitrogen making it difficult to meet effluent nitrogen regulations in some regions of the country. To study variation in UV₂₅₄ absorbing organic carbon and organic nitrogen, leachate samples ranging from cells with ages, 2 to 30 years from a large landfill in Kentucky were collected and fractionated on basis of their particle size and hydrophobic nature into humic acids, fulvic acids and a hydrophilic fraction. The effectiveness of long term landfilling, aerobic biological treatment and membrane treatment for organic matter and organic nitrogen removal was examined. Humic materials which were the major UV₂₅₄ absorbing substances were mainly > 1 kDa and they degraded significantly with landfill age. The hydrophilic organic fraction which was the major contributor to organic nitrogen was mainly < 1 kDa and it became increasingly recalcitrant with landfill age. Proteins contributed around one third of the organic nitrogen for all landfill ages.

Keywords: UV₂₅₄ absorbance; landfilling age; organic nitrogen; hydrophobic nature; particle size distribution

4.1 Introduction

Due to industrial and commercial development, the generation of municipal solid waste (MSW) is continuing to grow. Among all methods including recycling, composting and incineration, sanitary landfilling is still the most common and widely accepted method of MSW disposal in

the USA. New landfills are being constructed due to their economic advantages and practical convenience (Renou et al., 2008). Being a very cost effective approach for leachate disposal, landfill leachates are frequently discharged into publically owned treatment works (POTWs) (Zhao et al., 2012).

In recent years, the presence of bio-refractory compounds in landfill leachate has gained considerable attention (Vilar et al., 2011). It is widely accepted that humic substances contained in leachate are not readily biodegradable (Poblete et al., 2011) and can pass through the biological treatment processes in the POTWs and elevate the organic matter level in the effluent (Zhao et al., 2012).

Subsequently, ultra-violet (UV) disinfection has become quite popular in wastewater treatment because it can eliminate the formation of regulated disinfection by-products (DBPs) (NYSERDA, 1999). Though, $\lambda = 260$ nm is the most effective germicidal wavelength, in practice, POTWs utilize $\lambda = 254$ nm instead as it can be readily generated by mercury lamps (Tchobanoglous et al., 2004). The POTWs generally require that the UV_{254} transmittance in a wastewater stream be 60% - 65 % to insure that UV disinfection can work properly (Basu et al., 2007). The landfill leachates when discharged to POTWs can quench UV_{254} light, thereby interfering with the plant's UV disinfection systems and may significantly reduce their efficiency (Zhao et al., 2012).

With the integration of nitrification and denitrification systems into most POTWs, the organic nitrogen fraction accounts for as high as 80 % of the total nitrogen in POTW effluents (Qasim,

1998). Also, with recalcitrant dissolved organic nitrogen being identified as an issue of concern, stricter discharge limits have been imposed for total nitrogen ([Chesapeake Bay Program, 2004](#)). When used for disinfection in municipal wastewater systems, chlorination can generate carcinogenic DBPs in addition to nitrogenous DBPs which have dissolved organic nitrogen (DON) as a potential source ([Mitch and Sedlak, 2004](#)).

A major portion of the composition of organic nitrogen in wastewater effluents is still unknown with the sum of known specific components accounting for less than 10 % of the DON ([Pehlivanoglu-Mantas and Sedlak, 2008](#)). A recent study by [Westgate and Park \(2010\)](#) has shown that proteins correlate with the DON in the WWTP effluents. The study by [Westgate and Park \(2010\)](#) estimated the contribution of the proteins to the DON to be as high as 60 %.

The stabilization state, which is related to the age of a landfill, is considered one of the important factors on which the chemical composition of a landfill leachate depends ([Kjeldsen et al., 2002](#)). The general properties of stabilized landfill leachates and how they differ from the younger leachates has been well documented. However, there is very limited literature available to determine how the UV_{254} light absorbing organic matter and the organic nitrogen evolve over long term landfilling age.

This study of particle size and hydrophobic nature based fractions was conducted to help better understand as to how the UV_{254} absorbing organic matter and organic nitrogen in landfill leachate changes in composition over long term landfilling. An understanding of leachate

composition can lead to potential techniques for the removal of biorefractory organic matter causing absorbance of UV₂₅₄ light and elevated organic nitrogen levels. .

4.2 Materials and methods

4.2.1 Leachate collection, sampling and aerobic biological treatment

The leachate samples investigated in the study were collected from a landfill located in Kentucky (KY), USA. The KY landfill is comprised of eight individual units designated Units 1 through 8. Leachate samples collected for the study were from Units 3, 5, 7 and 8. The leachates are designated as KY-2.5, KY-9, KY-16 and KY-30 where the numbers refer to the average landfilling age. The characteristics of the KY leachates can be found in [Table 4-1](#).

The leachates were shipped directly from the site to Virginia Tech, Blacksburg, VA and were stored at 4 °C to reduce microbial activity. Leachate buckets were shaken well to resuspend settled particles before sampling and analysis.

Biological treatment of the KY leachates was conducted by continuous aeration in the lab. Since, leachates contain microorganisms from the waste layer of the landfill, no external seed was added. Biological flocs similar to activated sludge flocs were observed during the aeration process. Each leachate was aerated using a porous ceramic air diffuser and distilled water was added to compensate the water lost by evaporation. KY-2.5 and KY-9 leachate samples were aerated for 53 days and aerated leachates were sampled on the 21st, 38th and 53rd days. The KY-16 and KY-30 leachate samples were aerated for just 21 days because they contained little

biodegradable material. The detention time for aeration was decided on the basis of the time taken required for the leachates to reach a stabilized state i.e., a point after which there was little additional biological degradation.

4.2.2 Hydrophobic nature and particle size based fractionations

Landfill leachate samples were fractionated into humic acids (HA), fulvic acids (FA) and hydrophilic (Hpi) fractions based on their hydrophobic nature and solubility characteristics. Methods developed by [Thurman and Malcolm \(1981\)](#) and [Leenheer \(1981\)](#) were used in this study.

The XAD-8 resin (currently Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO) was packed and cleaned following the method described by [Leenheer \(1981\)](#). Approximately 3.5-4.5 mL of cleaned XAD-8 resin slurry was packed in a borosilicate glass column (1.0 cm×10 cm, Thomas Scientific, Swedesboro, NJ). Leachate samples were first filtered with a 1.5 µm micro glass fiber filter and then acidified to pH 2 using concentrated HCl. The humic acids precipitated and were separated with 0.45 µm cellulose nitrate membrane (47 mm, Sartorius Stedim Biotech, France). The humic acids collected along with the glass fiber filter were re-dissolved into a 0.1 M NaOH solution. The re-dissolved HA solution was used for analysis. The supernatant containing fulvic acids and the hydrophilic organics was then passed through the XAD-8 resin column at a flow rate of 10-15 bed volumes/hour. Fulvic acids were sorbed and retained onto the resin column. Then 0.1 M NaOH was used to elute the fulvic acids and this eluent was used for characterization of the FA fraction. The residual portion not sorbed by the resin is called the hydrophilic (Hpi) fraction.

The size fractionation apparatus consisted of 200 mL stirred ultrafiltration cells (Amicon model # 8200), a nitrogen gas tank (pressure: 120 kPa) and membrane discs (Millipore, Billerica, MA) with a range of molecular weight cut offs (MWCO). Details can be found in [Zhao et al. \(2012\)](#).

4.2.3 Analysis

Total organic carbon (TOC) was analyzed using a high temperature combustion TOC analyzer (TOC-5000A, Shimadzu, Japan). The chemical oxygen demand (COD) analysis was executed by the closed reflux, titrimetric method per Standard Method 5220-D ([APHA et. al., 2012](#)). The ultraviolet absorbance at 254 nm (UV₂₅₄ abs.) was measured with a spectrophotometer (Beckman Coulter, Brea, CA). The leachate samples were diluted if the absorbance values were above the detection limited for the instrument. UV₂₅₄ readings were multiplied by the corresponding dilution factor to give the final UV₂₅₄ absorbance values ([Zhao et al., 2012](#)).

Organic nitrogen (ON) was estimated by subtracting inorganic nitrogen from total nitrogen ([Westgate and Park, 2010](#)). The inorganic nitrogen consists of nitrates, nitrites and ammonia. Total nitrogen concentrations for the samples were determined by the persulfate digestion method, nitrates by the dimethylphenol method, nitrites by the diazotization method and ammonia by the salicylate method (Hach Company, Loveland, CO) with the measurements being made by a spectrophotometer (DR 2800, Hach Company, Loveland, CO). The protein measurements were carried out with accordance to the Frølund modified Lowry method for quantitative protein analysis ([Frølund et al., 1995](#); [Lowry et al., 1951](#)). The percentage of nitrogen in protein was taken to be 16 % ([Westgate and Park, 2010](#)).

Metal analysis for the samples was conducted using a Thermo Electron X-Series inductively coupled plasma with mass spectrometer (ICP-MS) per Standard Method 3125-B (APHA et. al., 2012). ICP-MS Samples and calibration standards were prepared in a matrix of 2% nitric acid by volume. The anions were measured with an Ion chromatograph (DX120, Dionex, Sunnyvale, CA) equipped with an AS9-HS column (Model No. 051786, Dionex, Sunnyvale, CA); the elute was 9.0 mM Na₂CO₃ and the flowrate was 1.0 mL/min. The pH of each leachate sample was measured by a pH probe (Accumet Model No.13-620-287A, Fisher-Scientific, Hampton, NH). The pH meter (Accumet Model No.10, Fisher-Scientific, Hampton, NH) was standardized against reference solution of pH 4 and pH 7.

4.3 Results and Discussion

4.3.1 Distribution of total organic carbon and UV₂₅₄ absorbance among the hydrophobic and hydrophilic fractions with landfilling age

Figure 4-1 shows the distribution of the TOC (Figure 4-1 (A)) and UV₂₅₄ absorbance (Figure 4-1 (B)) for the KY leachate samples into humic acids (HA), fulvic acids (FA) and the hydrophilic (Hpi) fraction. It can be observed that with increasing landfilling age, the proportions of the different hydrophobic fractions in the leachates change. The proportion of the organic carbon for the hydrophilic and fulvic acids fractions increase with landfill age while that of the humic acids decreases (Figure 4-1 (A)). The HA fraction decreases from 18.1 % in KY-2.5 to 2.1 % in KY-30, while the FA and Hpi fractions increase from 21.5 % to 26.8 % and from 60.4 % to 71 %, respectively. The fulvic acids are generally lower molecular weight compounds derived from

higher molecular weight humic acids (Tan, 2003), so, the increase in the FA fraction may be due to the HA fraction undergoing slow decomposition.

The increase in the proportion of the FA fraction with landfill age may be accounted for by conversion of the HA fraction to FA, but the increase in the proportion of the Hpi fraction shows that the Hpi fraction is becoming more recalcitrant with age. The removal of the Hpi fraction is 80 % from KY-2.5 to KY-30 but around 98 % of that removal is from KY-2.5 to KY-16. Thus, the 14 years of landfilling following KY-16 did not show any significant reduction, indicating the increased biorefractory nature of the Hpi fraction.

A practical parameter that provides insight into the nature of natural organic matter (NOM) and its fractions is specific UV absorbance (SUVA). SUVA is the ratio of ultraviolet light absorbance of wavelength to the concentration of TOC, i.e. $UV (m^{-1})/TOC (mg L^{-1})$. SUVA provides a quantitative measure of aromatic content per unit concentration of organic carbon (Karanfil et al., 2002). The specific UV absorbance at 254 nm ($SUVA_{254}$) for the leachates follows the order: HA > FA > Hpi with the $SUVA_{254}$ values of HA, FA and Hpi fractions ranging from 3.4 to 3.3 L/mg-M, 2.3 to 2.1 L/mg-M and 1.6 to 1.2 L/mg-M, respectively from KY-2.5 to KY-30. This indicates that the HA fraction is the component which is responsible for majority of the UV_{254} absorbance and aromatic content. A significant decrease in the HA fraction with long term landfilling indicates that the age of the landfill is important in determining the potential for leachates to impact the UV disinfection in POTWs.

Figure 4-2 shows the particle size distribution of the hydrophobic based fractions (humic acids – Figure 4-2 (A), fulvic acids – Figure 4-2 (B) and hydrophilic fraction – Figure 4-2 (C)) of the organic matter in the KY leachates. The contribution of the Hpi fraction < 1 kDa fraction (Figure 4-2 (C)) to the total Hpi organic matter varies from 78 % in KY-9 to 60 % in KY-30. It can be observed that the Hpi fraction which is the biggest contributor to the organic matter is mainly < 1 kDa. Among the humic substances, the contribution of the HA and FA fraction (Figure 4-2 (A) and Figure 4-2 (B)) is nearly equal in the younger KY-2.5 and KY-9 leachates whereas in the older leachates, the FA fraction contributes up to 92 % (KY-30) of the humic substances.

From the size distribution of the humic substances (HA and FA) it can be observed that majority of the organic matter is > 1 kDa in the younger leachates (KY-2.5 and KY-9). The contribution of the HA fraction > 1 kDa to the total HA fraction increases from the younger (58 % - KY-9) to the older leachates (77 % - KY-16), whereas the FA fraction decreases from the younger (59 % - KY-2.5) to the older leachate (23 % - KY-30).

The greatest decrease from young to older leachate can be seen for the HA fractions with almost complete loss of the size fraction < 100 kDa and a 90 % decrease for the fraction > 100 kDa. Most of organic matter left in the HA fraction consists of the higher MW (> 100 kDa) fraction for the older leachates. For the FA's however, it is the < 500 Da fraction which predominates in the older leachates with the portion of that fraction increasing from 40 % in KY-2.5 to 60 % in KY-30. As noted previously, with age the greater MW HA particles maybe degraded into smaller fractions and converted into lower MW FA's.

It can also be observed that for the HA's, the amount of the HA's > 1 kDa increased from 67 % in KY-2.5 to 76 % in KY-30. Most of this contribution comes from the 3 kDa to 100 kDa fraction which is 60 % in KY-2.5 and 84 % in KY-9. Thus, most of the organic matter in the HA fraction lies in the 3 kDa to 100 kDa MWCO range. The trend for the distribution of the organic matter in the FA's varies in the sense that fraction of the FA's > 1 kDa (57 % - KY-2.5 and 54 % - KY-9) predominates in the younger leachates but is in the minority in the older leachates (37 % - KY-16 and 23 % - KY-30). Thus, membrane filtration with a MWCO of 1 kDa would be effective for the removal of HA's for landfills of all ages, but for the older leachates, it would be less effective for the removal of FA's. Also, for the older leachates, KY-30 and KY-16, membrane filtration is not very attractive for the removal of the total organic matter because the fraction > 1 kDa for KY-30 and KY-16 is just 37 % and 30 %, respectively.

For the Hpi fraction in the younger leachates, the size fraction < 1 kDa comprises a majority of the organic matter (68 % - KY-2.5, 78 % - KY-9), but with age, the proportion of > 1 kDa organics increases from 24 % in KY-16 to 41 % in KY-30. The maximum decrease over a landfilling period in the landfill was 98 % for HA's and around 80 % for the FA's and Hpi's. However, the contribution of the Hpi fraction remains significant in the older leachates and thus tends to persist over long term landfilling. Also, while considering the effectiveness of the membrane filtration with a MWCO of 1 kDa for the removal of the Hpi's, it is suitable only for the older leachates where the fraction of the Hpi > 1 kDa is relatively high as compared to the younger leachates.

Figure 4-3 shows the particle size distribution of the UV₂₅₄ absorbing substances associated with the different hydrophobic nature based fractions (humic acids – Figure 4-3 (A), fulvic acids – Figure 4-3 (B) and hydrophilic fraction – Figure 4-3 (C)) for the KY leachates. The distribution of UV₂₅₄ absorbing substances is similar to that for the organic matter. For the humic substances, however, it can be observed that the UV₂₅₄ absorbance (Figure 4-3 (A) and Figure 4-3 (B)) due to the HA fraction is greater than that due to the FA's in the younger leachates (KY-2.5 and KY-9).

For the FA fraction in the older leachates, the UV₂₅₄ absorbing substances > 1 kDa dominate as opposed to the < 1 kDa size fraction dominating the organic matter, implying that the UV₂₅₄ absorbing substances and the organic matter are probably being contributed by different functional chemical species.

It can be observed that majority of the UV₂₅₄ absorbing humic substances are > 1 kDa with the absorption due to fractions > 1 kDa ranging from 44 % - 55 % for the different leachates. Thus, membrane filtration with a MWCO of 1 kDa will be helpful for the removal of UV₂₅₄ absorbing substances.

4.3.2 Comparison of on-site aerobic biological treatment with degradation due to long term landfilling

Figure 4-4 shows comparison of the particle size distribution of the organic carbon (Figure 4-4 (A)) and the UV₂₅₄ absorbing substances (Figure 4-4 (B)) in the untreated and biologically treated KY leachates. It can be observed that aerobic biological treatment is somewhat effective

for the removal of organic matter (Figure 4-4 (A)) in the leachates, even in the older ones, with the overall organic carbon removal being around 40 % for all the leachates.

Aerobic biological treatment is able to achieve removals in the range of 9 to 25 % for the UV₂₅₄ absorbance (Figure 4-4 (B)). A comparison between the percent removal of organic matter and UV₂₅₄ absorbing substances shows that the UV₂₅₄ absorbing substances are more recalcitrant. Thus, aerobic biological treatment is not effective for the removal of UV₂₅₄ absorbing substances compared to the degradation that occurs during long term landfilling. This suggests that the micro-organisms responsible for degradation of UV₂₅₄ absorbing substances require a longer detention time which is not available in aerobic biological treatment systems. The decrease in the organic matter over time is due to both biodegradation/biotransformation and dilution (Rowe, 1995).

The distribution of the organic matter between the untreated and biologically treated leachates shows the common trend of the maximum % removal taking place for organic matter > 100 kDa, especially for the younger leachates (94 % - KY-2.5, 92 % - KY-9). This trend is also seen for the removal of the UV₂₅₄ absorbing substances by aerobic biological treatment with the removal of the particles > 100 kDa being as high as 70 % for KY-2.5 whereas the overall removal of UV₂₅₄ absorbing substances by aerobic biological treatment in KY-2.5 is 25 %. This shows that aerobic biological treatment is more effective for the removal of organic matter and UV₂₅₄ absorbing substances > 100 kDa.

Around 50 % of the organic matter is biologically degradable in the < 1 kDa fraction, even for the older leachate samples. Hence, a treatment methodology of aerobic biological treatment

followed by membrane filtration with a MWCO of 1 kDa might be an effective technique for removal of organic matter for leachates over a range of ages. This method can help achieve 71 %, 60 %, 61 % and 60 % organic matter removal in the KY-2.5, KY-9, KY-16 and KY-30 leachates, respectively.

4.3.3 Distribution of organic nitrogen and proteins with landfilling age

Figure 4-5 shows the trend for the degradation of the organic nitrogen (Figure 4-5 (A)) and proteins (Figure 4-5 (B)) in the KY leachate with increasing landfilling age. It can also be observed that organic nitrogen and proteins undergo degradation with landfilling age. The decreases in organic nitrogen are 46 % for the younger leachates (KY-2.5 to KY-9) and 28 % for the older leachates (KY-16 to KY-30) (Figure 4-5 (A)). However, the removal of proteins is 24 % for the younger and 53 % for the older leachates (Figure 4-5 (B)). This means that the organic nitrogen is more recalcitrant with age, however, the degradability of the protein fraction increases with age.

The contribution of the Hpi fraction to the organic nitrogen is around 78 % for KY-2.5 which is the youngest leachate, whereas it is around 50 % for all the other leachates. Hence, the Hpi fraction is the biggest contributor to the organic nitrogen among the various hydrophobic fractions. The 67 % removal of the Hpi organic nitrogen from KY-2.5 to KY-9 is much greater than the 46 % removal which takes place for the organic nitrogen. The removal of the organic nitrogen by aerobic biological treatment in the Hpi fraction for the older leachates is quite low at 30 %. This implies that the Hpi organic nitrogen in the younger leachates is much more

biodegradable compared to the other leachates. Thus, the Hpi organic nitrogen becomes increasingly recalcitrant with age.

The Hpi fraction is the biggest contributor to the proteins among the hydrophobic fractions. Its contribution increases for the older leachates, especially for KY-30 where it contributes 86 % of the proteins. The protein in the Hpi fraction exhibits 40 % removal from KY-16 to KY-30 whereas the overall protein removal was around 53 %. The higher proportion of the Hpi protein's contribution to the total protein in the KY-30 leachate is due to the predominance of the Hpi fraction and very small quantities of the HA and FA fraction being present in the sample. This also points to the higher degradability of the HA and FA proteins in the older leachates.

These results suggest that most of the organic nitrogen and proteins come from the Hpi fraction which is mostly < 1 kDa. Thus, membrane filtration will not be effective for the removal of organic nitrogen and proteins.

Figure 4-6 shows the correlation between the amount of the organic nitrogen and the proteins contained in the untreated and biologically treated leachate. It also shows the contribution of the proteins in the Hpi fraction to the organic nitrogen in that fraction. Proteins are generally considered a major source of organic nitrogen, thus understanding their contribution in leachates is useful. It can be observed that the proteins contribute around one-third of the organic nitrogen. This amount remains the same, even for the biologically treated leachate, indicating that aerobic biological treatment is able to remove the organic nitrogen and proteins by equal proportions. This might also mean that components responsible for the remaining two-thirds of the organic nitrogen degrade in similar amounts as the proteins.

The components which contribute the remaining two-thirds of the organic nitrogen are not known and further investigation is needed to understand their source, chemical composition and their potential degradation mechanisms.

4.4 Conclusions

The results indicated that the humic substances in landfill leachates (mostly > 1 kDa) are mainly responsible for UV₂₅₄ absorbance in POTW effluents. Membrane treatment with a 1 kDa MWCO can significantly decrease the UV₂₅₄ absorbance due to the leachates in the POTW effluents. The UV₂₅₄ absorbing substances are relatively more biologically recalcitrant when compared with organic matter. A significant decrease in humic substances with long term landfilling indicated that age is important in determining potential for leachates to impact UV disinfection in POTWs. Microorganisms capable of degrading UV₂₅₄ absorbing substances were found to require a longer detention time which cannot be provided by on-site aerobic biological treatment. Hydrophilic fraction (mostly < 1 kDa) was found to be the biggest contributor of organic carbon, proteins and organic nitrogen and this fraction became increasingly recalcitrant with landfilling age. Proteins contributed around one-third of the organic nitrogen for all leachate ages.

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Table 4-1: Characteristics of KY leachates

Parameter	Unit	KY-2.5	KY-9	KY-16	KY-30
TOC	mg/L	1754.8 ± 105.3	1096.8 ± 72.6	284.0 ± 35.7	232.6 ± 27.6
COD	mg/L	6729.0 ± 126.9	3723.4 ± 63.4	942.1 ± 105.7	807.5 ± 95.2
UV ₂₅₄ abs.	cm ⁻¹	34.8 ± 4.7	21.6 ± 1.4	7.0 ± 1.2	4.7 ± 0.5
Total nitrogen	mg/L	1490.4 ± 83.4	1518.3 ± 43.6	605.9 ± 51.1	560.1 ± 61.5
NO ₂	mg/L	n.d. ^a	n.d.	n.d.	n.d.
NO ₃	mg/L	4.3 ± 0.7	1.4	n.d.	n.d.
NH ₃	mg/L	1281.3 ± 90.9	1328.2 ± 89.8	543.3 ± 30.2	537.5 ± 75.9
pH	—	7.8	7.5	8.0	7.7
PO ₄	mg/L	4.0 ± 0.6	4.9 ± 1.0	n.d.	n.d.
SO ₄	mg/L	31.6 ± 9.6	36.1 ± 6.1	7.6 ± 0.6	3.8 ± 0.3
Na	g/L	2.5	1.7 ± 0.3	1.2 ± 0.1	0.8 ± 0.1
Mg	mg/L	48.1 ± 6.5	45.1	76.6 ± 4.2	109.8 ± 0.1
Si	mg/L	31.2 ± 2.3	40.6	24.8 ± 1.7	23.1 ± 0.9
P	mg/L	3.2 ± 0.1	3.6 ± 0.6	1.5 ± 0.2	0.9 ± 0.1
Cl	g/L	2.3 ± 0.1	2.7	1.8 ± 0.1	1.2
K	mg/L	628.6 ± 51.3	596.0 ± 43.8	359.8 ± 27.5	339.1 ± 24.3
Ca	mg/L	27.0 ± 5.1	27.1 ± 2.2	54.7 ± 7.5	28.6 ± 0.9
Fe	mg/L	3.1 ± 0.1	4.7 ± 0.6	2.7 ± 0.6	2.4 ± 0.9
Mn	mg/L	0.1	0.1	0.1	0.1
Zn	mg/L	0.2	0.2	0.1	0.1

^a not detected

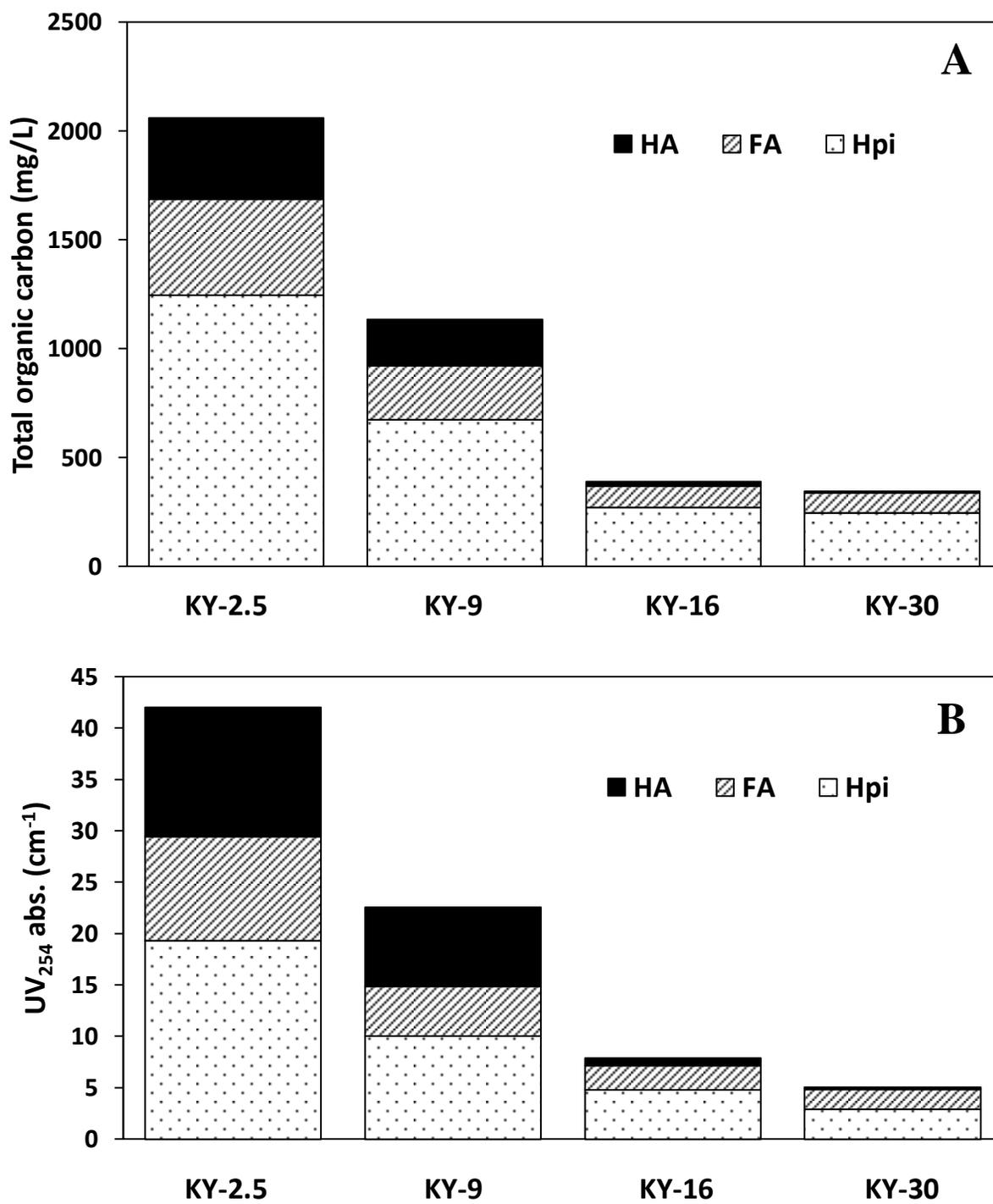


Figure 4-1: Distribution of total organic carbon (A) (TOC) and UV₂₅₄ absorbance (B) among hydrophobic and hydrophilic fractions in KY leachates

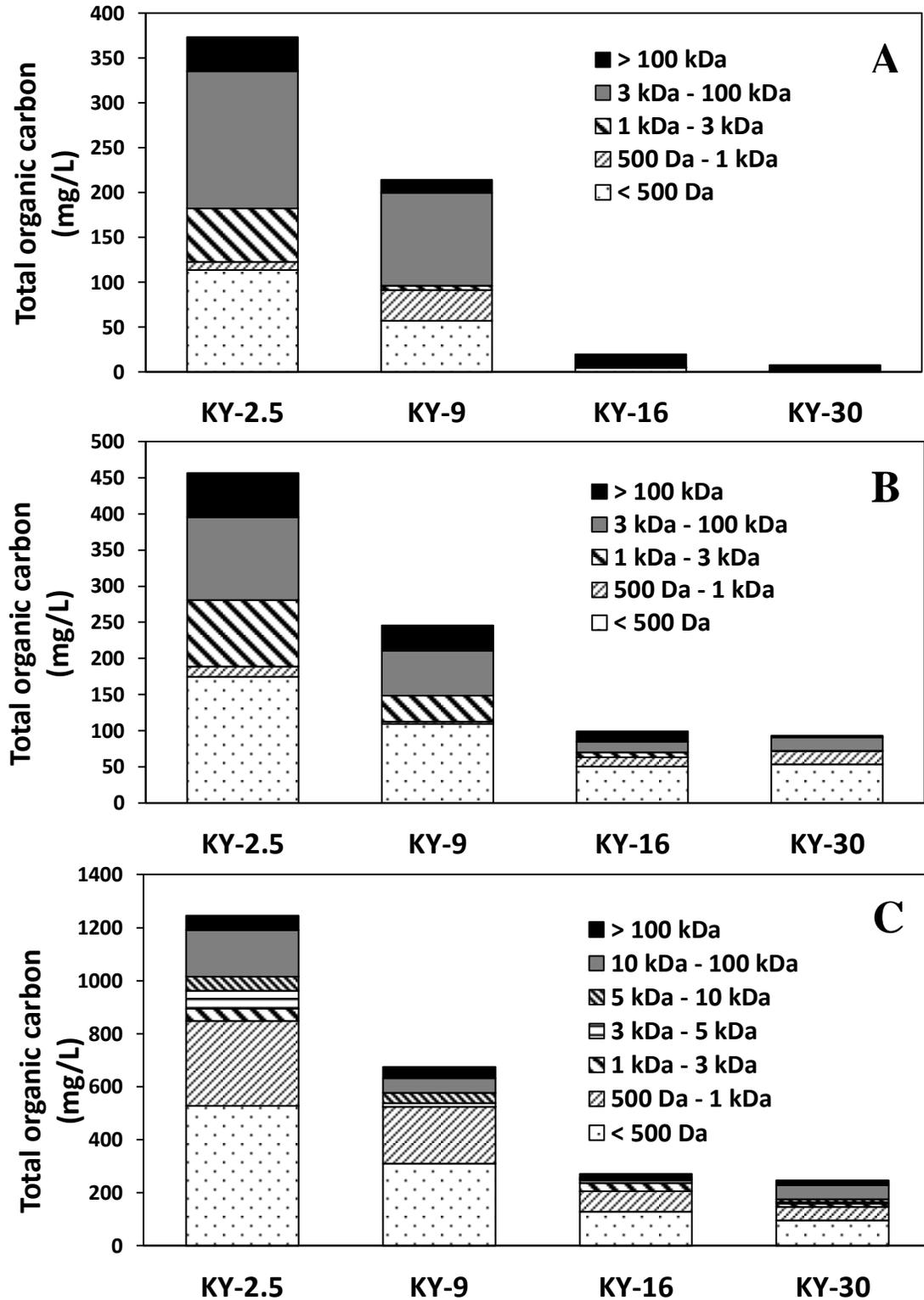


Figure 4-2: Particle size distribution of total organic carbon (TOC) in humic acids (A), fulvic acids (B) and hydrophilic fraction (C) in KY leachates

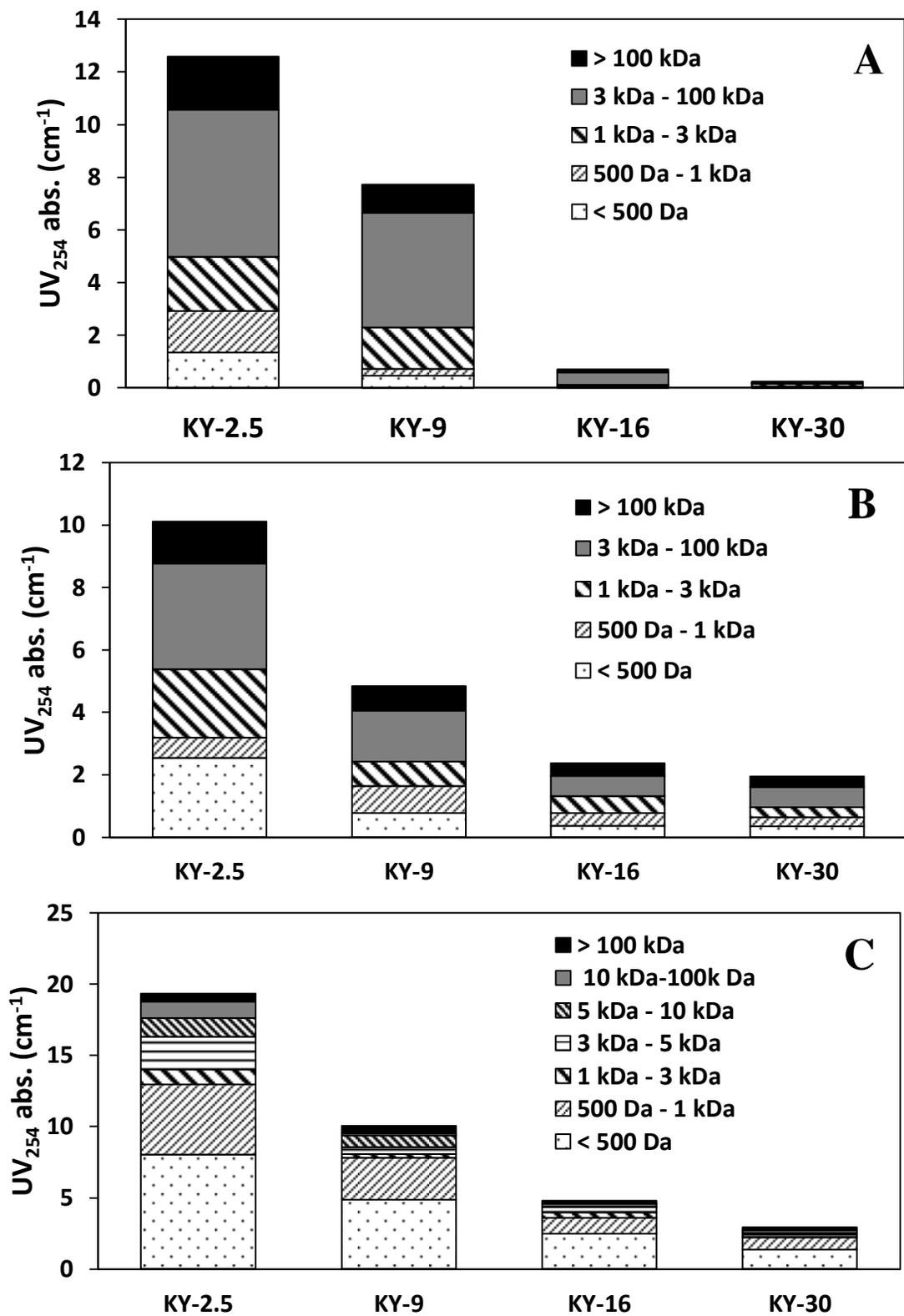


Figure 4-3: Particle size distribution of UV254 absorbing substances in humic acids (A), fulvic acids (B) and hydrophilic fraction (C) in KY leachates

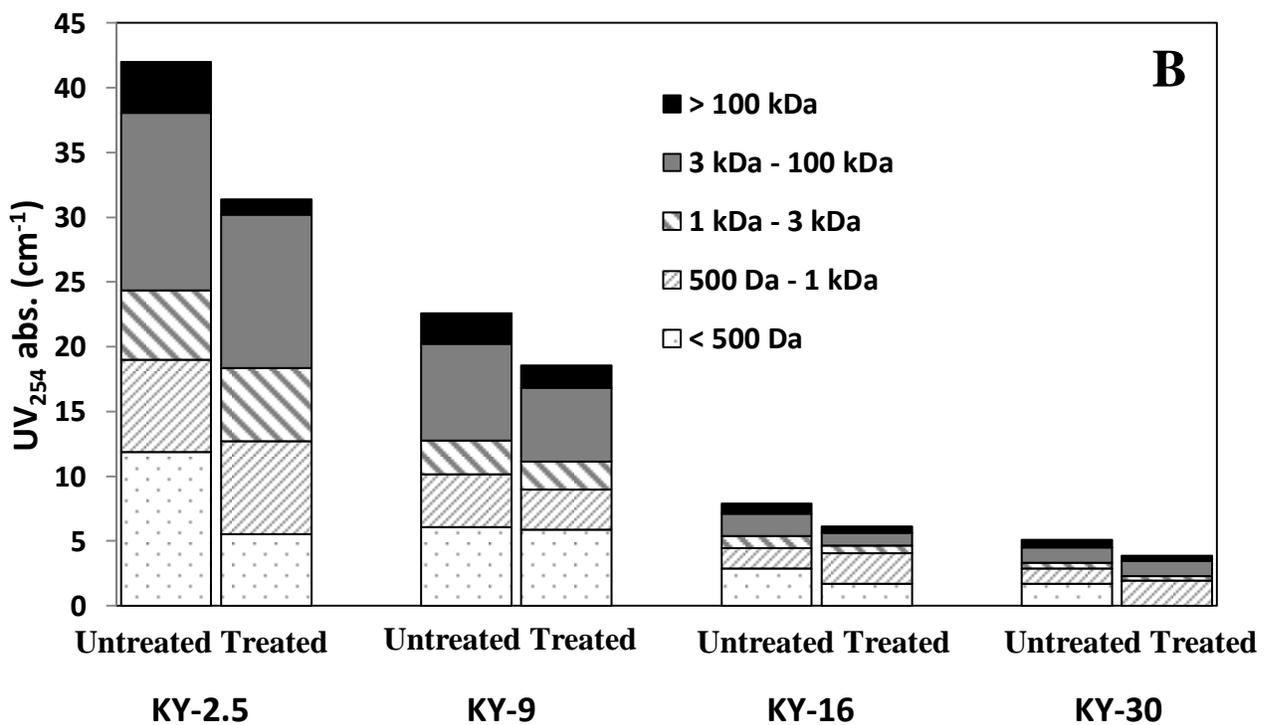
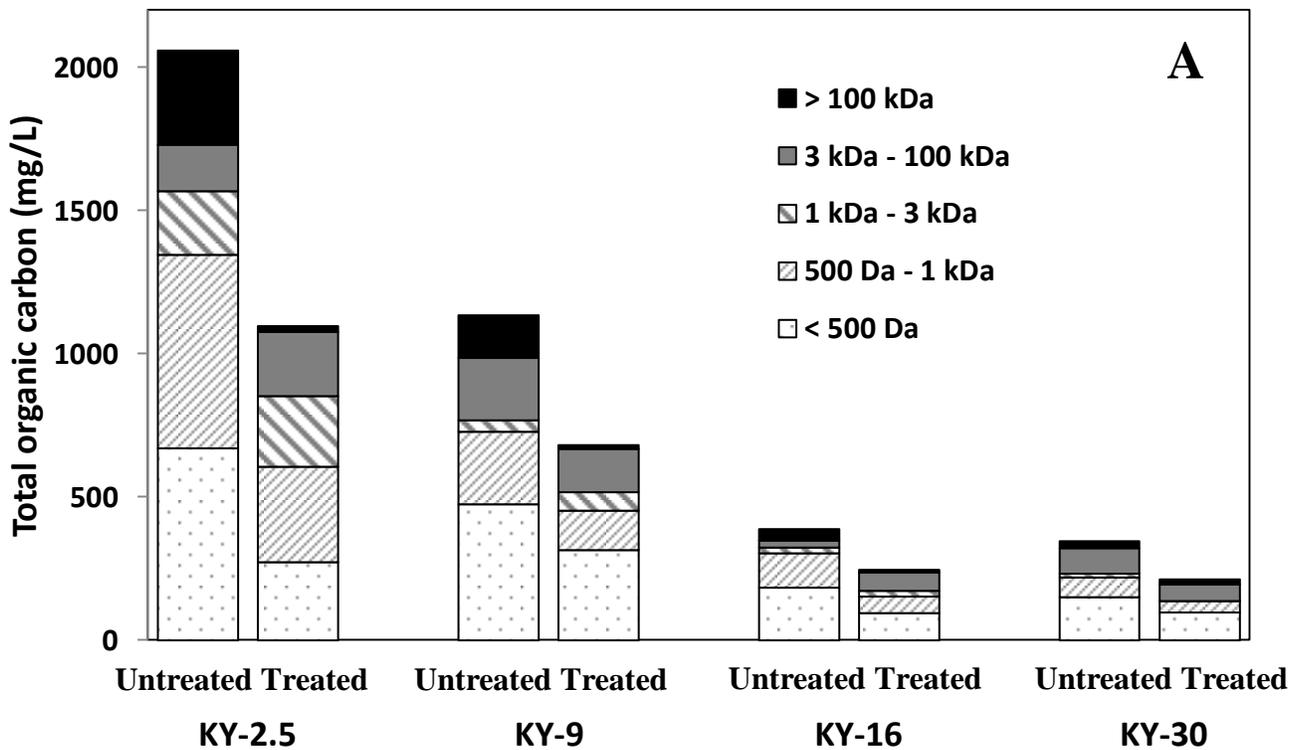


Figure 4-4: Comparison of the particle size distribution of total organic carbon (A) (TOC) and UV₂₅₄ absorbing substances (B) in the untreated and biologically treated KY leachates

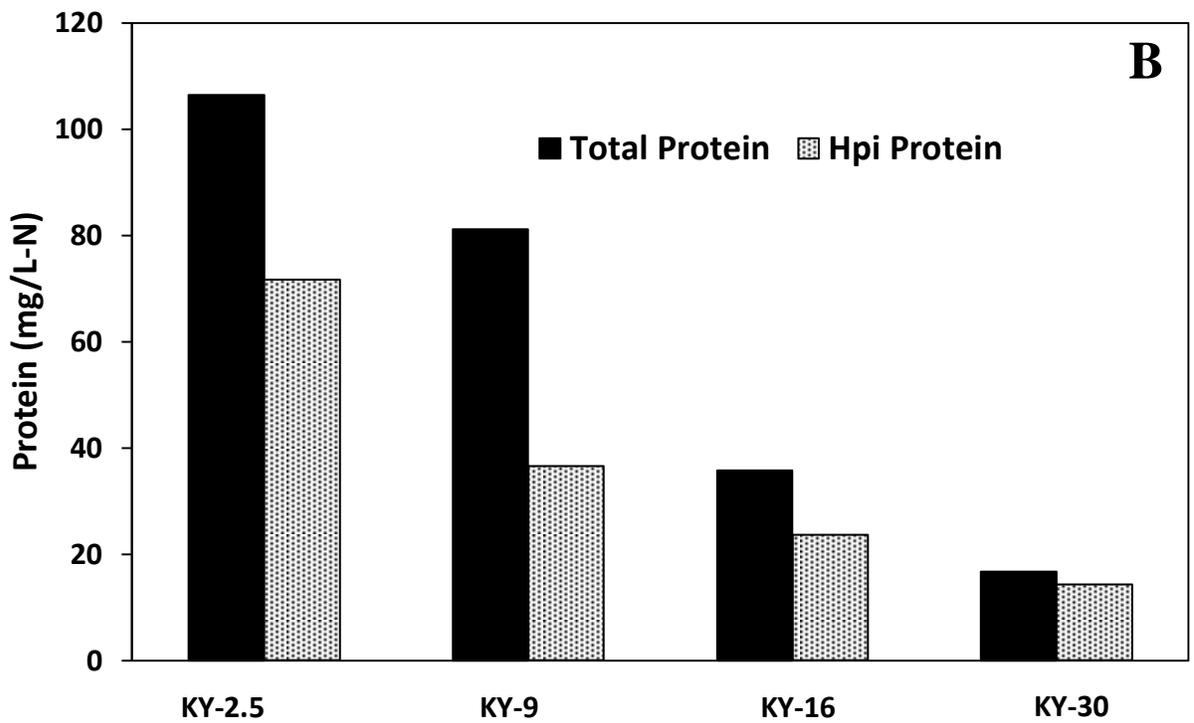
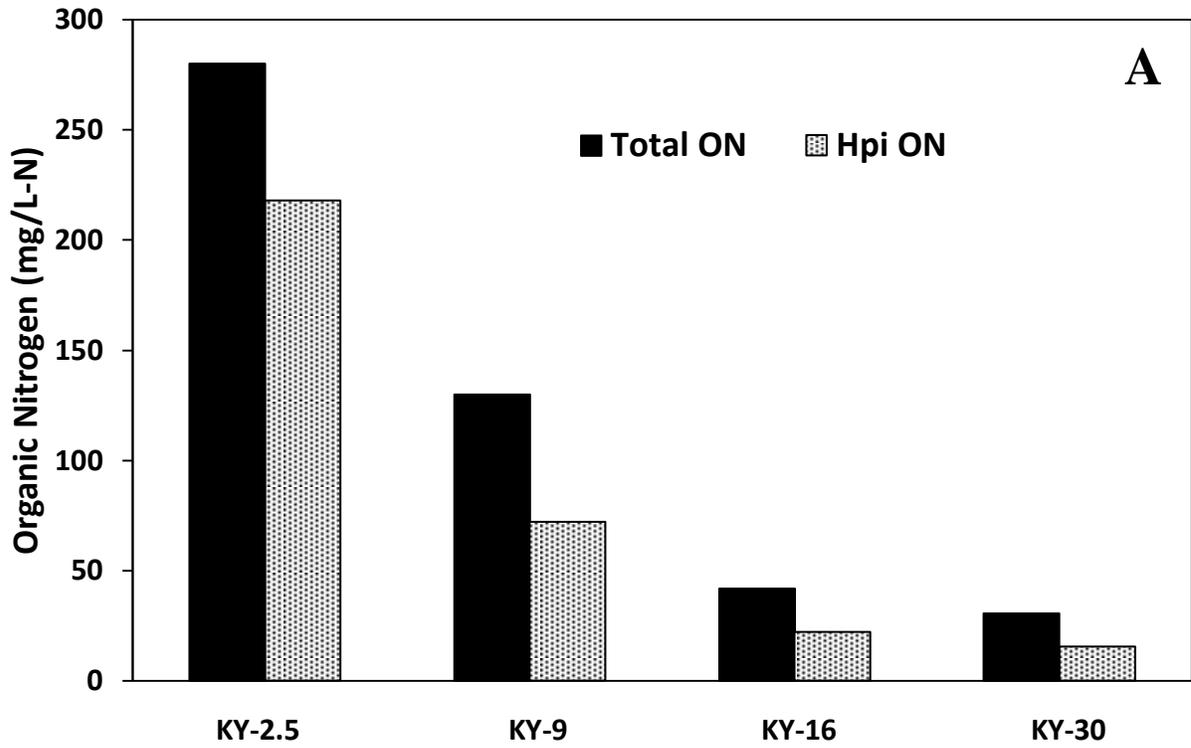


Figure 4-5: Contribution of the hydrophilic fraction to the organic nitrogen (A) and proteins (B) in the KY leachates

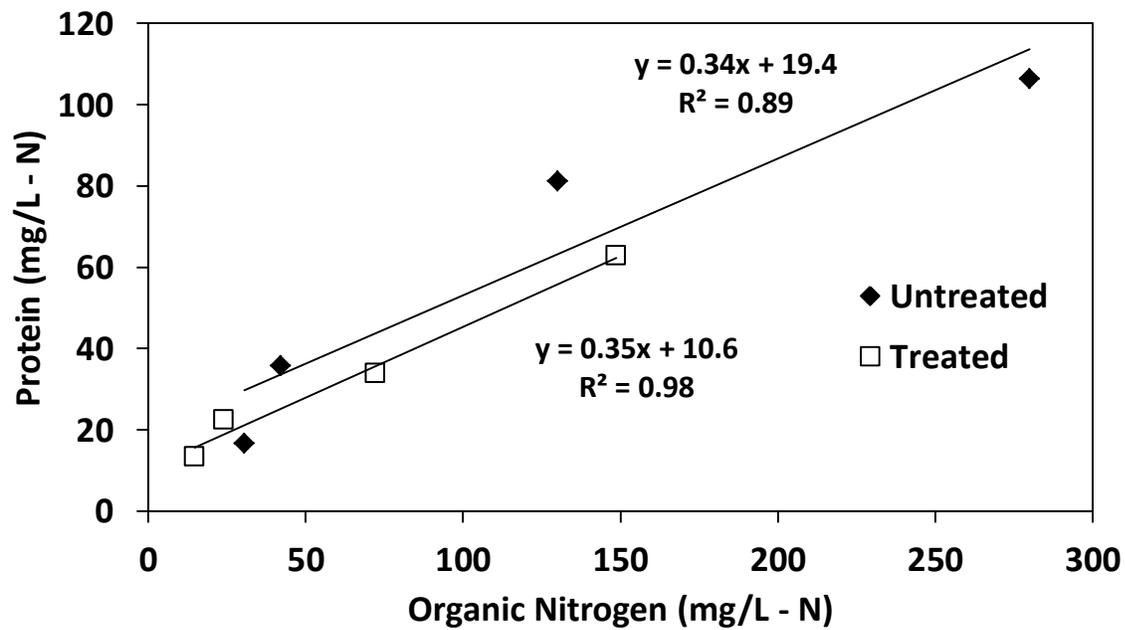


Figure 4-6: Correlation between organic nitrogen and proteins in untreated and biologically treated KY leachates

Chapter 5. Characterization and treatment of thermal hydrolysis pretreated anaerobic digestion centrate

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5.0 Abstract

Thermal hydrolysis is a sludge pretreatment technique that utilizes high pressure and temperature prior to anaerobic digestion. It causes increased volatile solids destruction, higher biogas production and improved cake dewaterability. It has been implemented successfully at a number of locations in Europe and one such system is under construction in the US. Disposal of the centrate/filtrate produced by the dewatering of the sludge is a major concern for treatment plants because the presence of UV₂₅₄ quenching substances in the centrate might interfere with UV₂₅₄ disinfection facilities. Also, with the lowering of the effluent nitrogen levels, development of treatment techniques for nitrogen-containing organics in the centrate is required. In this study, the particle size and hydrophobic fractions are characterized by their total organic carbon, UV₂₅₄ absorbance, organic nitrogen and protein content. This study also investigates the impact of biological treatment on the different particle size and hydrophobic fractions. It was observed that the optimum treatment depends on the size fraction and the hydrophobic behavior of the centrate. Coagulation-flocculation was observed to be better for the higher molecular weight (MW) fractions whereas a membrane bioreactor would be more suitable for the smaller MW fractions.

Keywords: thermal hydrolysis, anaerobic digestion, centrate treatment, characterization, particle size distribution, hydrophobic nature

5.1 Introduction

Thermal hydrolysis is a solids pretreatment technique that uses high temperature and pressure prior to mesophilic anaerobic digestion to improve digestion and dewatering. It can result in increased biogas production, doubling of digester loadings and can produce pathogen-free

biosolids with an increased cake solids concentration (Kopp and Ewert, 2009; Elliot and Mahmood, 2007; Zabranska et al., 2000). Since 1995, 20 plants have been built or are in construction (mainly in Europe) (Camacho et al., 2008). This technique is being implemented in the US for the first time (Figdore et al., 2010). The dewatering sidestream or centrate from the process contains higher ammonium-N than conventional anaerobic digestion processes (Kepp et al., 2001). Ammonia can contribute to eutrophication and can be toxic to sensitive aquatic biota. This reject water stream can also significantly impact the performance of secondary treatment systems for nitrification and nitrogen removal (Constantine, 2006). In wastewater treatment plants with sludge digestion, the return liquor typically comprises about one percent of the total plant flow volume, but 10-30% of the nitrogen load to the plant (Mulder et al., 2006; Constantine, 2006). With the permitted annual load limit for plant effluent total nitrogen being lowered in many regions of the country, several treatment techniques for the removal of nitrogen in the recycle stream, such as the DEMON process, are being explored (Figdore et al., 2011).

Most of the focus is with the removal of the inorganic nitrogen from the centrate. However, the organic nitrogen from the centrate can be a major contributor to the plant's effluent nitrogen (Johnson et al., 2010). With the integration of nitrification and denitrification systems into many of the present publically owned treatment works (POTWs), the organic nitrogen fraction can account for as high as 80 % of the total nitrogen in the POTW effluents (Qasim, 1999). A major portion of the composition of organic nitrogen in wastewater effluents is still unknown with the sum of known specific components accounting for less than 10 % of the organic nitrogen (Pehlivanoglu-Mantas and Sedlak, 2008). A study by Westgate and Park (2010) has shown that proteins correlate with the organic nitrogen in the wastewater treatment plant (WWTP) effluents.

This study estimated the contribution of the proteins to effluent organic nitrogen to be as high as 60 %.

It is widely accepted that humic substances are not readily biodegradable (Poblete et al., 2011) and can pass through the biological treatment processes in the POTWs elevating the organic matter level in the effluent in addition to the formation of harmful disinfection by-products (Zhao et al., 2012). Subsequently, ultra-violet (UV) disinfection has become quite popular in wastewater treatment because it can eliminate the formation of regulated disinfection by-products (DBPs) (NYSERDA, 1999). In practice POTWs utilize $\lambda = 254$ nm for their disinfection systems as it can be readily generated by mercury lamps (Tchobanoglous et al., 2004). The POTWs generally require that the UV_{254} transmittance in a wastewater stream be 60% - 65 % to ensure that UV_{254} disinfection can work properly (Basu et al., 2007).

However, the presence of UV_{254} quenching substances in the centrate can lead to a significant decrease in the efficiency of the UV_{254} disinfection systems at treatment plants (Zhao et al., 2012). Thus, a better understanding of the characteristics of the organic matter, nitrogen and UV_{254} quenching substances in the centrate is needed so that effective treatment techniques for recycle streams from thermal hydrolysis / anaerobic digestion systems can be developed.

Particle size and hydrophobic fractions of the untreated and biologically treated thermal hydrolysis / anaerobic digestion centrate were analyzed for total organic carbon (TOC), UV_{254} absorbance, organic nitrogen (ON) and proteins in this study . This investigation is one of the first to explore the distribution of organic matter and nitrogen in the untreated as well as

biologically treated thermal hydrolysis / anaerobic digestion centrate. The study also looks at the effectiveness of a physico-chemical technique like coagulation-flocculation for centrate treatment. Thus, the study can help us in the development of efficient techniques for the treatment of the centrate.

5.2 Materials and Methods

5.2.1 Centrate collection, sampling and aerobic biological treatment

The centrate investigated in this study was collected from the Anglian Water Cotton Valley sludge treatment center which is located at the Milton Keynes wastewater treatment works in Buckinghamshire, United Kingdom. The samples were shipped directly from the thermal hydrolysis sludge pretreatment facility to our lab at Virginia Tech, USA in plastic buckets and then stored at 4°C in the dark to reduce the microbial activity. The containers were shaken well to resuspend settled particles before sampling and analysis.

The centrate was biologically treated in the lab by continuous aeration using porous ceramic air diffusers for a period of 28 days. Since, the centrate contains microorganisms from anaerobic digestion sludge, no external seed was added. Biological flocs similar to activated sludge flocs were observed during the aeration process. Distilled water was added to compensate for the water lost due to evaporation. The detention time for aeration was decided on the basis of the time taken by the centrate to reach a stabilized state i.e. a point after which there was little additional biological degradation. The characteristics of the untreated and biologically treated centrate are listed in [Table 5-1](#).

5.2.2 Hydrophobic nature and particle size based fractionations

Centrate samples were fractionated into humic acids (HA), fulvic acids (FA) and a hydrophilic (Hpi) fraction based on their hydrophobic nature and solubility characteristics. Methods developed by [Thurman and Malcolm \(1981\)](#) and [Leenheer \(1981\)](#) were used in this study.

The size fractionation apparatus used consisted of 200 mL stirred ultrafiltration cells (Amicon model # 8200), a nitrogen gas tank (pressure: 120 kPa) and membrane discs (Millipore, Billerica, MA) with a range of molecular weight cut offs (MWCO). Details can be found in [Zhao et al. \(2012\)](#). The molecular weight cut off (in kDa) can be converted into pore size (in nm) with the equation: $R = 0.66MW^{1/3}$ ([Erickson, 2009](#)) where D is the pore size in nanometer and MW is the molecular weight in kDa.

5.2.3 Coagulation-flocculation

Coagulation-flocculation treatment was carried using a Jar Test apparatus (Phillips and Bird Inc., Richmond, VA). All experiments were carried out in 250 mL glass beakers containing a fixed amount of ferric chloride coagulant and 100 mL of the untreated centrate. The beakers in the Jar Test apparatus were stirred at 100 rpm for 5 minutes and at 40 rpm for 25 minutes and then allowed to settle for 1 hr. The dose was optimized by performing experiments at varying coagulant dosages (0.5, 1, 2, 3, 5 and 6 g/L).

5.2.4 Analysis

Total organic carbon (TOC) was analyzed by a high temperature combustion TOC analyzer (TOC-5000A, Shimadzu, Japan). The chemical oxygen demand (COD) analysis was executed by the closed reflux, titrimetric method per Standard Method 5220-D (APHA et al., 2012). The color analysis was carried out by the ADMI Tristimulus Filter Method 2120-E (APHA et al., 2012). The Ultraviolet absorbance at 254 nm (UV_{254} abs.) was measured with a spectrophotometer (Beckman Coulter, Brea, CA). The samples were diluted if the absorbance values were above the detection limited for the instrument. UV_{254} readings were multiplied by the corresponding dilution factor to give the final UV_{254} absorbance values (Zhao et al., 2012).

Organic nitrogen (ON) was estimated by subtracting inorganic nitrogen from total nitrogen (Westgate and Park, 2010). The inorganic nitrogen consists of nitrates, nitrites and ammonia. Total nitrogen concentrations for the samples were determined by the persulfate digestion method, nitrates by the dimethylphenol method, nitrites by the diazotization method and ammonia by the salicylate method (Hach Company, Loveland, CO) with the measurements being made by a spectrophotometer (DR 2800, Hach Company, Loveland, CO). The protein measurements were carried out with accordance to the Frølund modified Lowry method for quantitative protein analysis (Frølund et al., 1995; Lowry et al., 1951). The percentage of nitrogen in protein is taken to be 16 % (Westgate and Park, 2010).

Metal analysis for the samples was conducted using a Thermo Electron X-Series inductively coupled plasma with mass spectrometer (ICP-MS) per Standard Method 3125-B (APHA et al., 2012). ICP-MS Samples and calibration standards were prepared in a matrix of 2% nitric acid by

volume. The anions were measured with an Ion chromatograph (DX120, Dionex, Sunnyvale, CA) equipped with an AS9-HS column (Model No. 051786, Dionex, Sunnyvale, CA); the elute was 9.0 mM Na₂CO₃ and the flowrate was 1.0 mL/min.

5.3 Results and Discussion

5.3.1 Particle size distribution: Comparison between untreated and biologically treated fractions

Figure 5-1 (A) shows the particle size distribution of total organic carbon in the untreated and biologically treated fractions. For the untreated sample, the concentration of organic matter changes little from the fraction 300 kDa to 5 kDa (27 %) and from 8 µm to the unfiltered sample (5.5 %). There is a sizable decrease in the organic matter from the MWCO of 1.5 µm to the MWCO of 300 kDa (60 %). The 1.5 µm fraction corresponds to 65 % of the TOC which increases to 95 % for the 8 µm fraction. Around 60 % of the TOC is > 300 kDa indicating the importance of treatment techniques which can remove the larger size particles. Aerobic biological treatment is able to remove around 34 % of the TOC for the untreated sample. A previous study by Luo et al. (1998) showed that biological treatment can degrade organic matter of low molecular weight (MW). It was observed for this filtrate that biological treatment was able to achieve almost 50 % organic removal for fractions < 300 kDa (except for 500 Da) whereas just around 35 % removal was observed for the fractions > 300 kDa. This indicates that the smaller sized fractions were more biodegradable than the larger size fractions.

Figure 5-1 (B) shows the particle size distribution for the UV₂₅₄ quenching substances. Similar to Figure 5-1 (A), there seemed to be no significant increase in the UV₂₅₄ absorbance for fractions with MWCO of 100 kDa to 5 kDa and those > 300 kDa. The 1.5 µm fraction contributed 93 % of

the total UV₂₅₄ quenching while the 300 kDa fraction contributed around 50 %. There was almost equal UV₂₅₄ absorbance distribution between fractions < 300 kDa and those > 300 kDa. Aerobic biological treatment was observed to be relatively ineffective for the removal of UV₂₅₄ blocking material. For fractions > 300 kDa, almost no UV₂₅₄ absorbance removal was observed with around 20-30 % of the UV₂₅₄ absorbance removal in the fractions < 300 kDa. This indicated that the fractions > 300 kDa were the major contributors to UV₂₅₄ absorbance in addition to being more bio-refractory than the < 300 kDa fractions. Also, the percentage TOC removal by biological treatment was observed to be more than that for the UV₂₅₄ quenching substances for all the size fractions indicating that the biodegradable material did not quench UV light.

Figure 5-2 (A) shows the distribution of the ammonia in the untreated and biologically treated centrate size fractions. During aerobic biological treatment, due to the presence of both nitrifying and denitrifying bacteria in the centrate up to 90 % removal of the ammonia occurred, leaving behind negligible amounts of nitrate and nitrite species. Thus, aerobic biological treatment can be effective for the removal of the inorganic nitrogen from the centrate.

Figure 5-2 (B) shows the distribution of the organic nitrogen and proteins in the untreated and biologically treated centrate size fractions. There was a small but gradual increase in the organic nitrogen from < 500 Da to the 300 kDa fraction and from the > 300 kDa to the unfiltered sample. The ON distribution showed a major portion to be present in the fractions > 300 kDa (65 %). Around 80-90 % protein removal was observed for the fractions < 300 kDa whereas for the fractions > 300 kDa protein removal was around 60-70 % by aerobic biological treatment of the centrate. This indicated that the larger MW (> 300 kDa) proteins were less biodegradable than

the smaller MW proteins (< 300 kDa). Also, aerobic biological treatment was observed to be relatively ineffective for organic nitrogen removal for any of the size fractions.

The analysis in [Figure 5-3](#) for the centrate size fractions showed that the proteins were around 30 % of the organic nitrogen for the untreated centrate and 16 % for the treated centrate. For fractions < 300 kDa ([Figure 5-2](#)), the percentage of organic nitrogen from the proteins was greater than that for the fractions > 300 kDa. This indicated that the organic nitrogen < 300 kDa should be more biodegradable than the fractions > 300 kDa due to the biodegradable nature of proteins. The organic nitrogen remained almost the same even after the biological degradation of the contributing proteins. This suggests that proteins are probably being transformed into a form which still contributed to the organic nitrogen. This persistence of high quantities of organic nitrogen is a potential source of elevated total nitrogen levels for treatment plants using thermal hydrolysis. A comprehensive study is needed for the identification of the species that contribute to the biologically recalcitrant organic nitrogen.

5.3.2 Hydrophobic nature based distribution: Comparison between untreated and biologically treated fractions

[Figure 5-4 \(A\)](#) shows the distribution of the organic matter in the humic acids (HA), fulvic acids (FA) and hydrophilic (Hpi) fraction in the untreated and biologically treated centrate. It also shows the distribution of the organic matter based on the particle size for these hydrophobic fractions. It was observed that most of the organic matter was present in the HA and the Hpi fraction with their contributions being around 38 % and 41 %, respectively. It was also observed that the HA's were the largest MW fractions with the amount of organic matter in the fraction >

300 kDa being around 55 % while that < 1 kDa being just 18 %. The FA's which are generally considered the smaller MW humic substances (Tan, 2003) have a relatively even distribution of organic matter among the size fractions. Around 40 % of the organic matter in the FA was > 100 kDa (Table 5-2). However, for the Hpi's, most of the organic matter was quite small in size with 44 % of the organic matter being < 1 kDa. The HA and FA fractions (humic substances) combined contributed around 60 % of the total organic matter in the centrate. Thus, a membrane bioreactor might be helpful in the removal of more than half of the organic matter, especially the humic substances.

The overall organic removal by biological treatment in the HA, FA and Hpi fractions was 16 %, 39 % and 43 %, respectively. It was observed that the contribution of the < 1 kDa fraction to the HA increased from 18 % in the untreated centrate to 39 % in the biologically treated centrate. Thus, for the HA fraction, much of the organic matter > 300 kDa appeared to be converted into the smaller MW fractions on biological treatment. The FA and Hpi fraction, however, seemed to be easier to biodegrade than the HA's for most of the size fractions. Thus, though aerobic biological treatment might be relatively efficient for the degradation of the smaller MW fractions (FA and Hpi), it is not effective for the larger MW fractions (HA).

Figure 5-4 (B) shows the distribution of the UV₂₅₄ absorbance among the hydrophobic nature based fractions. It also shows the particle size distribution of the UV₂₅₄ absorbance for the hydrophobic fractions. It was observed that the humic substances (humic acids and fulvic acids) were mainly responsible for UV₂₅₄ quenching. This was different from the contribution of these fractions to the TOC. The HA's and FA's combined contributed more than three quarters of the

total UV₂₅₄ absorbance. The contribution of the Hpi's was less than 25 % even though its contribution to the TOC was around 42 %. Thus, the Hpi fraction might be the greatest contributor to the organic matter but its capacity to quench UV₂₅₄ light is the least among the hydrophobic fractions.

The particle size distribution of the UV₂₅₄ absorbance due to the HA fraction showed that around 50 % of the total UV₂₅₄ absorbance was due to particles > 300 kDa. The HA's had around 80 % of the total UV₂₅₄ absorbance from particles which were > 1 kDa, indicating that UV₂₅₄ quenching was mainly due to the larger sized particles. The UV₂₅₄ quenching due to the FA's from particles > 100 kDa it was around 37 % (Table 5-3). The Hpi fraction, however, had most of the UV₂₅₄ quenching due to particles < 1 kDa. The particles < 1 kDa contributed to almost two-third of the Hpi fraction's UV₂₅₄ absorbance. Most of the UV₂₅₄ quenching was due to the humic substances. For humics it has been observed that their larger MW fractions contributed greatest to UV₂₅₄ quenching. A membrane bioreactor with a pore size of 4 nm or 300 kDa MWCO might be a good option.

For the larger molecular weight, HA's, biological treatment was able to remove only 15 % of the UV₂₅₄ quenching substances, whereas there was 47 % and 39 % removal, for the FA and Hpi fractions, respectively. Thus, aerobic biological treatment might be feasible for the FA and Hpi fractions but for the removal of the larger MW HA's, it is ineffective.

Figure 5-5 shows the distribution of organic nitrogen and proteins in the untreated and biologically treated hydrophobic-hydrophilic fractions for the centrate. It can be observed that

similar to the distribution of the organic matter, the HA and Hpi fractions were the major contributors to the organic nitrogen. The contribution of HA's and Hpi's was 48 % and 45 %, with the FA's contributing just 7 %. It was observed that the portion of the proteins in the higher MW humic substances (HA's and FA's) was greater than that in the smaller MW Hpi fraction. The contribution of the proteins to the organic nitrogen in the HA's, FA's and the Hpi's was 40 %, 59 % and 23 %, respectively. Aerobic biological treatment, as seen in [Figure 5-2](#), was not able to achieve sizable organic nitrogen removal for any of the hydrophobic fractions even though the proteins were degrading.

In [Figure 5-2](#), it was observed that the proteins in the smaller MW fractions were more biodegradable as compared to those in the larger MW fractions. The degradation of the proteins in the HA, FA and Hpi fractions was 54 %, 53 % and 91 %, respectively. Thus, the proteins in the Hpi fraction degraded to a much larger extent when compared with those in the higher MW HA's and FA's.

The degradation of the organic matter, UV₂₅₄ quenching substances and organic nitrogen in the hydrophobic fractions, indicated that aerobic biological treatment was not capable of efficiently degrading the higher MW HA's and FA's. Physico-chemical treatment techniques like coagulation-flocculation are generally considered a better method for the removal of the higher MW fractions like HA's ([Vik et al., 1988](#)).

5.3.3 Particle size and hydrophobic nature based distribution: Comparison between untreated and coagulation-flocculation treated centrate fractions

Figure 5-6 shows the TOC (A) and the UV₂₅₄ absorbance (B) for the unfiltered and the 300 kDa MWCO centrate fractions, before and after coagulation-flocculation. Aerobic biological treatment was found to be ineffective for the treatment of the > 300 kDa fractions so coagulation might be an option as it usually removes the larger sized particles. The optimum dose for the treatment of the centrate was observed to be 5 g/L of ferric chloride.

Coagulation-flocculation resulted in 58 % and 46 % removal of the organic matter and UV₂₅₄ absorbance, respectively for the unfiltered centrate. These removals were much better than the 35 %, organic matter and 4 %, UV₂₅₄ absorbance removals achieved by biological treatment. Even for the 300 kDa fraction, coagulation-flocculation resulted in 36 % and 34 % removal of the TOC and UV₂₅₄ absorbance, respectively. Biological treatment resulted in 43% and 20 % removal of organic carbon and UV₂₅₄ absorbance for this fraction. Thus, coagulation-flocculation was found to be better for removal of UV₂₅₄ absorbing material.

It was also observed that the organic matter and UV₂₅₄ quenching substance removal achieved through coagulation-flocculation was greater for the unfiltered centrate than the 300 kDa MWCO fraction. This supported the idea that coagulation was more effective for the removal of larger sized particles. The removal of the UV₂₅₄ absorbance which can be achieved by coagulation-flocculation maybe attributed to the removal of the higher MW HA's.

Figure 5-7 shows the organic nitrogen and proteins for the unfiltered and the 300 kDa MWCO centrate fractions, before and after coagulation-flocculation. It was observed that the proteins in

the unfiltered sample were 63 % removed as compared to the 29 % removal which was observed for the 300 kDa fraction. This was opposite of the higher degradation of the proteins in the < 300 kDa fractions by biological treatment. Another observation which distinguished it from biological treatment of the < 300 kDa fractions was that coagulation-flocculation removed one third of the non-protein components of the organic nitrogen. This might be due to the removal of the smaller organic nitrogen compounds. Thus, coagulation-flocculation appears to be better than biological treatment when it comes to organic nitrogen removal in fractions < 300 kDa.

5.4 Summary and Conclusions

Thermal hydrolysis pretreatment prior to anaerobic digestion can be used to treat all types of sludges, industrial or municipal. This technique has a number of advantages over the conventional anaerobic digestion process. These are increased sludge biodegradability, enhanced biogas production, reduction in sludge produced and stabilization of the final biosolids product. The centrate produced by dewatering of the final biosolids can cause serious concerns for the POTWs into which this process is integrated. The centrate is capable of strongly quenching UV₂₅₄ light and interfering with the POTW's UV₂₅₄ disinfection facility. Also, the non-biodegradable organic nitrogen can add to the treatment plant's effluent nitrogen making it difficult to meet the effluent nitrogen regulations in some regions of the United States.

This study presented a particle size and hydrophobic nature based characterization of the centrate. It compared the different physico-chemical and biological treatment processes which can be implemented and what impact the treatment has on the particle size and hydrophobic distribution. It also tried to identify the hydrophobic fractions of the centrate which were the

main contributors of UV₂₅₄ absorbance and the organic nitrogen. The major conclusions of the study are summarized below.

- Biological treatment was observed to be more effective for the removal of organic matter and UV₂₅₄ quenching substances for fractions < 300 kDa. Hence, a membrane bioreactor with a pore size of 4 nm or 300 kDa MWCO would be effective for the treatment of the recycle stream as it can remove upto 80 % of the organic matter and 60 % of the UV₂₅₄ quenching substances.
- Organic nitrogen was observed to be more biologically recalcitrant when compared with organic carbon.
- Biological treatment was observed to be effective for the degradation of proteins but had little impact on organic nitrogen. However, the treatment of the recycle stream with a membrane bioreactor with a 300 kDa MWCO can result in upto 65 % organic nitrogen removal.
- Though, the HA's and the Hpi's were the major contributors to the organic matter, but the humic substances (HA's and FA's) were mainly responsible for the UV₂₅₄ quenching. Humic substances were the larger MW fractions and were not efficiently removed by biological treatment.
- The HA's and the Hpi's which contributed more than 90 % of the organic nitrogen are biologically recalcitrant.
- Coagulation-flocculation was observed to be a better treatment process for fractions > 300 kDa, exhibiting better UV₂₅₄ quenching substances and organic removal rates than biological treatment.

- Coagulation-flocculation also showed potential for the removal of organic nitrogen in lower MW fractions where biological treatment was found to be ineffective.

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Table 5-1: Characteristics of the thermal hydrolysis/anaerobic digestion centrate

Parameter	Unit	Untreated	Biologically treated
TOC	mg/L	2431.5 ± 55.3	1592.7 ± 41.2
COD	mg/L	7225 ± 70	5250 ± 45
UV ₂₅₄ abs.	cm ⁻¹	37.7 ± 1.7	32.6 ± 2.8
Total nitrogen	mg/L-N	2203.3 ± 102.1	537.4 ± 63.3
NO ₂	mg/L-N	7.7 ± 0.5	n.d. ^a
NO ₃	mg/L-N	20.1 ± 3.7	27.1 ± 1.4
NH ₃	mg/L-N	1895.5 ± 168.7	280.3 ± 53.4
pH	—	7.7	7.3
Color	ADMI	14904 ± 134	12420 ± 256
PO ₄	mg/L-P	115.4 ± 6.4	136.1 ± 13.5
SO ₄	mg/L	23.0 ± 8.8	55.1 ± 13.1
Na	mg/L	121.8 ± 25.7	133.5 ± 4.3
Mg	mg/L	2.7	5.0 ± 0.2
Si	mg/L	37.3 ± 2.3	33.7 ± 0.5
Cl	mg/L	180.7 ± 6.3	219.2 ± 21.7
K	mg/L	212.7 ± 17.9	200.8 ± 6.5
P	mg/L	174.5 ± 5.7	161.5 ± 2.9
Ca	mg/L	40.5 ± 0.7	26.2 ± 0.7
Cr	µg/L	64.9	51.9 ± 0.4
Mn	µg/L	27.7 ± 5.7	12.7 ± 0.7
Zn	mg/L	0.1	0.1

^a non-detectable

Table 5-2: Particle size distribution of total organic carbon (TOC) for the hydrophobicity fractions

Sample	Untreated centrate (mg/L)			Biologically treated centrate (mg/L)		
	HA	FA	Hpi	HA	FA	Hpi
< 1 kDa	185	145	504	339	120	310
1 kDa - 3 kDa	29	67	57	148	4	31
3 kDa - 10 kDa	140	111	88	29	37	36
10 kDa - 100 kDa	82	21	128	140	75	139
100 kDa - 300 kDa	43	89	149	27	51	95
> 300 kDa	575	134	214	198	61	40
Total	1054	568	1138	881	348	651

Table 5-3: Particle size distribution of UV₂₅₄ absorbance for the hydrophobicity fractions in the centrate

Sample	Untreated centrate (cm ⁻¹)			Biologically treated centrate (cm ⁻¹)		
	HA	FA	Hpi	HA	FA	Hpi
< 1 kDa	3.6	3.5	6.8	4.3	2.2	3.8
1 kDa - 3 kDa	1.1	1.9	0.3	0.8	0.0	0.0
3 kDa - 10 kDa	3.4	2.4	0.3	0.6	1.7	0.5
10 kDa - 100 kDa	0.2	0.2	0.7	1.7	1.9	0.1
100 kDa - 300 kDa	1.3	2.9	0.3	1.2	0.4	0.1
> 300 kDa	9.0	1.7	1.8	7.3	0.5	1.8
Total	18.6	12.7	10.2	15.9	6.7	6.2

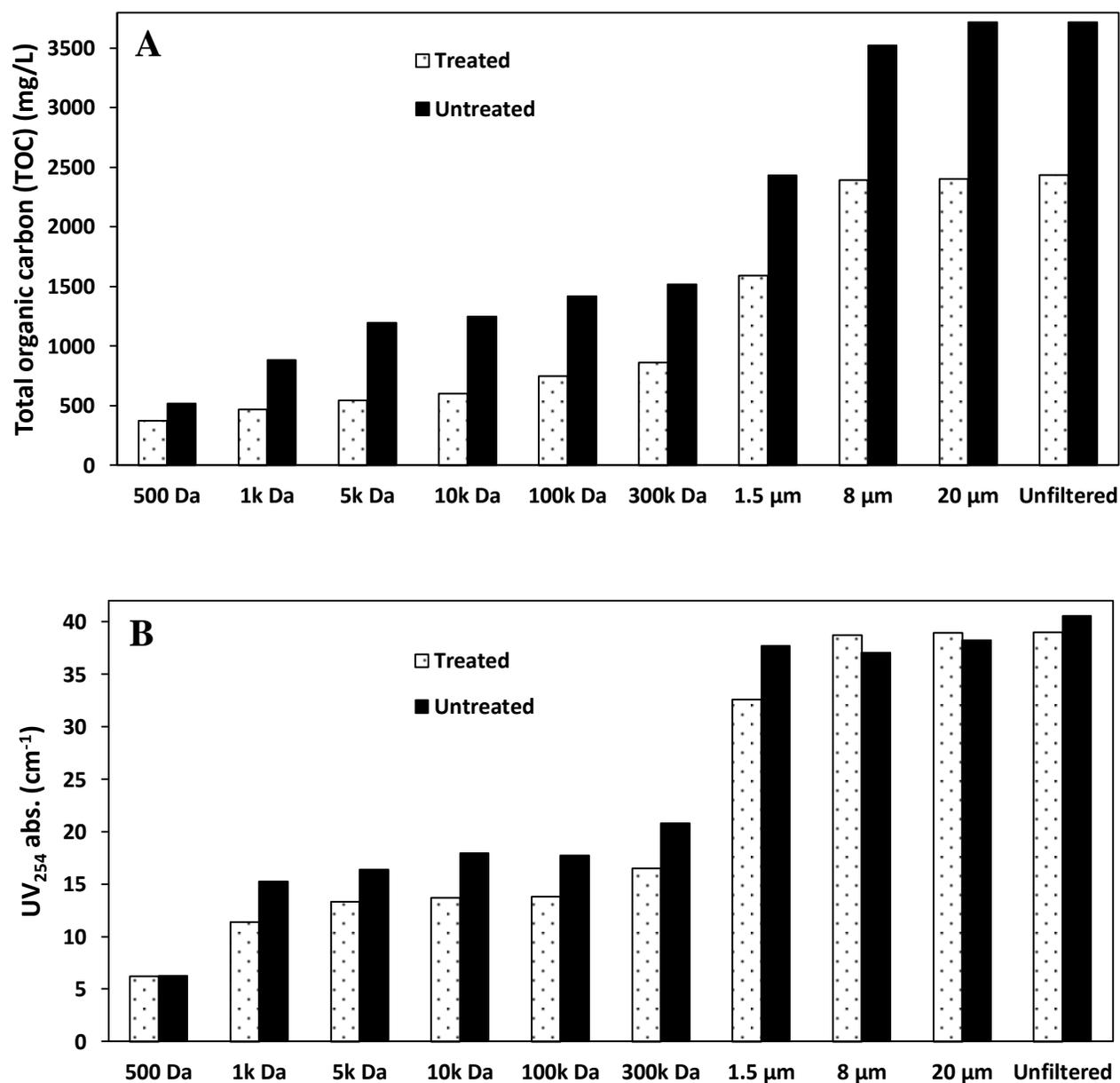


Figure 5-1: Particle size distribution of the total organic carbon (TOC) (A) and the UV₂₅₄ absorbance (B) in the untreated and biologically treated thermal hydrolysis/anaerobic digestion centrate

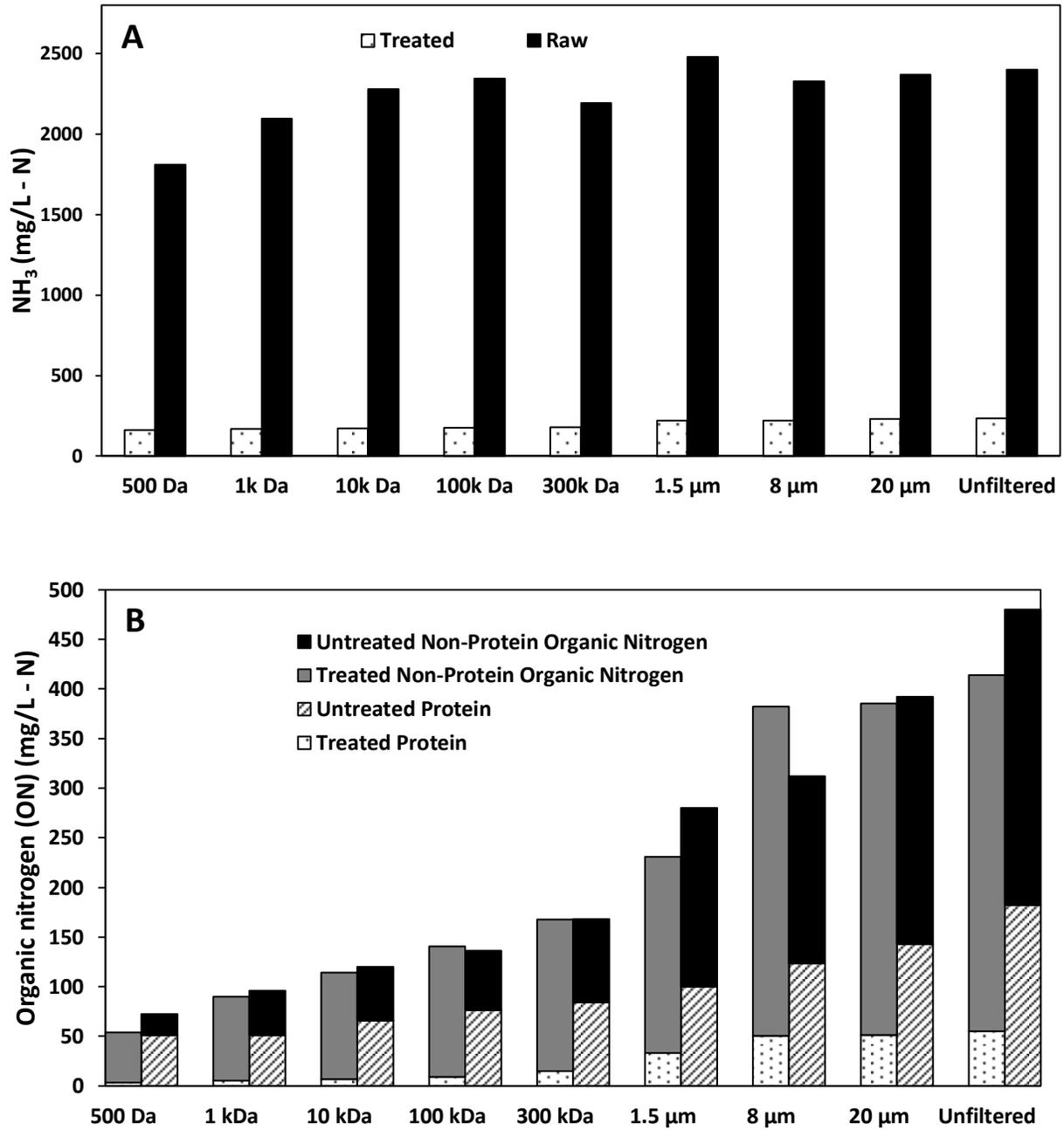


Figure 5-2: Particle size distribution of the ammonia (A) and organic nitrogen (ON), proteins (B) in the untreated and biologically treated thermal hydrolysis/anaerobic digestion centrate

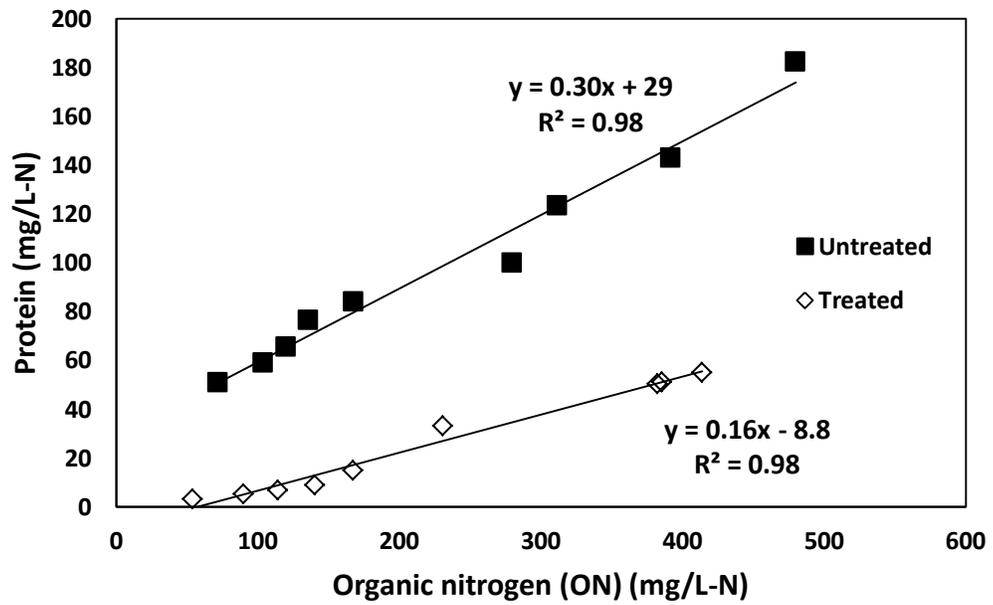


Figure 5-3: Correlation between the amount of protein and organic nitrogen (ON) in the untreated and biologically treated thermal hydrolysis/anaerobic digestion centrate

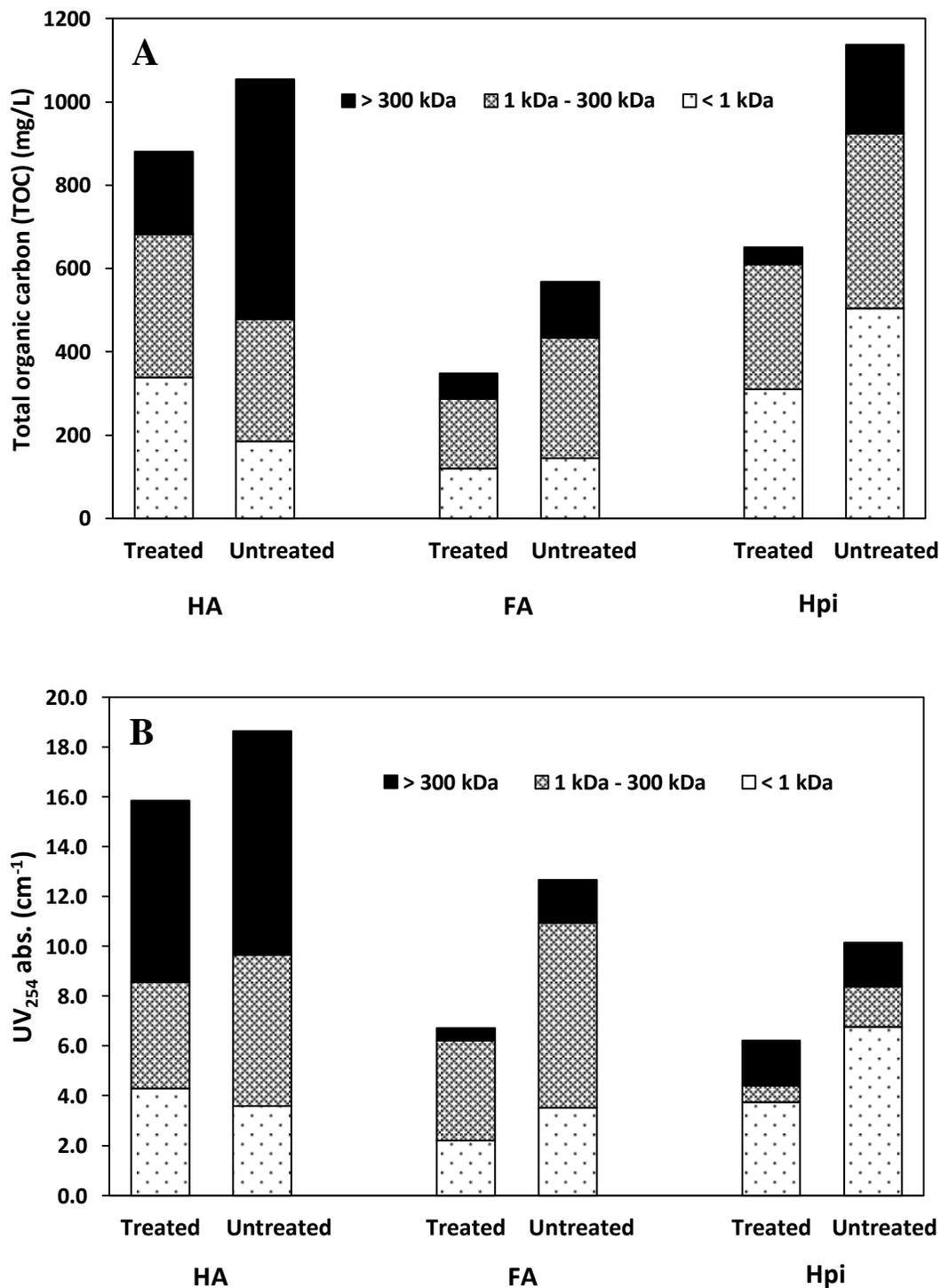


Figure 5-4: Distribution of the total organic carbon (TOC) (A) and UV₂₅₄ absorbing substances (B) among the hydrophobic nature based fractions in the untreated and biologically treated thermal hydrolysis/anaerobic digestion centrate

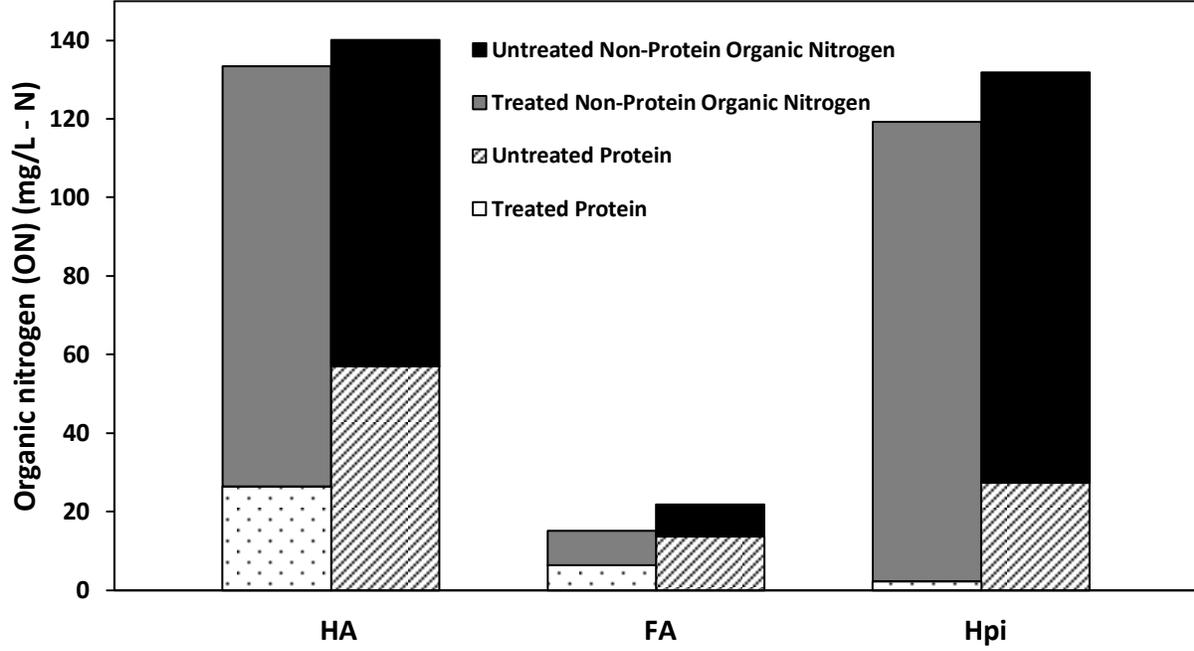


Figure 5-5: Distribution of organic nitrogen (ON) and proteins among the hydrophobic nature based fractions in the untreated and biologically treated thermal hydrolysis/anaerobic digestion centrate

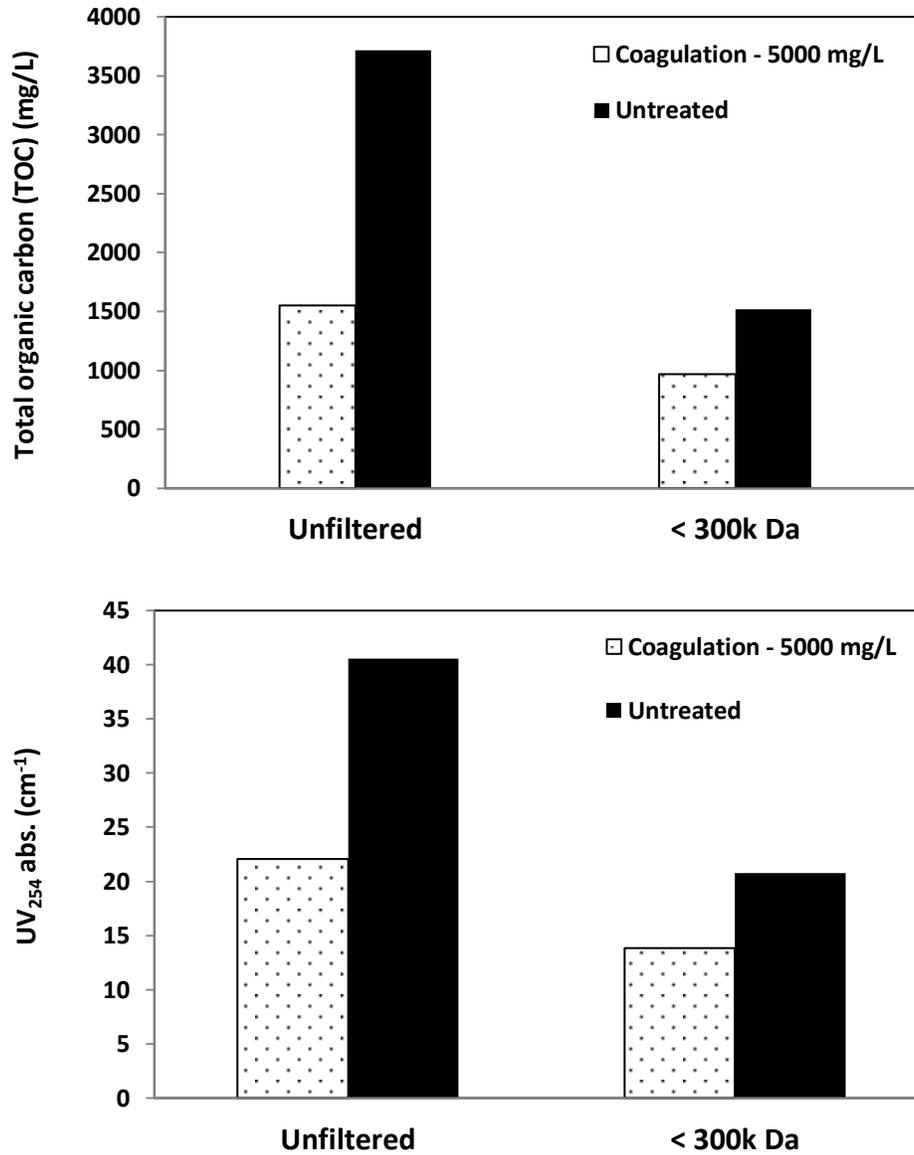


Figure 5-6: Distribution of the total organic carbon (TOC) (A) and UV₂₅₄ absorbance (B) before and after coagulation-flocculation of the size fractions for the thermal hydrolysis/anaerobic digestion centrate

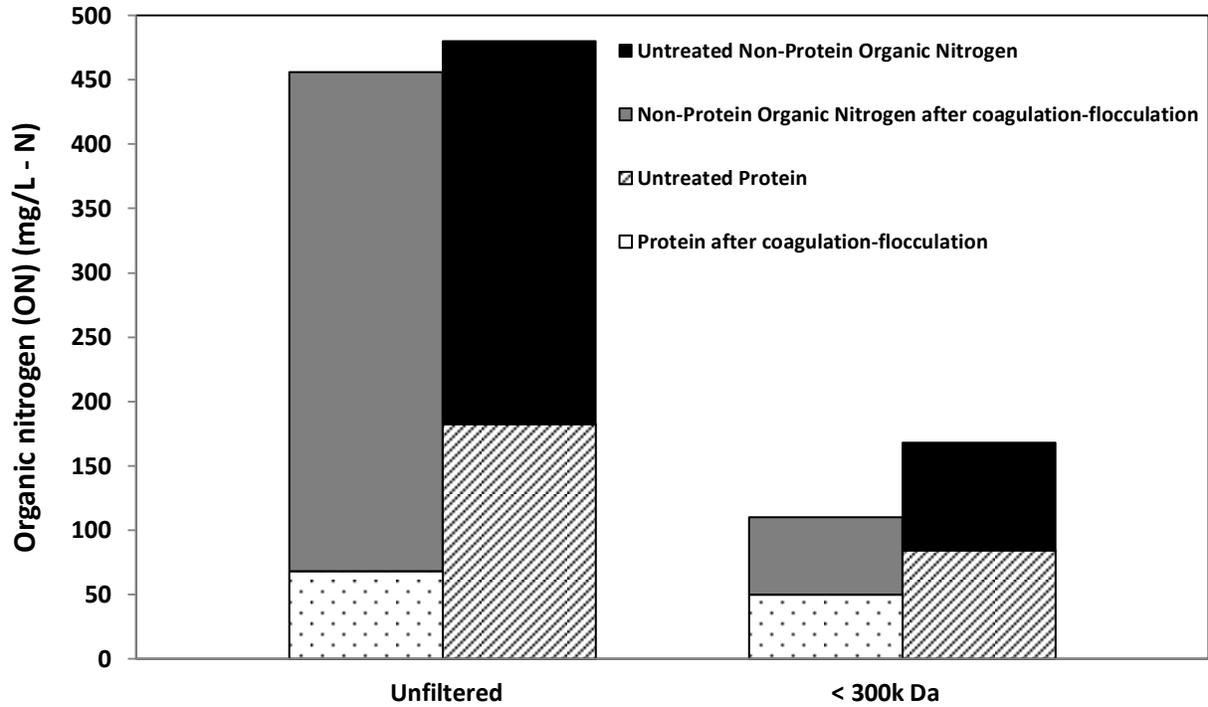


Figure 5-7: Distribution of the organic nitrogen (ON) and proteins before and after coagulation-flocculation of size fractions for the thermal hydrolysis/anaerobic digestion centrate

Appendix: Chapter 3

1. Statistical analysis of hypothesis from Table 3-2

p value (probability level) for the alternate hypothesis that the TOC removal percent $> UV_{254}$ removal percent is $5.611e-05$. Under the confidence level of $\alpha = 0.05$, the null hypothesis was rejected and the alternate hypothesis was accepted. Statistics analysis was conducted with R language.

R code:-

```
> TOCremovalpercent <- c(37.4,42.25,36.49,37.5,34.82,55.78)
> UVremovalpercent <- c(17.85,9.82,2.7,-2.3,2.51,29.09)
> t.test(TOCremovalpercent,UVremovalpercent,alt="greater",var.equal=T,paired=T)
```

Paired t-test

data: TOCremovalpercent and UVremovalpercent

t = 10.9141, df = 5, p-value = $5.611e-05$

alternative hypothesis: true difference in means is greater than 0

95 percent confidence interval:

25.0822 Inf

sample estimates:

mean of the differences

30.76167

2. Statistical analysis of regression in Figure 3-5

p values (probability level) for correlation curve slopes of HA, FA and Hpi fractions for their UV abs. (cm^{-1}) and TOC (mg/L) were $1.17\text{e-}06$, $2.97\text{e-}05$ and $2.38\text{e-}06$ respectively. Under the confidence level of $\alpha = 0.05$, all the correlations were significant in terms of slope. Statistics analysis was conducted with R language.

R code:-

```
> HAUV <- c(12.6,7.73,4.91,4.76,2.28,1.19,0.24,0.71,0.55)
> HATOC <- c(373.82,207.75,186.05,109.28,85.91,34.56,7.73,18.78,13.91)
> lmHA <- lm(HAUV~HATOC)
> summary(lmHA,corr=T)
```

Call:

```
lm(formula = HAUV ~ HATOC)
```

Residuals:

Min	1Q	Median	3Q	Max
-1.34037	-0.04920	0.05140	0.07256	1.07602

Coefficients:

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	0.030789	0.353477	0.087	0.933
HATOC	0.033430	0.002171	15.400	$1.17\text{e-}06$ ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7487 on 7 degrees of freedom

Multiple R-squared: 0.9713, Adjusted R-squared: 0.9672

F-statistic: 237.2 on 1 and 7 DF, p-value: 1.174e-06

Correlation of Coefficients:

(Intercept)

HATOC -0.71

```
> FAUV <- c(10.1,4.84,3.59,3.5,3.68,3.25,2.73,2.36,1.94)
```

```
> FATOC <- c(392.24,211,188.35,152.07,113.65,90.36,84.93,89.68, 83.18)
```

```
> lmFA <- lm(FAUV~FATOC)
```

```
> summary(lmFA,corr=T)
```

Call:

```
lm(formula = FAUV ~ FATOC)
```

Residuals:

Min	1Q	Median	3Q	Max
-1.16138	-0.40322	-0.08467	0.58208	0.78944

Coefficients:

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	0.348123	0.448738	0.776	0.463
FATOC	0.023378	0.002457	9.515	2.97e-05 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.6982 on 7 degrees of freedom

Multiple R-squared: 0.9282, Adjusted R-squared: 0.918

F-statistic: 90.54 on 1 and 7 DF, p-value: 2.966e-05

Correlation of Coefficients:

(Intercept)

FATOC -0.86

```
> HpiUV <- c(14.3,10.25,6.46,5.44,5.15,5.84, 4.77, 3.21, 2.11)
```

```
> HpiTOC <- c(1014.5,678.04, 496.07, 351.6,283.98,277.23, 232.78, 175.53, 141.65)
```

```
> lmHpi <- lm(HpiUV ~ HpiTOC)
```

```
> summary(lmHpi, corr=T)
```

Call:

```
lm(formula = HpiUV ~ HpiTOC)
```

Residuals:

Min	1Q	Median	3Q	Max
-1.1028	-0.2513	0.0214	0.3347	1.1121

Coefficients:

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	1.1366064	0.4531262	2.508	0.0405 *
HpiTOC	0.0129542	0.0009334	13.879	2.38e-06 ***

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Residual standard error: 0.7466 on 7 degrees of freedom

Multiple R-squared: 0.9649, Adjusted R-squared: 0.9599

F-statistic: 192.6 on 1 and 7 DF, p-value: 2.382e-06

Correlation of Coefficients:

(Intercept)

HpiTOC -0.84

The R code for the figure 5 illustrating the linear regression of HA, FA and Hpi fractions for UV_{254} abs (cm^{-1}) and TOC (mg/L) :-

```
>plot(HpiTOC,HpiUV, xlab="", ylab="", pch=19, xlim=c(0,1100), ylim=c(0,14.5))
```

```
>lines(HpiTOC, fitted(lmHpi))
```

```
>points(FATOC,FAUV, pch=15)
```

```
>lines(FATOC, fitted(lmFA))
```

```
>points(HATOC,HAUV, pch=17)
```

```
>lines(HATOC, fitted(lmHA))
```

```
>legend("bottomright", c("HA", "FA", "Hpi"), pch=c(17,15,19))
```

3. Statistical analysis of the $SUVA_{254}$ for the leachate fractions (Table 3-3)

p value (probability level) for the repeated measure multivariate ANOVA test with null hypothesis that the mean $SUVA_{254}$ values for the HA, FA and Hpi fractions were equal is 2.42e-08. Under the confidence level of $\alpha = 0.05$, the null hypothesis was rejected and the alternate hypothesis that the mean $SUVA_{254}$ for atleast one of the fractions was different was accepted.

Then a general linear hypothesis testing model was used to perform multiple comparisons between the $SUVA_{254}$ values of the leachate fractions using the Tukey's all pair comparison. From SF 1, the order of the $SUVA_{254}$ for the leachate fractions followed: HA>FA>Hpi. Statistics analysis was conducted with R language.

R code:-

```
> SUVA <-  
c(2.77,1.92,1.55,4.7,3.25,2.05,2.65,2.31,1.3,3.68,3.29,2.28,3.37,2.57,1.45,3.72,2.29,1.49,3.79,2.  
64,1.87,3.13,2.33,1.54)  
> Leachate <-  
c("PAr","PAr","PAr","PAr","PAr","PAr","NHr","NHr","NHr","NHt","NHt","NHt","OL8","OL8  
","OL8","OL7","OL7","OL7","OL5","OL5","OL5","OL3","OL3","OL3")  
> Fraction <-  
c("HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","  
HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi")  
> means.Fraction <- tapply(SUVA,Fraction, mean, na.rm = TRUE)  
> residuals <- SUVA-means.Fraction[Fraction]  
> shapiro.test(residuals)
```

Shapiro-Wilk normality test

data: residuals

W = 0.9661, p-value = 0.5714

```
> mydata <- data.frame(SUVA,Leachate,Fraction)
> y <- aov(SUVA ~ Fraction + Error(Leachate/Fraction), data=mydata)
> summary(y)
```

Error: Leachate

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Residuals	7	4.29	0.6128		

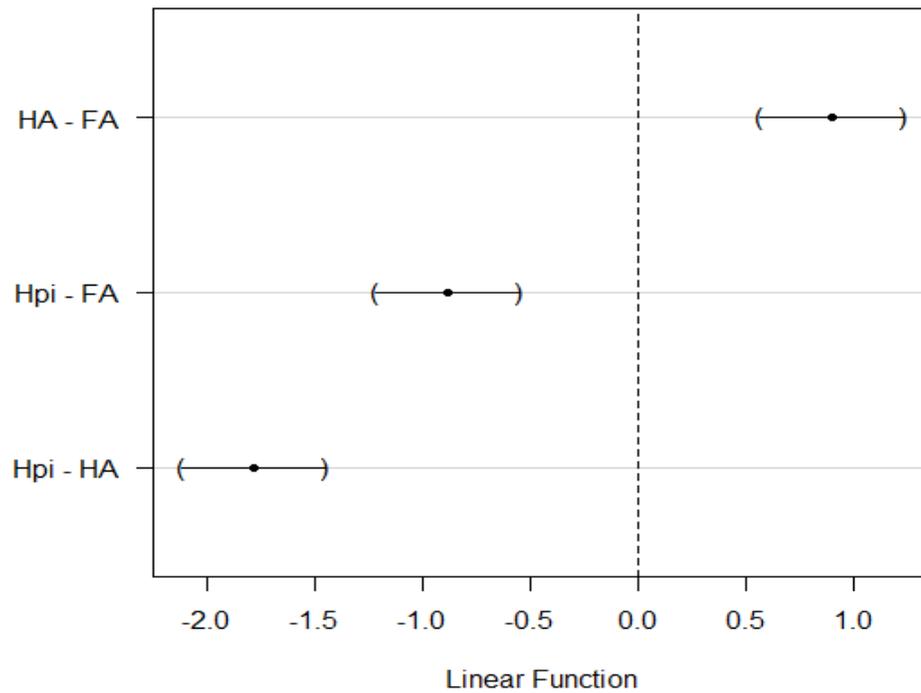
Error: Leachate:Fraction

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Fraction	2	12.745	6.373	78.72	2.42e-08 ***
Residuals	14	1.133	0.081		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
> am2 <- lme(SUVA ~ Fraction, random = ~1|Leachate/Fraction, data=mydata)
> x <- glht(am2,linfct=mcp(Fraction="Tukey"))
> plot(x)
```

95% family-wise confidence level



SF 1: Multiple comparisons of SUVA₂₅₄ values among the leachate fractions

4. Statistical analysis of the TOC percent < 1 kDa for the leachate fractions (Table 3-4)

p value (probability level) for the repeated measure multivariate ANOVA test with null hypothesis that the mean TOC percent < 1kDa values for the HA, FA and Hpi fractions were equal is 0.000949. Under the confidence level of $\alpha = 0.05$, the null hypothesis was rejected and the alternate hypothesis that the mean TOC percent < 1 kDa for atleast one of the fractions was different was accepted. Then a general linear hypothesis testing model was used to perform multiple comparisons between the TOC percent < 1 kDa values of the leachate fractions using the Tukey's all pair comparison. From SF 2, the order of the TOC percent < 1 kDa for the leachate fractions followed: Hpi>FA>HA. Statistics analysis was conducted with R language.

R code:-

```
> TOCpercent <- c(17.78,29.54,67.93,23.03,33.74,67.44,39.12,63.54,68.02,37.43,48.28,73.66)
> Leachate <-
c("PAr","PAr","PAr","PAt","PAt","PAt","NHr","NHr","NHr","NHt","NHt","NHt")
> Fraction <- c("HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi","HA","FA","Hpi")
> means.Fraction <- tapply(TOCpercent, Fraction, mean, na.rm = TRUE)
> residuals <- TOCpercent-means.Fraction[Fraction]
> shapiro.test(residuals)
```

Shapiro-Wilk normality test

data: residuals

W = 0.9681, p-value = 0.8895

```
> mydata <- data.frame(TOCpercent,Leachate,Fraction)
> y <- aov(TOCpercent ~ Fraction + Error(Leachate/Fraction), data=mydata)
> summary(y)
```

Error: Leachate

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Residuals	3	718.6	239.5		

Error: Leachate:Fraction

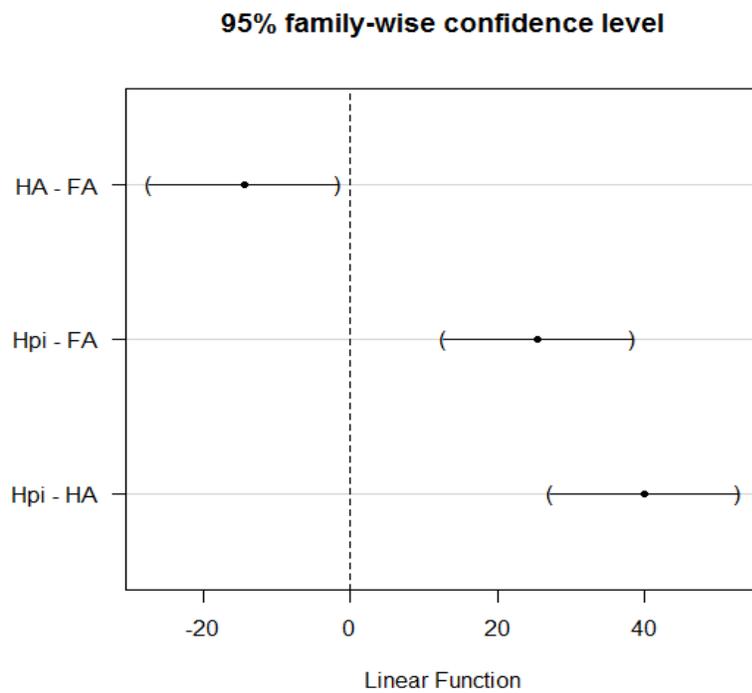
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Fraction	2	3269	1634.5	27.53	0.000949 ***
Residuals	6	356	59.4		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```
> am2 <- lme(TOCpercent ~ Fraction, random = ~1|Leachate/Fraction, data=mydata)
```

```
> x <- glht(am2, linfct=mcp(Fraction="Tukey"))
```

```
> plot(x)
```



SF 2: Multiple comparisons of TOC percent < 1 kDa values among the leachate fractions