Treatment of Landfill Leachates for removing organic matter, UV quenching substances and organic nitrogen using Anion Exchange Resins

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Abstract

Landfill leachates are often discharged to wastewater treatment plants (WWTPs) but their highly varied composition makes their treatment in WWTPs difficult. Landfill leachates contain bio-refractory organic matter which easily passes the biological treatment processes at WWTPs and increases the organic matter in the effluent. Leachates also interfere with the UV disinfection process at treatment plants. Another concern is the presence of large amounts of bio-refractory organic nitrogen in the leachates which makes it difficult for WWTPs to meet the tightening total nitrogen requirements.

Studies were conducted to evaluate the applicability of anion exchange resins to remove organic matter, UV quenching substance and organic nitrogen from landfill leachates. Leachate samples based on varying age and treatment methods were utilized. The anion exchange resins were found to work effectively for all studied leachates. The resins were found to remove more bio-refractory UV absorbing substances as compared to total organic carbon (TOC), suggesting that anion exchange resins could be employed for removal of UV absorbing substances. Multiple regenerations of the resin showed slight loss in the capacity to remove UV and organic carbon. Fractionation of leachate samples showed effective removal of humic acid (HA) fraction which is responsible for most of UV quenching. The resin was also found to effectively remove the bio-refractory hydrophilic (Hpi) fraction which tends to persist even after HA fraction has bio-degraded. Membrane filtration (1000 Da and 3000 Da Molecular weight cut off) in conjunction with ion exchange resins achieved better removal of organic matter and UV_{254} absorbing substances. In addition, this also significantly improved the performance of resins. Significant removal of organic nitrogen was also observed using anion exchange though it was less than both UV and TOC. Around 80% removal of organic nitrogen associated with bio-refractory Hpi fraction was achieved using anion exchange suggesting ion exchange as a viable alternative for removing organic nitrogen.

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Chapter1. Introduction

In both the industrialized and developing countries, large amounts of solid wastes are generated daily. As an economical and cost effective method, landfilling is a preferred mechanism over other options such as reuse by recycling, incineration and composting for disposal of industrial and municipal solid wastes (MSW) generated by the increasing population (Ahmed and Lan, 2012). Apart from its economical advantages, landfills also minimizes the enviromnetal risks associated with solid waste disposal and provides controlled conditions for the decomposition of waste into relatively inert and stabilized material (Robinson and Marris, 1983).

One of the main environmental problems associated with landfills is the production of leachates. When the rainwater percolates in a landfill, the liquid medium comes in contact with decomposing solid waste and solubilizes nutrients and contaminants. This highly polluted stream of liquid is referred to as "leachates" (Mariam and Nghiem, 2010). The composition of leachate varies greatly from one landfill to another and also over time in a particular landfill (Baig et al., 1999). These variations can be due to variety of factors such as type of waste accepted, landfill environment, filling technique, etc. Despite these variations, the general composition of leachate may include large amounts of organic matter, ammonia – nitrogen, inorganic salts, and some amounts of chlorinated organic salts and heavy metals (Renou et al., 2008). The presence of these toxic and/or recalcitrant compounds in leachates presents problems in their direct disposal to natural water bodies or if they infiltrate into groundwater.

Due to considerable difference between characteristic of domestic wastewater and leachates, it is necessary to pre-treat the leachates before their disposal to treatment plants so that they do not adversely impact the biological treatment process at WWTPs. The most economical and commonly practiced treatment method is the discharge of pre-treated leachate into sewers which flow to wastewater treatment plants (WWTPs). Alternativiely, the pretreated leachate is hauled by tank truck to the final treatment facility.

Owing to its relatively low cost, biological treatment is initially used to remove the readily biodegradable organic matter from leachates. For younger leachates (< 5 years old) (Rodriguez et al., 2004; Bashir et al., 2010a) biological treatment is particularly effective as the bulk of organics have high volatile fatty acids (VFA's) which are readily biodegradible (Trebouet et al., 2001). But, this becomes difficult for stabilized leachates due to the presence of refractory organic material which are often comprised of humic and fulvic acids (He et al., 2006; Bashir et al., 2010a). Also it has been observed that after biological treatment (Mejbri et al., 1995) and long term landfilling (Chian, 1977), there is an increase in 500 – 1000 MW bio-refractory fulvic substances indicating the degradation of humic acids into fulvic acids. These recalcitrant substances can easily pass the biological treatment operation at WWTP's and increase the organic matter in the effluent (Zhao et al., 2012).

Another concern is the presence of UV absorbing substances in leachates. The WWTPs often need to disinfect the effluent wastewater before discharging them to surface water sources. Generally, chemical disinfectants such as chlorine have been used for disinfection. But the increased awareness regarding the various disadvantages associated with using chlorine based disinfectant, such as, potential for disinfectant by product (DBP) formation which are carcinogenic in nature have encouraged the WWTPs to shift to UV as a means of disinfection. Recently, it was established that landfill leachates tend to inhibit the performance of UV disinfection systems at WWTP's (Zhao et al., 2012). It has also been reported that biological processes were effective in removing organic carbon but were unable to remove the bulk of UV absorbing substances (Zhao et al., 2013). Thus, physical chemical processes are also often employed in conjunction with biological processes for the treatment of leachates (Deng and Englehardt, 2006). These processes are generally comprised of coagulation/flocculation (Ghafari et al., 2010), activated carbon adsorption (Foo et al., 2009), chemical oxidation (Altin, 2008), membrane filtration (Trebouet et al., 2001) and ion exchange (Bashir et al., 2010a).

In recent years, regulatory agencies have proposed stricter discharge limits on the total nitrogen in the effluent from WWTPs. Organic nitrogen has been identified as a significant component of total nitrogen in wastewater effluents. The use of nitrification – denitrification systems at many WWTPs have been found to increase the organic nitrogen concentration in the effluent (Pehlivanoglu-Mantas and Sedlak, 2008). Organic nitrogen can be a source of potentially carcinogenic nitrogenous disinfection by products (N-DBP's) thereby adversely affecting the reuse of the effluent wastewater.

Landfill leachates generally contain large amounts of organic nitrogen and can be the major source of organic nitrogen in WWTPs (Zhao et al., 2012) which may not be removed completely in the WWTPs. Also, the organic nitrogen is more bio-refractory than the organic carbon (Zhao et al., 2012) and cannot be removed effectively by the biological processes alone. Various size distribution studies have been conducted and it has been found that the bulk of organic nitrogen has a molecular weight less than 1000 Da (Parkin and McCarty, 1981; Zhao et al., 2012; Pehlivanoglu and Sedlak, 2008). Therefore, membrane filtration might be utilized but it may not be entirely efficient due to fouling problems caused by organic matter (Kweon and Lawler, 2005).

The ion exchange mechanism has been known to remove humic and fulvic substances (Fettig et al.,1999) but their practical application has been limited to their use for removing metal ions from water and wastewater (Kurniawan et al., 2006). For landfill leachates as well, they have been mostly used as a polishing step to remove inorganic anions and heavy metals (Primo et al., 2009; Bashir et al., 2010b). There is very limited literature regarding their use for removing organic matter from leachates. But, recently a few studies have focussed on the successful use of anion exchange resins to remove non biodegradable organic matter from leachates (Bashir et al., 2010a; Boyer et al., 2011).

This study aimed at studying the applicability of anion exchange resins to remove organic matter, UV quenching substances and organic nitrogen from landfill leachates. The performance of resins for treating leachates was evaluated based on their ability to reduce UV_{254} , total organic carbon (TOC) and organic nitrogen from the leachates.

In Chapter 3, three anion exchange resins Dowex Marathon MSA, Dowex Marathon 11, and Dowex TAN1 were used for treatment of landfill leachate from a Pennsylvania landfill. Kinetic studies were conducted with the three resins and it was found that 30 minutes of effective contact time was sufficient to achieve equilibrium for total organic carbon (TOC) and UV_{254} removal. Isotherms showed TAN1 to have highest resin capacity and solute affinity but the percentage removal of TOC and UV_{254} suggested that both TAN1 and MSA perform in similar manner. Dowex 11 performed poorly relative to other two resins both in terms of TOC and UV_{254} removal. Also, the competing effect of inorganic anions such as nitrate on the removal of organic matter for the three anion exchange resins was investigated. The leachate sample was spiked with different nitrate concentrations but no adverse effect on the removal of TOC and UV_{254} absorbance was observed at the highest nitrate nitrogen concentration of 156 mg/L.

In Chapter 4, leachate samples with ages of 2 and 16 years from Kentucky landfill and a biologically treated leachate from Pennsylvania (PA) landfill were utilized to identify if different leachate properties affect the resins. All resins were found to remove more UV absorbing substances as compared to TOC suggesting that anion exchange resins could be employed for removal of UV absorbing substances. Resins could be effectively regenerated although some loss in the resin capacity was observed. Fractionation of leachate samples into humic acid (HA), fulvic acid (FA) and hydrophilic fraction (Hpi) revealed that with increasing regenerations the capacity of resin to remove the FA fraction is negatively impacted. The resin was able to consistently remove the HA fraction which is responsible for bulk of UV quenching. The resin was also found to effectively remove the bio-refractory Hpi fraction which tends to persist even after HA fraction has bio-degraded. Membrane filtration in conjunction with anion exchange resins was also employed and it was observed that this significantly improves the performance of resins to remove both the UV absorbing substances and TOC. It was also observed that out of the three studied resins (Dowex 11, Dowex MSA and Dowex TAN1), Dowex 11 seemed to be getting fouled by the HA and FA fractions suggesting its suitability for samples with less HA and FA fractions. Dowex TAN1 and MSA were able to effectively treat all leachates, irrespective of their origin.

In Chapter 5, anion exchange resins, Dowex TAN1 and MSA were evaluated for their ability to remove organic nitrogen from leachates. Two leachate samples with different stabilization stages (young and old) from a Kentucky landfill and a biologically treated leachate from Pennsylvania landfill were utilized for this study. Both TAN1 and MSA performed similarly and were found to remove more than 50% organic nitrogen at a batch resin dose of 200g/L. Regenerations conducted with the resins showed slight variability in the removal data. Fractionation of PA leachate into humic acid (HA), fulvic acid (FA) and hydrophilic (Hpi) fractions showed around 80% removal of bio-refractory Hpi fraction using anion exchange. Also, the organic nitrogen associated with HA fraction constituted the smallest fraction and had the greatest difficulty in its removal using anion exchange. Membrane filtration using 1000 and 3000 Da Molecular weight cutoff (MWCO) was performed on the leachate samples. For biologically treated leachate, almost all the organic nitrogen was < 1000 Da suggesting that membrane filtration may not be useful for this leachate. But for young leachate substantial removal was observed after membrane filtration which further enhanced the performance of anion exchange resins.

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Chapter 2. Literature Review

2.1 Leachate characteristics

Leachate is defined as high strength wastewater which is produced when the rainwater percolating down the landfill comes in contact with the degrading solid waste. The process results in solubilization of contaminants and nutrients from the solid waste into the percolating rainwater (Kurniawan et al., 2006). The composition of leachate generally varies depending on various factors such as type of waste discharged to the landfill, climatic conditions, site hydrology, etc. But, it is well accepted that leachates present serious threat to the natural environment. Many studies have confirmed the potential dangers associated with leachates due to their toxic effects (Clement et al., 1997; Crawford and Smith, 1986). Leachate treatment therefore is essential before it can be discharged to the natural water bodies.

Apart from the physical and chemical properties of the leachate, the amount of leachate generated from a landfill is also essential in determining the adequate treatment process. Though leachate production is influenced by the inherent water content of wastes, there is a direct relation between the quantity of leachate produced and the amount of external water going in the landfill. In general, the various components that lead to leachate generation are precipitation and surface runoff. In addition, physical characteristics of the landfill such as filling technique also affect the leachate production. Less compacted waste results in higher leachate production (Lema et al., 1988).

Some of the parameters often used to characterize leachates are biological oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), ratio of BOD/COD, pH, suspended solids (SS), Total suspended solids (TSS), ammonia nitrogen, total nitrogen, heavy metals, etc. The age of landfill greatly affects the quality of leachate (Kjeldsen et al., 2002; Chian and DeWalle, 1976). In the initial years (< 5 years), the leachate is characterized as young (Amokrane et al., 1997) and possesses higher amounts of biodegradable organic matter (Trebouet et al., 2001). During this phase, the leachate has considerably high amounts of BOD, COD, and low ammonia nitrogen (Ehrig, 1998). Leachates produced from landfills that have been operating for more than 10 years are characterized as old or stabilized (Mavinic, 1988). Old leachates have considerably lower values of BOD, COD and high ammonia nitrogen. The organic fraction in old leachate is majorly composed of non-biodegradable organic compounds (Chian and DeWalle, 1976) with very low BOD/COD values (<0.1). Moreover, the pH of leachate generally increases as the leachate becomes more stabilized. This clearly indicates that a single treatment method will not be an effective solution as the properties of leachate change depending on the age of landfill and hence, combined treatment options should be evaluated to achieve suitable treatment.

2.2 Fractionation

Fractionation of leachates into respective components has generally been done using size based or hydrophobicity based fraction.

2.2.1 Hydrophobicity Based fractionation

The organic component of leachate can be separated into hydrophilic and hydrophobic fractions. These fractions can be further separated into their acid, base and neutral fractions (Leenher, 1981).

The hydrophilic fraction generally comprises of low molecular weight alcohols and organic acids. The hydrophobic fraction can be separated into two other fractions based on their molecular weights – Fulvic acids (medium molecular weight) (Tan, 2003) and humic acids (high molecular weight). The separation of leachate samples into humic acids, fulvic acids and hydrophilic fractions is done in accordance with the methods proposed by Thurman and Malcolm (1981) and Leenheer (1981). Humic acids are collected by acidifying the solution to pH 2. The humic acids precipitate out of the solution after which the supernatant is passed through XAD-8 non-ionic resin which sorbs the fulvic acids. The remaining solution that passes through the XAD-8 resin is termed as hydrophilic fraction (Christensen et al., 1998).

The humic acids and fulvic acids are often together termed as humic substances. Thurman and Malcolm (1981) reported that humic substances comprised around 50-90% of dissolved organic carbon present in the leachate. Lou et al., (2009) also found the hydrophobic fraction (humic substances) was the major fraction and constituted more than 50% of the leachate. Chian (1977) also reported an increase in the 500-1000 MW fulvic substances after the long term landfilling. This is in agreement with the widely accepted fact that the humic substances are bio-refractory in nature (Poblete et al., 2011) and can easily pass the biological treatment operations in wastewater treatment plants (Zhao et al., 2012).

2.2.1 Size Based fractionation

Various size fractionation studies have been conducted to characterize the organics in landfill leachates (Lou et al., 2009; Slater et al., 1985; Li et al., 2009). It was found that up to 50% of organic fraction in terms of COD was less than 1k Da fraction. Other studies have demonstrated that approximately 47% - 92% of organics in terms of TOC was less than 1k Da. This is of considerable importance because of the difficulty in removing the smaller weight molecular fractions (Zhao et al., 2012).

He et al., (2006) conducted size fractionation studies on the fractions separated based on hydrophobicity. It was reported that the humic acid fraction generally comprises of large molecules which are greater than 10k Da.

In recent years, regulatory agencies have proposed stricter discharge limits on the total nitrogen in the effluent from wastewater treatment plants (WWTPs). Organic nitrogen has been identified as a significant component of total nitrogen in wastewater effluents. The use of nitrification – denitrification systems at many WWTPs have been found to increase the organic nitrogen concentration in the effluent (Pehlivanoglu-Mantas and Sedlak, 2008). Organic nitrogen fractions as high as 80% of total nitrogen have been reported (Qasim et al., 1999).

Organic nitrogen can be a source of potentially carcinogenic nitrogenous disinfection by products (N-DBP's) thereby adversely affecting the reuse of the effluent wastewater. It may also be responsible for eutrophication (Pehlivanoglu and Sedlak, 2004), posing a problem in the disposal of effluent wastewater to the surface water-bodies.

Landfill leachates generally contain large amounts of organic nitrogen (30 – 200 mg/L-N) and can be the major source of organic nitrogen in WWTPs (Zhao et al., 2012) which may not be removed completely in the WWTPs. Also, the organic nitrogen is more bio-refractory than the organic carbon (Zhao et al., 2012) and cannot be removed effectively by the biological processes alone. Efforts have been made to identify the composition of organic nitrogen but most of the wastewater derived organic nitrogen (70%) still remains unknown (Pehlivanoglu and Sedlak, 2008). Hydrophobicity based studies have revealed the bulk of organic nitrogen to be hydrophilic in nature (Zhao et al., 2013). Various size distribution studies have been conducted and it has been found that bulk of organic nitrogen have molecular weight less than 1k Da (Parkin and McCarty, 1981; Zhao et al., 2012; Pehlivanoglu and Sedlak, 2008).

Recently, it was reported that landfill leachates discharged to WWTPs adversely affect their UV disinfection system (Zhao et al., 2012). The WWTPs often need to disinfect the effluent wastewater before discharge to surface waters. Generally, chemical disinfectants such as chlorine have been used for disinfection. But the increased awareness regarding the various disadvantages associated with using chlorine based disinfectant (Wu et al., 2003; Zhang et al., 2005), such as, potential for disinfectant by product (DBP) formation which are carcinogenic in nature (Nikolaou, et al., 2004) have encouraged the WWTPs to shift to UV as a means of disinfection. More than 2000 UV systems are in operation at various WWTPs in United States and Canada. The germicidal wavelength used for the disinfection is at 254nm due to the ease of production (Tchobanoglous et al., 2004).

Leachate Treatment

Some of the widely used leachate treatment methods are described below:

Natural Leachate treatment systems

Typical natural systems for leachate treatment include leachate recirculation, wetlands, and aquatic systems. Recirculating leachate back in the landfill is one of the least expensive methods (Lema et al., 1988). The stabilization time is greatly reduced (from 15-20 years to 2-3 years) in case of re-circulated leachate (Pohland and Harper, 1985). Rodriguez et al. (2004) showed around 70% decrease using recirculation in an anaerobic pilot plant. But, the limitation of this is that due to continuous recirculation, the landfill becomes saturated and excess leachate flow needs to be removed separately (Strachan et al., 2000).

Co-treatment with Municipal Wastewater

This was a preferred method of disposal of leachate due to its relatively low operating cost and the ease of operation (Ahn et al., 2002). But, the presence of high amounts of refractory organics and heavy metals in the leachate tends to affect the biological processes in the WWTPs (Cecen and Atkas, 2004). The advantage of co treatment of leachate with sewage is that leachate contains excess nitrogen whereas sewage contains excess phosphorous which eliminates the need for nutrient addition.

Biological treatment

Biological treatment of leachate is commonly used as a first treatment step due to its simplicity and cost-effectiveness (Renou et al., 2008). The microbial population degrades the organics to carbon di-oxide under aerobic conditions and biogas under anaerobic conditions (Lema et al., 1988). Biological treatment is very effective in removing organic and nitrogenous matter in young leachate with high BOD/COD ratio. Aerobic processes such as sequencing batch reactor are often suited for nitrification/denitrification processes (Diamadopoulos et al., 1997) and have been shown to achieve up to 75% COD removals and 99% NH_4^+ - N removals (Lo, 1996). The disadvantage of aerobic processes is that they are very energy intensive and produce large quantities of sludge. Anaerobic processes on the other hand conserve energy by producing biogas and less sludge but are usually very slow (Berrueta and Castrillon, 1992). Up to 95% BOD removal and 75% COD removal was obtained in an up-flow anaerobic sludge blanket reactor (UASB) for the treatment of municipal landfill leachate (Kettunen and Rintala, 1998).

The use of biological processes becomes relatively difficult for stabilized leachates due to the presence of bio-refractory humic substances (Bashir et al., 2010). Moreover, for young leachates as well, the biological treatment does not meet the permitted discharge limits (Kurniawan et al., 2006). Therefore, necessary pre and post treatment steps are often carried out using physical chemical methods to remove the residual organics.

Physical – Chemical Treatment

Due to inadequacy of biological processes to remove the organic pollutants to the desired extent, they are often used in conjunction with the physical/chemical treatment processes either as pre or post treatment option (Deng and Englehardt, 2006).

Various physical/chemical treatment processes that have been successfully utilized for leachates are coagulation/flocculation (Ghafari et al., 2010), activated carbon adsorption (Foo et al., 2009), chemical oxidation (Altin et al., 2008; Qureshi et al., 2002), Air stripping (Cheung et al, 1997), membrane filtration (Trebouet et al., 2001; Bohdziewicz et al., 2001) and ion exchange (Bashir et al., 2010).

Coagulation/flocculation has proven to be effective in treatment of non-bidegradable fractions in stabilized leachates (Urase et al., 1997). Zouboulis et al (2004) reported around 85% removal of humic acids using 20mg/L biofloculant dosage. The disadvantage associated with this is the high volume of sludge production.

The Adsorption using activated carbon has been found to achieve more COD removal than the chemical methods but the need for frequent regeneration makes it difficult to use (Renou et al., 2008). Hence, it is often used along with biological treatment (Morawe et al., 1995; Cecen et al., 2003). In a study conducted by Fettig et al. (1996), leachate samples were first ozonated and then subjected to adsorption in activated carbon columns. It was found that biodegradation took place inside the columns achieving more removal than the adsorption process alone.

Air Stripping has been used mainly for the removal of high concentration of ammonia nitrogen which can otherwise increase the toxicity of wastewaters (Marttinen et al., 2002). Ozturk et al., (2003) achieved 85% ammonia nitrogen removal whereas in a separate study conducted by Silva et al. (2004), 99.5% removal was observed. The main disadvantage of this process is the release of ammonia in the atmosphere which causes air pollution. Another operational issue is the adjustment of pH for the ammonia stripping to work.

The ion exchange mechanism has been known to remove humic and fulvic substances (Fettig et al.,1999) but their practical application has been limited to their use for removing metal ions from water and wastewater (Lin et al., 2008; Kurniawan et al., 2006). For landfill leachates as well, they have mostly been used as a polishing step. Primo et al., (2009) used anion exchange resins for removing nitrate ions from landfill leachate. Majone et al., (1998) successfully employed ion exchange for removing Cd (II) and Ni (II) from leachate, but, there has been limited use of ion exchange for removing non biodegradable organic compounds from leachates. Bashir et al., (2010) utilized anion exchnage resins for removing organic matter from stabilized leachates and achieved more than 90% color removal and 70% COD removal. Boyer et al., (2011) also utilized MIEX resins for removing the non biodegradable organic matter and achieved around 50% UV_{254} removal and 35% DOC removal.

With the hardening of discharge standards the conventional methods such as biological or physical-chemical do not perform satisfactorily and hence more effective methods are being sought. Membrane filtration proves to be a good alternative in that regard. The various membrane processes can be categorized as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO). Use of microfiltration is limited to removing suspended solids or as a prefiltration stage for other membrane processes. Ultrafiltration can remove maromolecules and has been effectively utilized in various leachate treatment studies. COD removals in the range of 60-70% have been observed using ultrafiltration (Marttinen et al., 2002; Trebouet et al., 2001). Reverse osmosis have shown to achieve around 98% removal of COD and 99% removal of heavy metals. But, the disadvantage of membrane treatment systems are its susceptibilty to fouling and problems in removing ammonia at elevated water temperatures. Fouling of membranes increases the osmotic pressure thereby increasing the energy uptake for the same removal. In general, ultrafiltration is performed as a pretreatment step to prevent the RO membranes from fouling and thereby increasing their life. In general, membrane treatment is a costly process and often combined with biological and physical-chemical processes. Pirbazari et al. (1996) employed the combination of adsorption and membrane process and achieved 97% COD removal.

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Chapter 3. Treatment of Landfill Leachate with Anion Exchange Resins

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3.1 Abstract

In this study, three anion exchange resins Dowex Marathon MSA, Dowex Marathon 11, and Dowex TAN1 were used for treatment of landfill leachate from a Pennsylvania landfill. Kinetic studies were conducted with the three resins and it was found that 30 minutes of effective contact time was sufficient to achieve equilibrium for total organic carbon (TOC) and UV_{254} removal. Isotherms showed TAN1 to have highest resin capacity and solute affinity but the percentage removal of TOC and UV_{254} suggested that both TAN1 and MSA perform in similar manner. Dowex 11 performed poorly relative to other two resins both in terms of TOC and UV_{254} removal. Multiple regenerations followed by column studies confirmed that the resin after repeated regeneration deteriorates slightly. Also, the competing effect of inorganic anions such as nitrate on the removal of organic matter for the three anion exchange resins was investigated. The leachate sample was spiked with different nitrate concentrations but no adverse effect on the removal of TOC and UV_{254} absorbance was observed at the highest nitrate nitrogen concentration of 156 mg/L.

Keywords: Landfill Leachate Treatment, Anion Exchange Resins, Regeneration, UV disinfection, Adsorption

3.2 Introduction

Municipal solid waste generation has increased continuously over the years. Methods such as incineration, composting and landfilling have been used for solid waste disposal. Due to its economic advantages, landfilling continues to be the most widely accepted and used method for disposal of MSW in many countries (Rodriguez et al., 2004). Disposal of the wastes in landfills minimizes the adverse environmental impacts associated with solid waste and provides controlled conditions for their decomposition (Robinson et al., 1983).

The rainwater and moisture percolating down through the landfill in combination with decomposing MSW produces a highly polluted form of wastewater referred to as "leachate" (Kurniawan et al., 2006). The leachates contain large amounts of organic matter, heavy metals, chlorinated organics, inorganic salts and other toxic materials that may have leached from the decomposing waste (Li et al., 2009). Thus they pose a hazard for the receiving water bodies. It is therefore imperative to treat the leachates before discharging them into the natural water bodies. The preferred method of disposal of leachate is discharging into waste water treatment plants (WWTP's). But due to considerable difference between composition of leachate and domestic wastewater, it is necessary to pre-treat the leachates so that they do not adversely impact the biological treatment process at WWTPs.

Various treatment techniques employed for water and waste water have been utilized for treating leachates. Of these, biological treatment is considered as the preferred method due to its cost effectiveness (Zhao et al., 2012). But, biological treatment is problematic for stabilized leachates because of the presence of refractory organic matter (Read et al., 2001). Also, the refractory organic matter remaining after biological treatment of leachate may pass unaltered through the biological processes at WWTPs. Thus, physical chemical processes are also often employed in conjunction with biological processes for the treatment of leachates (Deng and Englehardt, 2006). These processes are generally comprised of coagulation/flocculation (Ghafari et al., 2010), activated carbon adsorption (Foo et al., 2009), chemical oxidation (Altin et al., 2008; Qureshi et al., 2002), membrane filtration (Trebouet et al., 2001; Tsilogeorgisa et al., 2008) and ion exchange (Bashir et al., 2010a).

Ion exchange resins have primarily been used for removing metal ions from water and wastewater (Bashir et al., 2010a). In recent years, ion exchange resins have been used to remove natural organic matter (NOM) from drinking water sources (Cornelissen et al., 2008). Additionally, they have also been found to remove natural and synthetic compounds having weak functional groups (Li and Sengupta, 2004). Bolto et al (2002) utilized 20 anion exchange resins to study the removal of NOM isolates. Their studies conducted with a dissolved organic carbon acid extract without a neutral fraction achieved 98-100% NOM removal. In principle ion exchange resins should be able to treat landfill leachates because they contain organic matter (both biodegradable as well as refractory). But, the use of ion exchange to treat leachates have been limited to removing NH_4^+ and NO_3^- (Boyer et al., 2011). To date there have been few studies conducted on the use of ion exchange resins for treating landfill leachate for removal of organic matter (Bashir et al., 2010b).

In this study, three different anion exchange resins were used for the treatment of landfill leachate for the removal of organic matter. The performance of the resins for treating landfill leachate was evaluated based on their ability to reduce UV_{254} and TOC from the leachate. The initial study consisted of identifying the effective contact time needed by the resins for treating leachate. Thereafter, the regeneration performance of the resin was studied in both batch and dynamic mode using column experiments to evaluate the efficacy of ion exchange method for treating leachate. Since landfill leachates contain high amounts of inorganic salts, the potential of nitrate to compete with the organic matter for exchange sites on the resin was also evaluated.

3.3 Materials and Methods

3.3.1 Leachate Sampling

The leachate samples that were used in this study were collected from an on-site MSW leachate treatment plant from Pennsylvania(PA), USA. The leachate treatment plant at the PA landfill performs nitrification/denitrification using a sequencing batch reactor activated sludge system with addition of methanol for denitrification. The plant has a daily capacity of 113.6 m^3

and HRT of 6-7 days. The leachate after treatment from the sequencing batch reactor is discharged through a sewer to a municipal wastewater treatment plant for further treatment.

The leachate samples were shipped in polyethylene containers directly from landfills to Virginia Tech where they were stored in the lab refrigerated at 4^{o}C to prevent microbial activity from affecting the samples. Before sampling, the leachate containers were shaken vigorously to resuspend the settled particles. Some characteristics of the PA leachate are listed in Table 3-1.

3.3.2 Ion Exchange Resins

Treatment of leachate was investigated using three different anion exchange resins manufactured by the Dow Chemical Company, Dowex Marathon MSA, Dowex Marathon 11, and Dowex TAN1. The resins used were those suggested by the manufacturer for the treatment of the leachate. The properties of these resins are listed in Table 3-2. The resins were rinsed with deionized (DI) water prior to their use.The regeneration of exhausted resins was carried out by mixing the resin in 5% NaCl solution (regenerant brine) for 180 minutes. The resin, prior to regeneration with regenerant brine, was washed with DI water to remove the traces of leachate that might be present on the resin. After the regeneration, the resin was again thoroughly washed with DI water to remove the regenerant brine.

3.3.3 Analytical Methods

All chemicals used in this experiment were of analytical grade. All the glassware used in this experiment were first detergent washed with water, rinsed, soaked in 10% nitric acid, rinsed with deionized water and baked at 450°C for 4 h. Characterization of untreated and treated leachates was done using various techniques. Total organic carbon (TOC) was analyzed using high temperature combustion with a TOC analyzer (TOC-5000A, Shimadzu, Japan). The ultraviolet absorbance at 254 nm (UV_{254} absorbance) was measured using a spectrophotometer (Beckman Coulter, Brea, CA). The pH of samples was measured using a pH meter (Model No. 910, Accumet, Cambridge, MA) with a pH probe (Model No. 13-620-287, Accumet, Petalinga Jaya, Malaysia). The specific UV absorbance at 254 nm ($SUVA_{254}$) has been calculated as $\{(UV_{254} \times 100)/TOC\}$. The nitrate concentration was determined by the dimethylphenol method (Hach Company, Loveland, CO) with the measurements being made by a spectrophotometer (DR 2800, Hach Company, Loveland, CO).

The leachate samples were microfiltered through a 1.5µm glass microfiber filters(42.5mm, Whatman 934-AH Glass Microfiber filters, GE Healthcare Biosciences Corp., Piscataway, NJ) to remove the suspended particles . The microfiltration was performed using 300 mL filtration cells (GELMAN, Ann Arber, MI) operating with a vaccuum pump.

3.3.4 Experimental Methods

Batch Studies

The batch experiments were carried out to investigate the ion exchange equilibrium by using varying resin concentration and 100 ml of leachate in 250 ml beakers. The beakers were stirred constantly during the experiments using a magnetic stir bar. Initial tests consisted of performing the kinetic studies to determine the optimal contact time needed by the resins. For these studies, an aliquot of sample was taken at specified intervals of 1, 5, 10, 20, 30, and 60 minutes and analyzed for both UV_{254} and TOC. Multiple regenerations of resin were also carried out and their treatment performance was evaluated to assess the loss in the removal capacity of the resin. Competitive adsorption between nitrate and organic matter was also studied by varying the nitrate - N concentration from 10 to 156 mg/L.

Column Studies

Column studies were conducted to determine the performance of resin in a dynamic mode. A 1.0 cm X 10 cm borosilicate glass column (Thomas Scientific, Swedesboro, NJ) was packed with 6 ml of resin and the leachate was fed from the top using a pump at a constant flow rate of 15 bed volumes per hour. The effluent solutions were collected and every 15 ml was analyzed to determine the residual concentration of both UV_{254} and TOC.

3.4 Results

3.3.1 Kinetic Studies

Figure 3 -1 (A) and (B) show the removal of UV_{254} and TOC with contact time, respectively, for PA leachate treated with 100 g/L Dowex Marathon MSA, Dowex 11, both 100 g/L and 150 g/L of Dowex TAN1. It was found that a contact time of 20-30 minutes was sufficient to achieve equilibrium for UV_{254} and TOC removal for all the three resins. Previously Dowex MSA and Dowex 11 have been utilized for treatment of raw waters (Humbert et al., 2005) and similar results were obtained with 30 minutes being observed as the effective contact time. It can also be observed that for all the three resins used, the TOC and UV_{254} absorbance decreased sharply in the initial few minutes (5 minutes). This was characterized by the steep slope of the curve and reflected a very rapid adsorption rate. From 5-30 minutes there was a gradual decrease which was characterized by a gentle slope of the curve. And after 30 minutes the system achieved equilibrium demonstrated by the nearly zero slope of the curve.

Nearly 50% TOC removal was observed for all the three resins after only 1 minute of contact time. After 30 minutes of contact time when equilibrium was achieved, the removal performance of the resins was TAN1 (80%), MSA (72%), and Dowex 11 (72%).

From Figure 3- 1(A), it can be seen that the UV removal performance of Dowex 11 was poorer than the other two resins. After 1 minute of contact time, the UV removal performance of

Dowex 11, MSA and TAN1 was 45%, 55% and 60%, respectively. After 30 minutes when steady state was achieved, Dowex 11 could achieve only 73% UV removal as compared to 92% and 89% for TAN1 and MSA, respectively.

$SUVA_{254}$ is a good predictor of the aromatic content of the dissolved organic matter (Weishar et al., 2003). The $SUVA_{254}$ value of the untreated leachate was 2.90 L/mg-m. It can be seen that $SUVA_{254}$ values were reduced by nearly 60% for both TAN1 ($SUVA_{254}$ = 1.08 L/mg-m) and MSA ($SUVA_{254}$ = 1.25 L/mg-m) after 30 minutes of contact time but no reduction was observed for Dowex11 ($SUVA_{254}$ =2.88 L/mg-m). This indicates the preference of TAN1 and MSA for the removal of organic matter with a high aromatic character and the inability of Dowex11 to remove organic matter with higher aromatic character.

Figure 3-1 also shows the kinetic removal of TOC and UV_{254} removal for different concentration of TAN1 resin. The comparison was made between 100 g/L and 150 g/L TAN1 to evaluate the behavior of resin at different concentration for the same mixing time. It can be seen that the TOC concentration decreased rapidly with time for the two resin concentrations. Also at a given mixing time, with increase in dosing, faster removal of both UV and TOC was observed. For example, in the initial 5 minutes – 90% UV and 82% TOC removal was achieved for 150 g/L as compared to 83% UV and 72% TOC removal for 100 g/L TAN1 resin.

3.3.2 Adsorption isotherm

Adsorption isotherms are used to describe the relationship between the amounts of organic matter (TOC) adsorbed on the resin and the equilibrium concentration of TOC in the leachate. Langmuir and Freundlich are the most commonly utilized adsorption isotherms. The Langmuir isotherm describes homogeneous, monolayer adsorption on the surface which has specific number of equal energy sites whereas the Freundlich isotherm is used to represent heterogeneous adsorption. Generally, the removal of natural organic matter by anion exchange resins is heterogeneous in nature (Cornelissen et al., 2008). Hence, Freundlich adsorption isotherm has been used to describe the removal of TOC by anion exchange resins. Mathematically it can be expressed as,

$$q_e = k_f C_e^{1/n}$$

Linearly, it can be expressed as,

$$\ln(q_e) = \ln(k_f) + 1/n \ln(C_e)$$

where, q_e (mg/g) is expressed as mass of TOC removed per mass of resin, C_e is the equilibrium concentration of TOC in the leachate and n and k_f are the Freundlich constants. K_f is an indicator of the adsorption capacity and in case of ion exchange resins reflect the resin capacity. n is an indicator of the strength of adsorption and here represents the solute affinity (Bassandeh et al, 2013). Higher k_f for a given n reflects higher resin capacity (Cornelissen et al, 2008). The value of the Freundlich parameters are listed in Table 3-3.

The higher k_f value of TAN1 showed that it had the highest exchange capacity followed by MSA and Dowex11. Generally a value of parameter n between 1 and 10 indicates favorable adsorption. It is worth noting that although TAN1 had the highest k_f value, it had a relatively low n value (less than 1) indicating that very low amount of organic matter per gram of resin is being removed and it is not a favorable adsorption. This can be attributed to a high initial TOC in the leachate samples. TOC adsorption isotherms for the three resins are presented in Figure 3-2.

Figure 3- 3(A) and (B) respectively, depict the percentage removal of UV and TOC achieved by these resins. It clearly indicates that performance of the resin to remove both UV and TOC follow the order TAN1> MSA> Dowex11. Despite the differences in capacity of TAN1 and MSA shown by the Freundlich isotherm parameters, the percentage removal achieved by TAN1 and MSA indicate that they behaved in similar manner. At the low resin dose of 50 g/L, there is marked difference in the UV removal capacity but as the resin dose increases, they start behaving similarly. A similar result was achieved for TOC removal. On the other hand, Dowex 11 behaved poorly relative to both TAN1 and MSA at all the resin concentrations.

3.3.3 Sequential Resin Treatment

From the isotherm parameters it is clear that TAN1 was the best resin with highest k_f and n values, but the percentage removal of TOC and UV absorbing substances indicated that there is some similarity in behaviour of TAN1 and MSA. The resin properties outlined in Table 2 indicated that TAN1 and MSA had similar physical properties with the only difference being in the total exchange capacity which was higher for MSA. Thus to assess if there is an observable difference in the behavior of these two resins or are they behaving in identical manner, sequential resin treatment was performed. Figure 3-4 represents the results of sequential resin treatment on the leachate. Dowex 11 was not included in this analysis. Here the leachate was first treated with either MSA or TAN1 and then the treated leachate was subjected to the other resin.

In Figure 3-4, the resin concentration of 50 g/L essentially implies that the leachate was first subjected to either 50 g/L TAN1 or MSA and the treated leachate was again subjected to 50 g/L of other resin. It was observed for both the UV and TOC removal that the leachate treatment by subjecting it to MSA first and then TAN1 and vice versa, have similar results. For 50 g/L resin concentration, MSA + TAN1 arrangement decreased the UV_{254} absorbance from 13.32 cm^{-1} to 0.809 cm^{-1}(93.9% removal) and TAN1 + MSA arrangement decreased it to 0.828cm^{-1} (93.8% removal). For higher resin concentration of 200 g/L, some variation is observed. MSA + TAN1 arrangement performed slightly better with final UV_{254} absorbance of 0.446 cm^{-1} (96.7% removal) whereas TAN1 + MSA had absorbance of 0.534 cm^{-1} (95.9 % removal). For organic matter removal, no observable difference was observed with 91.3% removal observed in both the cases at 200 g/L resin concentration.The performance in terms of UV absorbance can be construed to be slightly better for subjecting the leachate to MSA + TAN1 arrangement. Overall, it appears that both TAN1 and MSA behave in similar manner.

3.3.4 Regeneration

The ion exchange process is economically viable only if the resins could be effectively regenerated and they perform for long time without getting fouled. Since the leachate had really high concentration of organic matter, there were concerns regarding the effective regeneration of the resins.

In this regard, a number of regeneration cycles were performed and since the behavior of MSA and TAN1 was similar, only MSA was used for the 23 regenerations. Also, TAN1 resin beads deteriorated while stirring in batch experiments so MSA was selected for investigation into the regeneration potential. The regeneration cycles were conducted at a resin concentration of 50 g/L and the results are shown in Figure 3-5. It can be observed from Figure 3-5(A) that the UV_{254} absorbance of treated samples varies between $2cm^{-1}$ – $3cm^{-1}$. In terms of the percentage reduction of UV quenching substances, it varied from 76% – 86%. The trend shows that removal does not change much with number of regenerations. The initial three regenerations indicate a decrease in removal efficiency of the resin but afterwards the removal stabilizes with UV absorbance around 2.5 - $3cm^{-1}$. After the 10th, 16th and 18th regeneration cycle, the effective contact time between the resin and leachate was increased from 30 minutes to 90 minutes to assess effect of contact time on the removal efficiency. It was observed that the UV_{254} absorbance after the 10th, 16th and 18th regeneration was similar to the absorbance of the original resin. For all other regeneration cycles, the contact time between the resin and leachate was kept 30 minutes. It appears that as the number of regenerations increases, the contact time needed to achieve performances similar to the new resin also increases.

The organic matter removal also followed a similar trend as UV_{254} absorbance for the leachate as shown in Figure 3-5(B). The TOC value after the third regeneration was 148.35 mg/L as compared to 119.50 mg/L observed in the case of original resin. This resulted in decrease of organic matter removal from 73.8% to 68.2% after the third regeneration cycle. The initial few regeneration cycles indicate that the performance of the resin deteriorates somewhat after the initial usage. But, from 5th regeneration on, the TOC value stabilized and was typically observed to be in the range of 145.00 mg/L to 160.00 mg/L. The TOC value after the 23rd regeneration cycle was 152.90 mg/L or 67.2% removal of organic matter. Also, the TOC value after the 16th and 18th regeneration cycle was 142.9 mg/L and 146.9 mg/L respectively which are not similar to the TOC value observed after the use of original resin. This suggests that increasing the contact time from 30 minutes to 90 minutes has no effect on organic matter removal.

Thus, increasing the contact time improved the performance in terms of UV removal but had no effect on TOC removal suggesting that the removal mechanisms for UV and TOC removal are different. This also suggests that as the number of regeneration cycle increases, the adsorption of UV quenching substances on resin becomes slower.

3.3.5 Column Studies

Column experiments were conducted with Dowex MSA resin to assess the performance of resin under dynamic conditions. It was also used to assess conclusively if the resin over the number of regeneration has deteriorated in its capacity to remove the UV absorbing substances and TOC. MSA resin regenerated for 26th time in batch mode was compared with the new MSA resin. The results are shown in Figure 3-6. Figure 3-6(A) represents the UV_{254} of the column effluent in terms of the bed volume (BV). Figure 3-6(B) depicts a plot of the normalized TOC concentration in terms of C/C_o versus bed volume, where C represents the TOC value of the column effluent and C_o represents the TOC value of the column influent.

Both Figure 3-6(A) and 3-6(B) show that the performance of resin in removing UV and TOC decreased after repeated regenerations. It could be observed that for the new resin, the UV_{254} absorbance of column effluent starts plateauing at around 20 bed volumes and after 35 bed volumes the UV_{254} absorbance is around 0.64 cm^{-1}. This corresponds to the UV_{254} removal of around 95%. For the same bed volume the UV_{254} absorbance of column effluent for regenerated MSA (R26) was around 0.9 cm^{-1}. This corresponds to the UV_{254} removal of 93%. Thus, though the performance of resin decreases after repeated regenerations, it is still able to achieve satisfactory removal of UV quenching substances. Another observation that can be made is that the performance of resin in column mode for UV removal is much better than the performance in batch experiments as indicated by the low UV values of the column effluent.

For TOC removal also, there is a clear difference between the performance of new MSA and R26 MSA resin. After 35 bed volumes, the new resin achieved C/C_o of 0.41 which corresponds to 58% TOC removal. The regenerated resin (R26 MSA) treated 35 bed volumes after which it achieved the C/C_o of 0.5. This corresponds to the removal of 39%. Thus the decrease in the performance of resin to remove TOC is more pronounced than UV for the regenerated MSA resin in comparison to the new resin.

Ion exchange may be effective as a means of treatment because ion exchange is a reversible process. Once the resin is exhausted, it can theoretically be regenerated and restored to its initial ionic form. Ion exchange resins are expensive and thus their ability to be reused multiple times due to regeneration makes it a viable cost effective process. It can be observed above that in terms of UV_{254} removal which is one of a primary concern when disposing landfill leachate to treatment plants, after 35 BV there is very little difference in the performance of new (95% removal) and 26th time regenerated resin (93% removal). Though there is some drop in the performance of the new and the regenerated resin for removal of organic carbon, but this does not impact the resins' ability to remove UV absorbing organics. It has been found that landfill leachates adversely affect the UV operations at treatment plants (Zhao et. al, 2012) and hence, ion exchange which seems to be effectively regenerated provides a potentially cost effective means for removing UV absorbing organics from landfill leachates.

3.3.6 Competitive behavior of Nitrate on UV and TOC removal

Competitive removal of organic matter in the presence of NO_3^- was evaluated by TOC and UV_{254} removal. A comparison was performed using all three resins. The plots of UV_{254} and TOC removal for different nitrate concentrations are shown in Figure 3-7 (A) and (B) respectively. The leachate sample had an initial NO_3^--N concentration of 10 mg/L and it was further spiked to achieve total NO_3^--N concentrations of 60 mg/L and 156 mg/L. The resin concentration of 50 g/L was used in all the cases and conditions were kept identical to earlier batch experiments. It can be seen from Figure 3-7(A) that the removal performance of UV quenching substances for all three resins is not impacted by the increasing NO_3^--N concentrations. Similar behavior is observed in case of TOC removal as shown in Figure 3-7(B). This indicates that presence of high concentrations of NO_3^- does not impact the removal of organic matter and UV quenching substances. It appears that the resins are able to simultaneously remove organic matter, UV quenching substances and NO_3^-.

Table 3-4 highlights the NO_3^--N concentration remaining after the resin treatment for all three resins. It shows that significant NO_3^--N removal was observed in all cases. At the highest studied NO_3^--N concentration of 156 mg/L, the resins decreased the concentration to 29.8, 49.8 and 30.1 mg/L for MSA, TAN1 and Dowex 11, respectively. This high percentage removal of NO_3^- even when no further reduction of organic matter or UV_{254} is observed suggests that there are still active exchange sites present on the resin to remove other anions.

Another observation is that though at very high NO_3^--N concentration, good NO_3^--N removal was observed. At low NO_3^- of 10 mg/L, complete removal of NO_3^--N could not be achieved. The nitrate N removal follows the order MSA= Dowex11 > TAN1.

It is also worth mentioning that the background sulfate concentration in the leachate was 76 mg/L. And although no experiment was conducted to ascertain the competing effect of sulfate ion, the removal observed at 50 g/L resin concentrations for MSA, TAN1 and Dowex 11 were 55%, 13% and 56% respectively. Thus, it appears that TAN1 had very little affinity for either nitrate or sulfate, suggesting that if in cases where there is competition observed, TAN1 should be preferred over MSA and Dowex 11.

3.5 Discussion

Anion exchange resins – Dowex Marathon 11, Dowex Marathon MSA and Dowex TAN1 were utilized for the treatment of leachate samples subjected to prior on-site biological treatment at the landfill facility in Pennsylvania.

Most of the work using ion exchange resin for landfill leachates have been based on their utilization for polishing steps such as for removal of heavy metals (Majone et al., 1998), ammonia (Lin and Wu, 1996) and NO_3^- (Primo et al., 2009). Boyer et al., (2011) utilized MIEX- Cl for treating leachates and achieved 34% dissolved organic carbon (DOC) removal and 57% UV_{254} removal at MIEX-Cl dosage of 40ml/L. Similar experiments conducted by Bashir et al., (2010) using anion exchange resin achieved around 90% color and 70% COD removal. In this study also, it was found that the resins could remove more than 90% UV_{254} removal and around 85% TOC at resin dosage of 200 g/L. Thus it is in agreement with some of the previous studies which suggest that ion exchange could be utilized for treatment of leachates. Kinetic studies conducted by Boyer et al., (2011) using MIEX- Cl found that steady state removal of DOM in leachates takes place after 20 minutes of contact time. Previously Humbert et al., (2005) utilized Dowex MSA and Dowex 11 for treating raw drinking water containing high amount of DOC and found the contact time of 30 minutes to be sufficient for achieving equilibrium DOC and UV_{254} removal. In our case as well, the resins after contact time of 30 minutes achieved equilibrium UV_{254} and TOC removal suggesting that contact time for resins is not affected by the type of influent to be treated.

It has been generally established that for UV disinfection in WWTPs to work properly, the minimum transmittance of the wastewater stream should be around 60% (Basu et al., 2007). Zhao et al., (2012) reported that the even 5 % leachate in mixed wastewater stream adversely affects the UV disinfection process at WWTPs. In another set of experiments performed by Zhao et al., (2013), it was observed that significant TOC removal was achieved after biological treatment but there was very little or no removal observed in case of UV_{254}. This concluded that the UV absorbing organic matter is different from TOC and is biologically recalcitrant. This study, however, establishes that ion exchange is very effective in removing the UV absorbing organics (>90% removal). Also it should be noted that for the untreated leachate to be discharged to the WWTPs, the mixed wastewater stream can contain maximum 1.7% of the leachate to meet the 60% UV transmittance requirement but after treatment with anion exchange resins the amount of leachate that can be discharged in the mixed wastewater stream significantly increases to 33% to meet the same requirement. This suggests that ion exchange could be used to treat only a portion of the leachate discharge to prevent quenching of UV light and can be tailored to the overall wastewater flow. When wastewater flow and dilution is high, the ion exchangers could be bypassed or receive a minimum amount of flow. When wastewater flow is low, the entire leachate discharge stream could be treated by ion exchange. This would extend the life of the resins and reduce costs.

It has been widely reported that inorganic anions compete with dissolved organic matter for exchange sites on anion exchange resins and can significantly impact the removal of organic matter (Tan and Kilduff, 2007). Though this has been established for use of anion exchange resins for surface water treatment, it is applicable to leachates as they often contain very high concentrations of inorganic anions. In this study the effect of competing anions on removal of organic matter was evaluated by taking nitrate as the surrogate parameter. It was observed that nitrate concentration as high as ≈ 150 mg/L did not adversely impact the TOC and UV_{254} removal. Moreover, significant nitrate removal along with organic matter was also observed. This could be attributed to the high concentration of organic matter in leachate which increases the effective force for displacement of inorganic anions.

3.6 Conclusions

Various anion exchange resins were evaluated for treatment of landfill leachate in terms of UV_{254} and TOC removal. Equilibrium removal of organic matter and UV quenching substances was achieved after 30 minutes of contact. More than 60% removal of UV_{254} and TOC was observed after 5 minutes of contact time. Dowex 11 performed poorly both in terms of UV and

TOC removal. TAN1 and MSA achieved better results and performed in similar manner. At the resin concentration of 200 g/L, TAN1 achieved 85% TOC and 95% UV removal. MSA at this dosage achieved 83% TOC and 94% UV removal. Dowex 11 could achieve only 77% TOC and 78% UV removal. Regeneration of MSA was carried out in batch experiments and it was found that there is some loss in the resin capacity after initial regenerations. It was also found that increasing the contact time from 30 minutes to 90 minutes after repeated regenerations help the resin achieve similar results as the new resin as far as UV removal is concerned. Increasing contact time has no effect on the performance of resin to remove TOC. Column studies conducted with new MSA and regenerated MSA (26th regeneration) confirmed the decreased capacity of the resin. The competition between organic matter and nitrate anion for the exchange sites on resins was investigated and it was found that presence of nitrate did not adversely affect organic matter removal for all the three resins. At the nitrate nitrogen concentration of 156 mg/L, same TOC and UV removal was observed as in the case of 10 mg/L nitrate nitrogen. Additionally, the anion exchange resins were found to significantly remove the nitrate nitrogen (80% for Dowex 11 and MSA, 68% for TAN1).

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Table 3- 1: Characteristics of PA Leachate

Parameters	Unit	Values
Total Organic Carbon (TOC)	mg/L	459.46 ± 55.04
UV_{254}	cm^{-1}	13.3
pH	-	8.70

Table 3- 2: Anion exchange resin properties

Resin Properties	Anion Exchange Resins		
	Dowex Marathon 11	Dowex Marathon MSA	Dowex TAN1
Type	Strong base anion exchange resin	Strong base anion exchange resin	Strong base anion exchange resin
Matrix	Styrene-DVB, Gel	Styrene-DVB, Macroporous	Styrene – DVB, Macroporous
Functional Group	Quaternary Amine	Quaternary Amine	Quaternary Amine
pH range	0 -14	0 - 14	0 - 14
Ionic form	Cl^-(supplied) ,OH^-	Cl^-(supplied) ,OH^-	Cl^-(supplied) ,OH^-
Recommended maximum operating temperature	60^o C for OH^- 100^o C for Cl^-	60^o C for OH^- 100^o C for Cl^-	60^o C for OH^- 100^o C for Cl^-
Mean particle Size (µm)	550 ± 50	640 ± 50	NA
Total exchange capacity (eq/l)	1.3	1.1	0.7

Table 3- 3: TOC Isotherm parameters for various resins

Resins	K_f(mg g^{-1})/(g L^{-1})	n	R^2
Dowex TAN1	0.09	0.4536	0.99
Dowex MSA	0.007	0.3361	0.9854
Dowex 11	0.0005	0.3053	0.9897

Table 3-4: Nitrate concentration remaining after treatment with 50 g/L resin concentration. The column heading indicates the initial nitrate- nitrogen concentration

Anion Exchange Resins	Nitrate N – 10 mg/L	Nitrate N – 60 mg/L	Nitrate N - 156 mg/L
MSA – 50 g/L	3.80	10.5	29.8
TAN1 – 50 g/L	4.27	17.2	49.8
DOWEX11 – 50 g/L	5.37	12.1	30.4

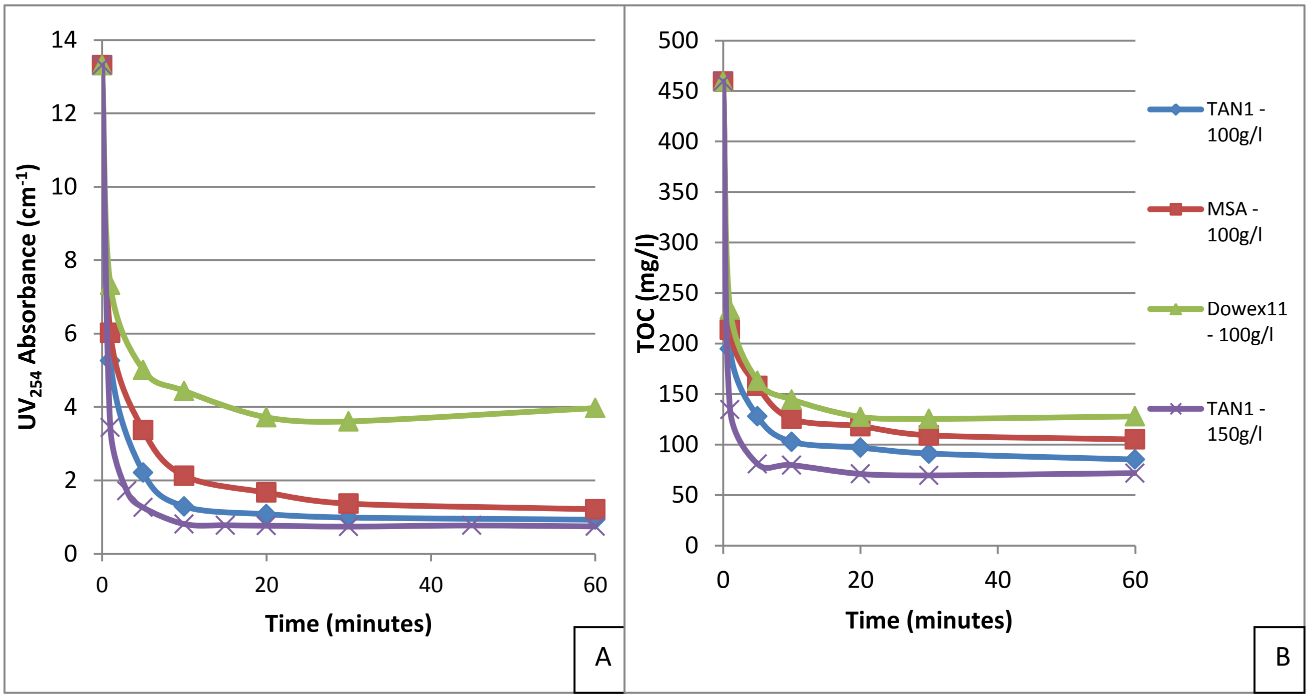

Figure 3- 1: Effect of Contact Time on (A) UV254 absorbance and (B) TOC removal for various resins

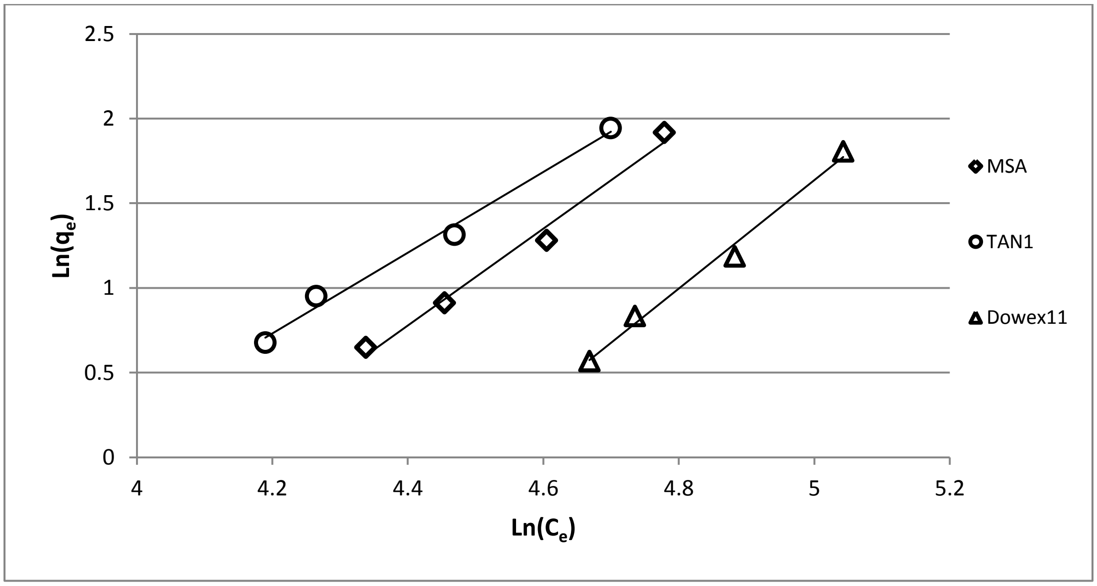

Figure 3- 2: TOC adsorption Isotherm for various resins

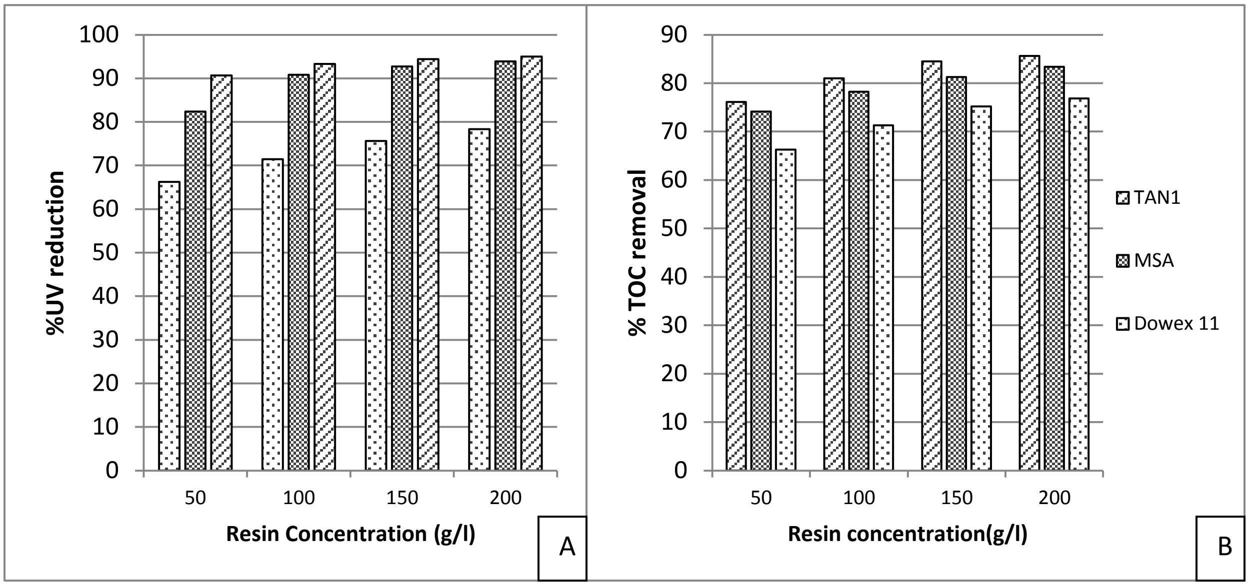

Figure 3- 3: Comparison of removal efficiency at various resin concentrations for (A) UV removal and (B) TOC removal

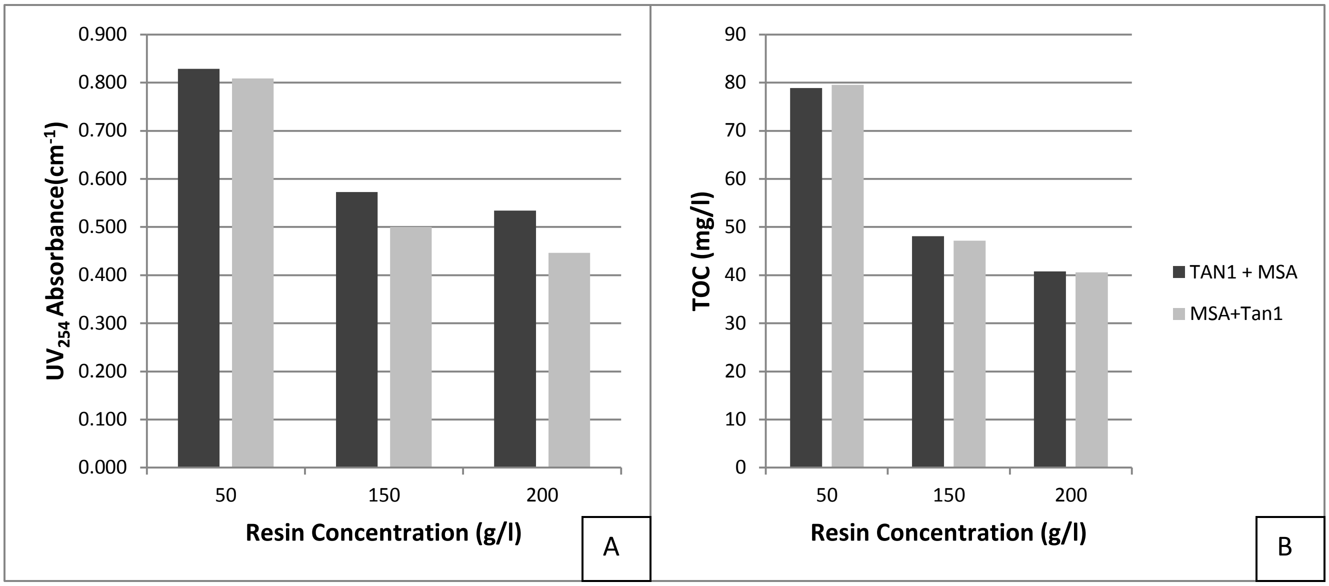

Figure 3- 4: Sequential resin treatment for leachate with varying concentrations of MSA and TAN1

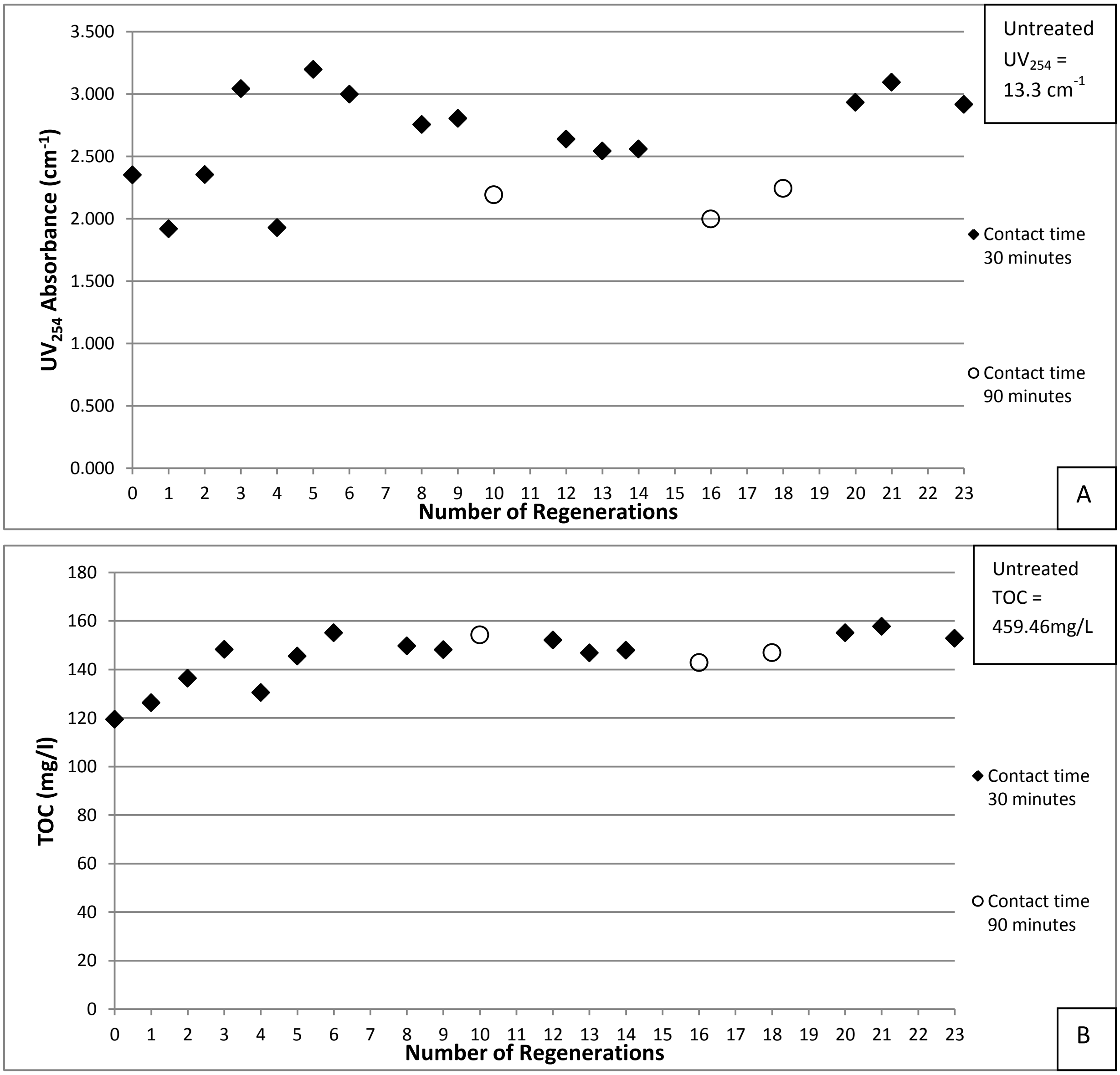

Figure 3- 5: Effect of regeneration on (A) - UV_{254} Absorbance, and (B) - TOC for 50 g/L MSA

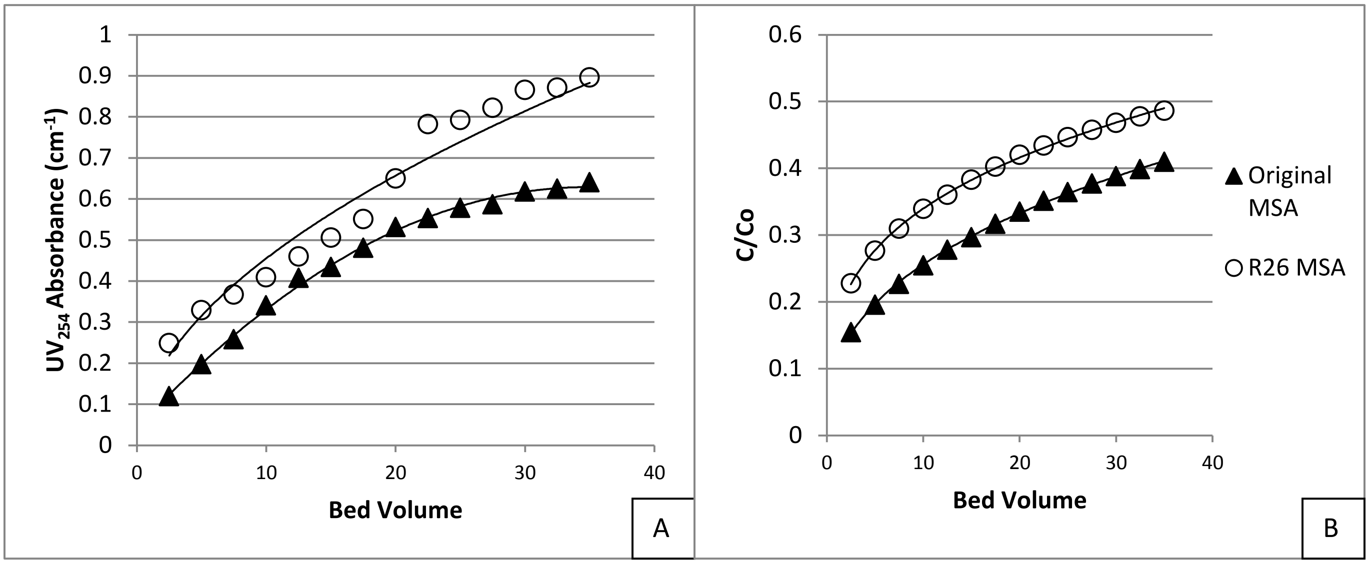

Figure 3- 6: (A) UV_{254} Absorbance, and (B) – Normalized TOC of new and regenerated MSA resin in column mode (C/Co)

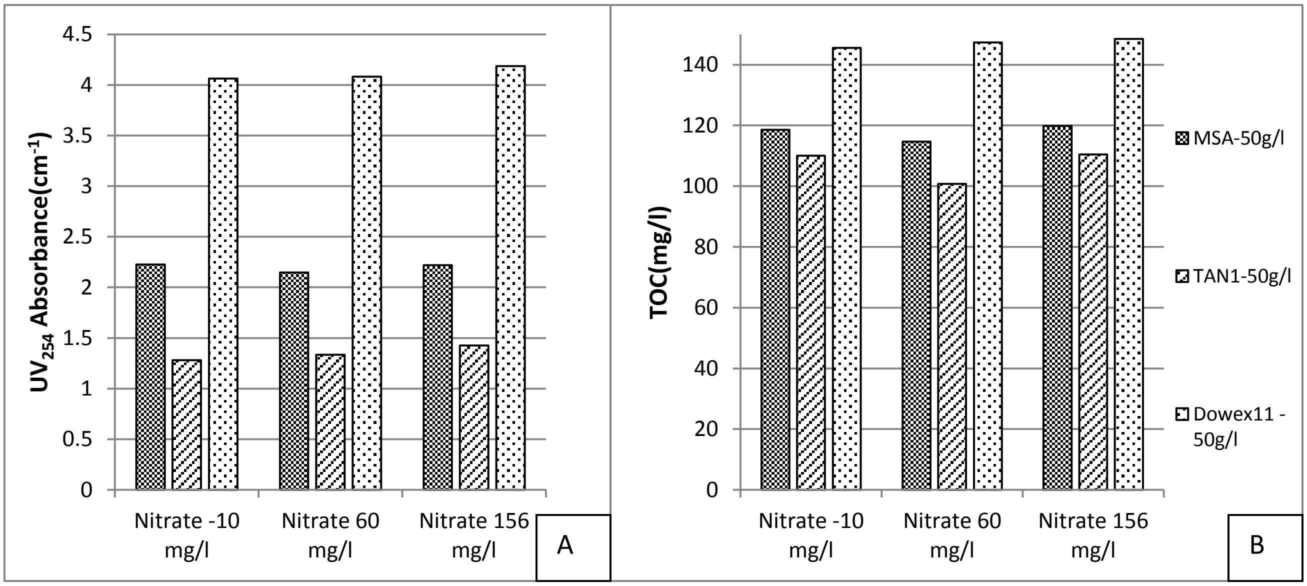

Figure 3- 7: Performance for the resins at different Nitrate concentrations for (A) – UV_{254} removal, (B) TOC removal at resin concentration of 50 g/L

Chapter 4. Evaluation of Ion Exchange and Membrane Filtration as viable alternative for Landfill Leachate treatment

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4.1 Abstract

Landfill leachates are often discharged to wastewater treatment plants but the presence of UV absorbing substances in leachates adversely affects the UV disinfection operations at WWTP's. Anion exchange resins were employed in this study to reduce the UV_{254} absorption and total organic carbon (TOC) values to levels which would permit the acceptable disposal to wastewater treatment plants. Leachate samples with ages of 2 and 16 years from Kentucky landfill and a biologically treated leachate from a Pennsylvania (PA) landfill were utilized for this study. All resins were found to remove more UV absorbing substances compared to TOC, suggesting that anion exchange resins could be employed for removal of UV absorbing substances. Resins could be effectively regenerated, although some loss in the resin capacity was observed. Fractionation of leachate samples into humic acid (HA), fulvic acid (FA) and hydrophilic fraction (Hpi) revealed that with increasing regenerations, the capacity of a resin to remove the FA fraction is negatively impacted. The resin were able to consistently remove the HA fraction which is responsible for bulk of UV quenching. The resin was also found to effectively remove the bio-refractory Hpi fraction which tends to persist even after HA fraction has bio-degraded. Membrane filtration in conjunction with anion exchange resins was also employed and it was observed that this significantly improves the performance of resins to remove both the UV absorbing substances and TOC.

Keywords: landfill leachate, Ion Exchange resin, hydrophobicity, membrane filtration

4.2 Introduction

In a landfill, the rainwater in combination with mositure and degrading solid waste results in a highly polluted stream of wastewater referred to as leachates (Kurniawan et al., 2006). These leachates may be toxic in nature and their composition vary greatly depending upon number of factors such as the age of landfill, climate, type of waste accepted, etc (Renou et al., 2008). There is a strong possibility of groundwater contamination due to seepage of leachate and therefore, they are often collected and discharged to wastewater treatment plants (WWTP's). But their highly varied and complex composition makes their treatment in WWTP's challenging.

Owing to its relatively low cost, biological treatment is initially used to remove the readily biodegradable organic matter from leachates. For younger leachates (< 5 years old) (Rodriguez et al., 2004; Bashir et al.; 2010a) biological treatment is particularly effective as the bulk of organics contain a high concentration of volatile fatty acids (VFA's) which are readily biodegradible (Trebouet et al., 2001). This becomes difficult for stabilized leachates due to the presence of refractory organic material which are often comprised of humic and fulvic acids (He et al., 2006; Bashir et al.; 2010a). Also it has been observed that after biological treatment (Mejbri et al., 1995) and long term landfilling (Chian, 1977), there is an increase in 500 – 1000 MW bio-refractory fulvic substances, most likely from the degradation of humic acids into fulvic acids. These recalcitrant humic substances (humic and fulvic acids) can easily pass the biological treatment operation at WWTP's (Zhao et al., 2012) and increase the organic matter in the effluent.

Another concern is the presence of UV absorbing substances in leachates. The WWTPs often need to disinfect the effluent wastewater before discharge to surface waters. Generally, chemical disinfectants such as chlorine have been used for disinfection. But the increased awareness regarding the potential for disinfectant by product (DBP) formation which are carcinogenic in nature have encouraged the WWTPs to shift to UV as a means of disinfection. More than 2000 UV systems are in operation at various WWTPs in United States and Canada. Recently, it was established that landfill leachates tend to inhibit the performance of UV disinfection systems at WWTP's (Zhao et al., 2012). In a study conducted by Zhao et al. (2013), it was also found that biological processes were effective in removing organic carbon but were unable to remove the bulk of UV absorbing substances.

On the other hand, Ion exchange mechanism has been known to remove humic and fulvic substances (Fettig et al.,1999) but their practical application has generally been limited to their use for removing metal ions from water and wastewater(Lin et al., 2008; Kurniawan et al., 2006). For landfill leachates as well, they have been mostly used as a polishing step to remove inorganic anions and heavy metals (Primo et al., 2009; Bashir et al., 2010b). There is very limited literature regarding their use for removing organic matter from leachates. Recently a few studies have focussed on the successful use of ion exchange resins to remove non biodegradable organic matter from leachates (Bashir et al., 2010a; Boyer et al.; 2011).

In this study, the applicability of anion exchange resins to remove UV quenching substances and organic matter from landfill leachates was investigated. Three different leachate samples were used to evaluate if leachate properties affect the effectiveness of the anion exchange resins.

The total organic carbon (TOC) and UV_{254} measurements were made to evaluate the performance of the resins. Specifically,the research aimed at finding answers to the following questions.

1) Does ion exchange work in an acceptable manner to treat landfill leachates i.e. can they remove the TOC and the component responsible for UV quenching effectively?
2) Can the ion exchange resins be effectively regenerated or does the organic matter present in leachates foul the resin?
3) Which component of landfill leachates : UV or TOC (humic acid, fulvic acid and hydrophillic component) are best removed by the resin and
4) What is the effect of combined membrane filtration and ion exchange on treatment of leachates

4.3 Materials and Methods

4.3.1 Leachate Sampling

The leachate samples that have been used in this study were collected from landfills located in Pennsylvania (PA) and Kentucky. The PA landfill has an on-site leachate treatment plant which performs nitrification/denitrification using a sequencing batch reactor activated sludge system. More details about the PA landfill leachate system can be found in Zhao et al.(2012).

The Kentucky landfill has 8 separate individual units designated Unit 1 to 8. Leachate samples for this study were taken from Unit 5 and Unit 8 whose average age are 16 and 2.5 years respectivley. No input has been made to Unit 5 (OL5) in over a decade whereas Unit 8 (OL8) is an active permitted landfill. The leachate from these units are stored underground onsite without any treatment under anaerobic conditions.

Based on their age and treatment methods, OL8 has been characterized as young leachate, OL5 as old leachate and PA leachate as biologically treated leachate.The leachates were shipped from landfills and stored in the lab at Virginia tech at 4^{o}C to prevent any microbial activity from affecting the samples. Before any sampling for experimental purpose, the leachate containers were shaken vigourously to suspend the settled particles.

4.3.2 Resin Characteristics

Treatment of leachates was investigated using three different anion exchange resins manufactured by the Dow Chemical Company, Dowex Marathon MSA, Dowex Marathon 11 and Dowex TAN1. These resins were selected because they were suggested by the manufacturer for leachate treatment as they are strong base anion resin and have excellent organic removal capability as well as rapid exchange capacity. They can be operated in both the Cl^- and OH^- form and over a pH range of 0 – 14. The properties of these resins are listed in Table 4-1.

4.3.3 Experimental Process

Leachate pretreatment

The leachate samples were microfiltered through a 1.5µm glass microfiber filters (42.5mm, Whatman 934-AH Glass Microfiber filters, GE Healthcare Biosciences Corp., Piscataway, NJ) to remove the suspended particles. The microfiltration was performed using 300 mL filtration cells (GELMAN, Ann Arber, MI) operating with a vaccuum pump.

Batch Experiments

Several batch experiments were conducted with varying resin concentrations to identify the optimal resin concentration and to assess the best resin for the research objectives. The batch experiments were conducted in 250 ml beakers with 100 ml of leachate. The beakers were stirred constantly during the experiments using a magnetic stir bar. Initial tests consisted of performing the kinetic studies to determine the optimal contact time needed by the resins. It was found that after 30 minutes of contact time, equilibrium is achieved for both UV and TOC removal. Multiple regenerations of resins were also carried out and their treatment performance evaluated to assess the loss in the removal capacity of the resins.

4.3.4 Leachate Fractionation

The samples before and after treatment with anion exchange treatment were separated into Humic acid (HA), Fulvic acid (FA) and Hydrophillic (Hpi) components based on their hydrophobicity by passing them through DAX-8 non-ionic resin (Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO) in accordance with the methods proposed by Thurman and Malcolm (1981), Leenheer (1981) and Christensen et al. (1998).

The DAX-8 resin was cleaned in accordance with the method proposed by Leenheer (1981). The cleaned resin slurry (approximately 4 mL) was packed in 1.0 cm X 10 cm borosilicate glass column (Thomas Scientific, Swedesboro, NJ). Treated leachate samples were acidified to pH 2 by adding concentrated HCL to precipitate the Humic acids (HA). The precipitated Humic acids (HA) were separated and collected on 0.45 µm cellulose nitrate membrane (47 mm, Sartorius Stedim Biotech, France). The humic acids collected on the 0.45 µm cellulose membrane redissolved in 0.1N NaOH solution which was used for further analysis. The supernatant consisting of Fulvic and Hydrophillic components was passed through DAX-8 resin column at a flow rate of 15 bed volumes per hour. Fulvic acid were retained on the resin column and the unabsorbed Hydrophillic fraction that passed through the resin column. The Fulvic acids retained on the DAX-8 resin was eluted by backwashing the resin column with 0.1N NaOH solution and the resultant eluent characterized as FA solution was used for further analysis.

4.3.5 Membrane Filtration

The apparatus for membrane filtration of the leachate samples consisted of a 200 mL stirred ultrafiltration cells (Amicon model # 8200), a nitrogen gas tank maintained at 120 kPa pressure and membrane discs (Millipore, Billerica, MA) with diameters of 63.5 mm. In this study, the molecular weight cutoffs (MWCO) for the membrane discs used were 1000 Da and 3000 Da(PLAC and PLBC, Millipore, Billerica, MA).

4.3.6 Chemical Analysis

All chemicals used in this experiment were of analytical grade. All the glassware used in this experiment were first washed with soapy water, soaked in 10% nitric acid, rinsed with deionized (DI) water and baked at 450^{o} C for 4 h. Total Organic Carbon (TOC) was analyzed using high temperature combustion with a TOC analyzer (TOC-5000A, Shimadzu, Japan). The ultraviolet absorbance at 254 nm(UV_{254} absorbance) was measured using spectrophotometer (Beckman Coulter, Brea, CA). The pH of samples was measured using a pH meter (Model No. 910, Accumet, Cambridge, MA) with a pH probe (Model No. 13-620-287, Accumet, Petalinga Jaya, Malaysia). The specific UV absorbance at 254 nm ($SUVA_{254}$) has been calculated as UV_{254} X 100/TOC in the units of L/mg-m.

The regeneration of exhausted resins was carried out by mixing the resin in 5% NaCl solution (regenerant brine) for 180 minutes (Nyugen et al., 2011). The regeneration experiments were conducted in batch mode. The resins were washed with DI water prior to regeneration with regenerant brine to remove the traces of leachate that might be present on the resin and again after the regeneration to remove the traces of regenerant brine.

4.4 Results & Discussions

4.4.1 Treatment performance of Ion Exchange resins

Figure 4-1 shows the performance of resins in removing TOC and UV_{254} absorbance for the PA, OL8 and OL5 leachate samples.There is an observable difference between the TOC and UV_{254} absorbance of the three untreated leachate samples. PA leachate has undergone prior biological treatment on-site whereas OL8 leachate is from a newer landfill and has not undergone any treatment (young leachate). OL5 leachate is from an inactive landfill which has been closed for more than 16 years (stabilized leachate). The difference between OL8 and OL5 is that the former has high organic matter constituent that can undergo bio-degradation but OL5 has mostly a high percentage of non-biodegradable material due to degradation over long term landfilling.

Figure 4-1-(B) , (D) and (F) show the TOC removal capacity of the resins for PA, OL8 and OL5 leachate. It can be observed that as the resin concentration increases from 50 g/L to 200 g/L, the organic matter removal also increases. For the PA leachate, at the resin concentration of 50 g/L, the removal of TOC was 67%, 74% and 76% for Dowex 11, Dowex MSA and Dowex TAN1 respectively. At 200 g/L, the removal observed was 77%, 84% and 87% for Dowex 11, Dowex MSA and Dowex TAN1 respectively. Thus, for organic carbon removal of PA leachate, Dowex 11 performed poorly relative to TAN1 and MSA.

For OL8 leachate, Dowex 11 was not utilized because of its performance for the PA leachate. It was observed that TAN1 performed better than Dowex MSA. Around 78% and 72% removal is observed at 200 g/L for TAN1 and MSA, respectively whereas at 50 g/L, MSA and TAN1 achieved 58% and 64% removal respectively.

For OL5, only 100 g/L resin concentration was used for all the three resins. All resins performed similarly and achieved around 77% removal of organic matter.

Figure 4-1-(A), (C) and (E) show the capacity of resins to remove the UV quenching substances from the PA, OL8 and OL5 leachates, respectively. Again, as the resin concentration increases, the removal of UV quenching substances increases. It can be seen that the resins followed the similar pattern for UV removal as was observed for TOC removal. Dowex 11 again had a relatively poor performance with 78% removal as compared to 94% and 95% removal for MSA and TAN1, respectively at a resin concentration of 200 g/L. At 50 g/L, Dowex 11 achieved only 66% removal of UV quenching substances as compared to 82% and 90% in case of MSA and TAN1, respectively.

For OL8, the percentage removal achieved was around 89% and 90% for MSA and TAN1 at 200 g/L. At 50 g/L MSA and TAN1 achieved 79% and 85% removal. In case of OL5, MSA, TAN1 and Dowex11 achieved 90%, 91% and 91% UV_{254} removal, respectively.

In all cases, the resins were able to remove more UV absorbing substances than TOC, suggesting their preference for removing aromatic type molecules (Humbet et al, 2005). This suggests that anion exchange resins are a potential alternative for removing substances that are causing UV quenching problems in WWTPs. Also, Dowex11 was able to achieve similar removal performance as TAN1 and MSA in case of OL5. In studies conducted by Zhao et al. (2013) it was found that long term landfilling leads to nearly complete degradation of humic substances present in leachate. This suggests that the humic and fulvic components in the PA leachate might be affecting the performance of Dowex11. This is further evaluated in this study.

Also, the earlier use of anion exchange resins were limited to treatment of stabilized landfill leachate (Bashir et al., 2010a) but this study shows that good removal of both TOC and UV absorbing substance was observed even in the case of a very young leachate (OL8) which had not undergone any treatment, suggesting that ion exchange can be a viable treatment alternative for old and fresh leachates.

4.4.2 Effect of Regeneration

The ion exchange resins are generally expensive (Grote and Schumacher) and hence for this process to be economically feasible ion exchange resins are reused multiple times. This is possible because, in principle ion exchange is a reversible process. So, theoretically if the media becomes exhausted, it can be regenerated back to its ionic form and can be reused. To determine the effect of organic ions on the ability to regenerate the resins, the regeneration potential of the anion exchange resins was investigated.

For regeneration, Dowex 11 was not considered because of its poor initial performance. Six regenerations were performed with both TAN1 and MSA at different resin concentrations for PA leachate and their performance was found to be similar. It was also observed that the resin beads of TAN1 were deteriorating physically during the stirring. Therefore, to further explore the regeneration capacity of the resin, regenerations were performed with only MSA at the representative dose of 50 g/L for PA leachate and shown in Figure 4-2.

The regeneration cycles for both TAN1 and MSA for OL8 and OL5 leachate are presented in Figure 3 and Figure 4, respectively.

Figure 4- 2(A) and (B) show the regeneration performance of MSA at resin concentration of 50 g/L. It can be observed from Figure 4- 2(A) that the UV_{254} absorbance of treated samples varies between $2cm^{-1}$ – $3cm^{-1}$. The trend shows that removal does not change much with the number of regenerations. The initial three regenerations indicate a decrease in removal efficiency of the resin but afterwards it stabilizes with a final UV absorbance nearly around 2.5 - $3cm^{-1}$. For the 10th, 16th and 18th regeneration cycle, the effective contact time between the resin and leachate was increased from 30 minutes to 90 minutes.

It was observed that the UV_{254} absorbance after the 10th, 16th and 18th regeneration was similar to the absorbance of the new resin. For all other regeneration cycles, the contact time between the resin and leachate was kept 30 minutes. It can be observed that after initial 3 regenerations, the UV_{254} absorbance hovers around $3cm^{-1}$ until the contact time was increased. In the later regenerations (20th, 21st and 23rd cycles), it can be again seen that the UV_{254} is around $3cm^{-1}$ suggesting that there is a slight deterioration in the performance of the resins to remove UV absorbing substances, but most of the deterioration occurs over first three regenerations.

The TOC removal also followed the similar trend as UV_{254} absorbance for the leachate. The TOC value after the third regeneration was 148.35 mg/L as compared to 119.50 mg/L observed in the case of new resin. This resulted in decrease of organic matter removal from 73.8% to 68.2% after the third regeneration cycle. But, from 5th regeneration onwards, the TOC value stabilized and was typically observed to be in the range of 145.00 - 160.00 mg/L. Also, the TOC value after the 10th, 16th and 18th regeneration cycle was 154.35 mg/L, 142.9 mg/L and 146.9 mg/L respectively which was not similar to the TOC value observed after the use of new resin. This suggests that increasing the contact time from 30 minutes to 90 minutes would benefit UV removal but had no effect on organic matter removal.

Figure 4- 3 (A) and (B) show the effect of regeneration on the UV_{254} and TOC removal of both TAN1 and MSA for OL8 leachate which is from a newer landfill site and so contains higher level of TOC and UV absorbing substances. From the TOC data it can be observed that MSA

performance over 7 regeneration cycles is consistent. The TOC values are within 3% of the value achieved after the use of new MSA resin. For TAN1 also, the TOC values are similar to the value attained for the new resin. Considering UV_{254} removal, the performance of MSA seems to deteriorate slightly with increasing regeneration cycles. This is evident by the increasing UV_{254} absorbance values from 3.06 cm^{-1} in the case of new resin to 3.58 cm^{-1} achieved after 7th regeneration. For TAN1 also, after the 2nd regeneration the values seem to be showing an upward trend. In terms of percentage removal, it drops from 86% to 84% for MSA and 88% to 86% for TAN1 (observed at 5th regeneration)

Figure 4- 4(A) and (B) show the regeneration performance of TAN1 and MSA for OL5 leachate which is from a landfill that has been closed for 16 years and thus contains mostly non-biodegradable organic matter. Both the UV absorbance and TOC values are almost identical over the six regeneration cycles. There is a slight variation in the UV values for MSA but the regenerated values are all better than the new resin. Thus it indicates that resins for treating stabilized leachates could be effectively regenerated without any observable loss in its capacity.

4.4.3 Hydrophobicity distribution of TOC and UV for treated leachate samples

The treated PA leachates were fractionated on the basis of hydrophobicity into their humic acid (HA), fulvic acid (FA) and hydrophilic (Hpi) fractions to better understand the reasons for the slight loss in the resin capacity with regeneration. Data for the removal of each fraction as a function of the number of regeneration cycles is shown in Figure 5 for Dowex MSA at a resin concentration of 50 g/L.

The TOC of the fractionated components in the order of HA, FA and Hpi fractions was found to be 94.64 mg/L, 216.5 mg/L and 155.36 mg/L. Thus, the largest fraction in terms of TOC consisted of the FA fraction.

The HA, FA and Hpi fractions had UV_{254} absorbance values of 4.66 cm^{-1}, 6.01 cm^{-1}, and 2.52 cm^{-1} respectively. As was the case with TOC, the FA component had the highest UV_{254} absorbance. But comparing the $SUVA_{254}$ values (Table 4-2) of these components gave a different perspective. The $SUVA_{254}$ is directly proportional to the aromatic content of dissolved organic matter. In other words, a high SUVA value indicates high UV absorbance per unit concentration of organic carbon. Hence the higher the $SUVA_{254}$ value, the higher is the aromatic content. The $SUVA_{254}$ follows the order HA > FA > Hpi with the values for HA, FA and Hpi in the raw leachate being 4.92 L/mg-m, 2.78 L/mg-m and 1.62 L/mg-m, respectively. Thus high $SUVA_{254}$ of HA fraction indicates that it is responsible for majority of UV quenching followed by FA and Hpi components.

The data in Table 4-2 show the TOC and UV values for HA, FA and Hpi fraction of PA leachate treated by Dowex MSA at various resin concentrations. It can be seen that as the resin concentration increases from 50 g/L to 200 g/L, the TOC removal for the HA fraction goes up only slightly from 81% to 85%. For the FA fraction, the removal percentage increases moderately from 82% to 89% whereas for the Hpi fraction, there is a large increase with removal increasing from 60% to 73%. Thus as the resin concentration increases, a relatively higher amount of the Hpi and FA fraction is removed compared to the HA fraction.

The UV_{254} absorbance shows a different trend for HA fraction. The reduction in the UV_{254} absorbing HA fraction shows a large increase from 85% to 95% when the resin concentration is increased from 50 g/L to 200 g/L. The FA fraction reduction on the other hand shows a moderate increase from 92% to 96% and the Hpi fraction removal increases from 83% to 89%. Thus, a substantial increase in % removal of UV associated HA fraction at 200 g/L coupled with overall decrease in UV_{254} absorbance of the treated leachate at 200 g/L again substantiates the fact that HA fraction is more responsible for UV quenching than the other fractions.

Overall, observing both the UV and TOC removal, it can be seen that higher removal of humic and fulvic components take place than the hydrophilic component.

From Table 4-2, it can be seen that the $SUVA_{254}$ values decreases sharply for the HA fraction as the resin concentration increases from 50 g/L to 100 g/L (22% reduction in $SUVA_{254}$ at 50 g/L and 60% at 100 g/L) whereas only a small decrease is observed for the FA (54% $SUVA_{254}$ reduction at 50 g/L and 61% at 100 g/L) and Hpi fractions (56% $SUVA_{254}$ reduction at 50 g/L and 58% at 100 g/L). From 100 g/L to 200 g/L there is almost no change in $SUVA_{254}$ values for FA and Hpi fraction whereas again moderate decrease is observed for the HA fraction. This could be attributed to the fact that the resin has high selectivity for removing UV absorbing substances as observed in above section. The HA fraction has a high aromatic content and is responsible for much of the UV quenching and increasing the resin concentration results in more removal of the UV absorbing HA fraction whereas the FA and Hpi fractions which have a small aromatic content show a more uniform removal of TOC and UV_{254}. Also, it establishes that the organic matter responsible for UV_{254} absorbance behaves differently from the behavior of the TOC.

From Figure 4-5, it can be clearly seen that as far as TOC removal is concerned, the Hpi fraction is nearly constant across all the regeneration cycles. The Hpi TOC value generally lies in the 60 – 70 mg/L range for multiple regenerations. This implies that across the regeneration spectrum, around 55% - 60% removal of Hpi fraction occurs. This is particularly important because the Hpi fraction tends to persist even after long term landfilling and is bio-refractory in nature. The HA fraction also behaves in a similar manner, with TOC values observed to be in the range of 16 – 22 mg/L or removal of around 77% - 83% of total HA fraction. The removal of the FA fraction on the other hand seems to be impacted by the number of regeneration cycles. It can be seen that the TOC value for the FA fraction after first regeneration is 38.5 mg/L which starts increasing and reaches 60 mg/L after the sixth regeneration (decrease in removal efficiency from 82% to 72%) and afterwards it becomes constant around this value for the subsequent regeneration cycles.

Both the HA and Hpi removal are constant throughout the regeneration cycles but the FA removal deteriorates over the first six regeneration cycle and then stabilizes. This is consistent with the TOC observation in Figure 4-2(B) where the TOC value increases until the sixth regeneration cycle and then stabilizes. The possible reason for this could be that some of the high molecular weight HA fraction may be getting adsorbed irreversibly on the resin beads. The resin has high selectivity for removing UV absorbing substances and since HA and FA fraction both had high UV_{254} values, the resin has preference for them. But the possible fouling of resin by the HA fraction might be affecting the FA removal. Removal of the Hpi fraction on the other hand appears to be unaffected due to its smaller size composition (< than 1000 Da) (Zhao et al 2013).

For the HA fraction, the UV absorbance after the first regeneration was 0.71 cm^{-1} or 85% removal of the HA fraction. This jumped to 1.14 cm^{-1} after the third regeneration bringing the removal of HA fraction down to 76%. For the regeneration cycles afterwards, the UV absorbance was around 1.00 cm^{-1} indicating that there is loss in the removal effectiveness of the UV quenching HA fraction with increasing regeneration cycles. Also after the 10th, 16th and 18th regeneration when the contact time was increased to 90 minutes, it can be observed that the UV Absorbance of HA fraction is similar to the value after first regeneration. This indicates that over the subsequent regenerations, the HA fraction removal requires more contact time for achieving the same removal as the new resin. The UV absorbance for the FA fraction after first regeneration was 0.50 cm^{-1} achieving around 92% removal of FA fraction. Subsequent regenerations lead to decreasing removal of the FA associated UV quenching substances and reach UV absorbance of 0.93 cm^{-1} by the fifth regeneration leading to 84% removal. Afterwards for other regenerations the UV value remains close to 1.0 cm^{-1}, similar to the HA fraction. Also, there is no observable effect on the removal of the UV quenching FA fraction by increasing the contact time. The Hpi fraction also shows the similar trend to the FA fraction with the UV value increasing from 0.44 cm^{-1} after the first regeneration to 0.71 cm^{-1} after the sixth regeneration. The removal of Hpi fraction of UV quenching substances drops from 83% to 72%. Afterwards, it becomes fairly constant around 0.60 cm^{-1} for subsequent regeneration cycles.

The resin after few regeneration cycles does deteriorate both in terms of UV Absorbance and organic matter removal but it stabilizes after this initial deterioration, suggesting that the anion exchange resins could be effectively regenerated.

4.4.4 Combined Membrane Filtration and Ion Exchange treatment

In the above segments, a slight loss in the capacity of resin has been observed. This could potentially be caused by humic substances and so this stage of study included membrane filtration of leachates through 1000 and 3000 Da molecular weight cut off (MWCO) membranes to remove the bulk of HA and FA fractions as a pretreatment step for anion exchange resins.

Figure 4-6 shows the performance of membrane filtration on removing UV absorbing substances and TOC for PA and OL8 leachates. In case of the PA leachate, the effluent after passing through 3000 and 1000 Da had UV_{254} values of 6.45 cm^{-1} and 5.14 cm^{-1} respectively. The 3000 Da and 1000 Da Cutoff achieves, respectively, 52% and 61% removal of UV absorbing substances. For OL8 leachate, the UV_{254} absorbance after 3000 Da was 11.84 cm^{-1} and after 1000 Da was 10.46 cm^{-1}. This corresponds to removal of around 46% and 52% for 3000 Da and 1000 Da respectively. For TOC removal of PA leachate, 3000 Da and 1000 Da achieve 44% and 45% removal respectively. In case of OL8, the removal achieved were 51% and 54% for 3000 Da and 1000 Da. Hence, there is significant decrease in the UV and TOC values after the use of the membranes. Also, there was not much difference between 3000 and 1000 Da membranes as the effluent after passing through 3000 and 1000 Da membranes had similar TOC and UV values for both OL8 and PA leachates. This indicates the presence of fraction greater than 3000 Da MW fractions (generally HA and FA) in the leachates. Also, since both 3000 and 1000 Da membranes had a similar performance, subsequent regeneration experiments were performed with 1000 Da membrane filtered leachates.

In Figures 4- 6 (A) and (B), the performance of all three resins to remove UV_{254} and TOC is shown for the 1000 Da filtered PA leachate. It can be seen that Dowex 11 responds in a surprising manner with UV_{254} absorbance values slightly better than both TAN1 and MSA. This is in contrast to the performance of Dowex 11 on the bulk leachate sample that has not been subjected to membrane filtration. Dowex 11 performed similarly to both TAN1 and MSA for OL5 leachate (Figure 1(E), (F)) which, due to biodegradation over long term landfilling had almost no humic substances in the leachate. This suggests that Dowex 11 is suitable for treating leachates which have small amounts of humic and fulvic acid components i.e. leachates that contain only low molecular weight HA and FA components and these are likely to be from older landfills.

After the application of resins for PA leachates filtered through the 1000 Da membrane, the TOC removal was observed to be comparable for TAN1 and Dowex 11. Dowex MSA had a relatively poor performance. The % removal of TOC achieved after applying 50 g/L resin to the 1000 Da filtered leachate was 80%, 81% and 77% for Dowex 11, TAN1 and MSA, respectively. Compared to the original bulk leachate subjected to resins at the same concentration, this corresponded to an increase of about 14%, 5% and 4% for Dowex 11, TAN1 and MSA. Hence, for both TAN1 and MSA the performance is moderately better for membrane filtered leachate. For Dowex 11 though, it is substantially better for membrane filtered leachate. For UV removal also, the performance of resins on membrane filtered leachate was much better. At the same resin concentration of 50 g/L, Dowex 11 achieved an overall 93% removal for 1000 Da filtered leachate as compared to 66% observed for the treatment of original bulk leachate. For both MSA and TAN1, 92% UV removal was observed for 1000 Da filtered leachate, as compared to 82% (MSA) and 90% (TAN1) observed in case of bulk leachate. The performance of all three resins to treat membrane filtered PA leachate was similar in nature with close to 80% TOC removal and 90% UV removal being observed. To achieve the similar removal without membrane treatment would require higher resin dosages of 150-200 g/L of MSA and TAN1.

Figures 4- 6 (C) and (D) show the results of membrane filtration and ion exchange treatment for OL8 leachate. It can be seen that filtration by both 3000 Da and 1000 Da followed by resin treatment with 100 g/L MSA achieved similar results both in terms of TOC and UV removal. Membrane filtration in conjunction with resin treatment achieved an overall UV removal of 92%. For TOC removal, membrane filtration and resin treatment achieved an overall TOC removal of 80%. Comparing it with untreated bulk leachate subjected to 100 g/L MSA, there was a 6% overall increase in UV removal and 14% increase in TOC removal. In contrast, subjecting the untreated OL8 directly to 200 g/L MSA achieved only 72% TOC removal and 89% UV removal.

Thus it can be seen that the use of membrane filtration significantly improves the performance of the anion exchange resins to remove both the UV absorbing substances and TOC. Also, significantly reduced quantities of resin are needed after membrane filtration to achieve the desired UV and TOC removal. Even after membrane filtration it was observed that the anion exchange resins have a tendency to remove more UV absorbing substances than TOC. This suggests the presence of low molecular weight aromatic compounds in the leachate which could also be contributing to UV quenching.

Table 4-3 and 4-4 show the regeneration potential of the resins for treating the 1000 Da filtered leachate. It can be seen from Table 4-3 that all three resins showed effective regeneration as far as TOC removal is concerned but there is a slight deterioration in UV removal capacity of the resins. Dowex 11 and Dowex TAN1 on subsequent regenerations shows slowly increasing UV_{254} values whereas Dowex MSA showed a slight deterioration after first regeneration and then had similar performance for all subsequent regenerations.

Table 4-4 shows the regeneration potential of Dowex MSA and TAN1 for OL8 Leachate. Five regenerations were conducted with MSA and 2 regenerations were conducted with TAN1. For UV removal, after 2 regenerations it seemed that TAN1 could be regenerated but MSA suffered some deterioration. A few more regenerations were conducted with MSA and it was found that as number of regenerations increase, the UV_{254} value of the treated leachates also increases, showing that the resin is deteriorating slightly. In terms of % deterioration this corresponds to decrease in UV removal from 83% to 81%. For TOC removal the performance after fifth regeneration was similar to the new resin. This suggests that the resin after membrane filtration could be effectively regenerated. A slight loss in UV removal capacity could be due to the small amount of humic & fulvic component present after membrane filtration but it is within acceptable range of practical application.

4.5 Conclusions

1) Out of the three studied resins namely Dowex 11, Dowex MSA and Dowex TAN1, Dowex 11 faired relatively poorly and Dowex MSA and Dowex TAN1 both performed almost identically. Considering TAN1 and MSA, for biologically treated and stabilized leachates such as PA and OL5 leachate respectively, close to 80% organic matter removal and 90% UV_{254} removal was observed at the resin dosages exceeding 100 g/L. For OL8 leachate which is a raw young leachate, the organic matter removal of 72% and UV_{254} removal of 90% for resin dosages of 200 g/L was observed. Thus, it indicates that anion exchange resins can be effectively utilized for any leachate.
2) It was also found that the anion exchange resins preferentially remove UV quenching substances.
3) The resin performance over the number of regenerations does tend to deteriorate slightly. In case of PA leachate, it was observed that both UV and TOC deteriorate for initial few regeneration and then stabilize. Also, by increasing the effective contact time between resins and leachates, the UV deterioration could be avoided but it does not have any impact on TOC removal. Effective regeneration of resins is possible for treating stabilized landfill leachates (OL5). It was observed that for treating young leachate (OL8) the resins could be effectively regenerated as far as TOC removal is concerned but some loss is observed in their UV removal capacity.

4) Fractionation of leachate into HA, FA and Hpi fraction revealed that in case of TOC, Hpi and HA fraction removal is not affected over the increasing number of regeneration cycles but FA fraction removal is negatively impacted. For UV_{254} absorbance, the removal of all HA, FA and Hpi fractions are negatively impacted thereby leading to the deterioration of the resin. It could potentially be because of the fouling of resins by high molecular weight HA and FA fractions.

5) As the resin dosages is increased, the % increase in TOC removal follows the order Hpi > FA> HA. Whereas the % increase in UV removal follows the order HA>Hpi> FA. Also the high $SUVA_{254}$ of HA fraction and decrease in overall UV_{254} corresponding to the decrease in UV_{254} of HA fraction on increasing the resin dosages suggests that HA fraction is responsible for bulk of UV quenching.

6) Using membrane filtration prior to ion exchange improves the performance of the anion exchange resins to remove both the UV quenching substances and TOC. The performance of Dowex 11 improved significantly when using 1000 Da membrane filtered leachate as compared to the unfiltered leachate suggesting that high molecular weight HA and FA fractions were fouling it and hence should be used for treating leachates which have small fraction of HA and FA components. All three resins could be effectively regenerated with less variability in the TOC and UV values observed for subsequent regenerations. Slight losses in the UV values were observed for TAN1 and Dowex 11 but they were not substantially significant. Thus combined membrane filtration and ion exchange serves as a better treatment alternative and will significantly improve the resin life.

7) The performance of resins in removing TOC and UV quenching substances after filtering the leachate through 1000 and 3000 Da membranes was found to be similar. Thus, when using membrane filtration in conjunction with ion exchange resins, 3000 Da MWCO should be utilized as it would require less energy and save operational costs.

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Table 4- 1: Physical and Chemical Properties of resins (Data sourced from Product specification brochures)

Resin Properties	**Anion Exchange Resins**		
	Dowex Marathon 11	Dowex Marathon MSA	Dowex TAN1
Type	Strong base anion exchange resin	Strong base anion exchange resin	Strong base anion exchange resin
Matrix	Styrene-DVB, Gel	Styrene-DVB, Macroporous	Styrene – DVB, Macroporous
Functional Group	Quaternary Amine	Quaternary Amine	Quaternary Amine
pH range	0 -14	0 - 14	0 - 14
Ionic form	Cl^-(supplied) ,OH^-	Cl^-(supplied) ,OH^-	Cl^-(supplied) ,OH^-
Recommended maximum operating temperature	60^0 C for OH^- 100^0 C for Cl^-	60^0 C for OH^- 100^0 C for Cl^-	60^0 C for OH^- 100^0 C for Cl^-
Mean particle Size (µm)	550 ± 50	640 ± 50	NA
Total exchange capacity (eq/l)	1.3	1.1	0.7

Table 4- 2: HA, FA and Hpi values after first regeneration cycle of Dowex MSA at various resin concentrations for PA leachate

		TOC (mg/L)	% TOC removal	UV_{254} Absorbance (cm^{-1})	% UV removal	$SUVA_{254}$ (L/mg-m)
Untreated PA leachate	HA	94.64		4.66		4.92
	FA	216.5		6.01		2.78
	Hpi	155.36		2.52		1.62
50 g/L	HA	18.39	81	0.71	85	3.84
	FA	38.49	82	0.50	92	1.29
	Hpi	62.4	60	0.44	83	0.71
100 g/L	HA	15.72	83	0.31	93	1.96
	FA	33.99	84	0.37	94	1.09
	Hpi	50.28	68	0.34	87	0.68
150 g/L	HA	14.99	84	0.22	95	1.53
	FA	26.07	88	0.28	95	1.08
	Hpi	45.34	71	0.30	88	0.66
200 g/L	HA	14.24	85	0.22	95	1.56
	FA	24.38	89	0.26	96	1.08
	Hpi	42.6	73	0.28	89	0.65

Table 4- 3: Regeneration data of Dowex 11, Dowex MSA and Dowex TAN1 for 1000 Da filtered PA leachate

	Dowex 11		**Dowex TAN1**		**Dowex MSA**	
	TOC(mg/L)	UV$_{254}$ (cm^{-1})	TOC(mg/L)	UV$_{254}$ (cm^{-1})	TOC(mg/L)	UV$_{254}$ (cm^{-1})
PA leachate-1k Da	251.6	5.14	251.6	5.14	251.6	5.14
New Resin	89.92	0.88	85.52	1.10	104.60	1.06
1st Regeneration	90.83	0.92	106.1	1.24	105.80	1.20
2nd Regeneration	92.08	0.91	107	1.22	106.80	1.21
3rd Regeneration	91.4	0.95	115.3	1.27	109.20	1.26
4th Regeneration	92.73	0.95	106.75	1.30	104.83	1.28
5th Regeneration	-	-	103.05	1.32	101.10	1.21
6th Regeneration	-	-	-	-	106.40	1.26
7th Regeneration	-	-	-	-	100.00	1.18
8th Regeneration	-	-	-	-	99.25	1.20
9th Regeneration	-	-	-	-	98.39	1.19
10th Regeneration	-	-	-	-	96.53	1.17

Table 4-4: Regeneration data at 100 g/L Dowex MSA and TAN1 for 1000 Da filtered OL8 leachate

	Dowex MSA		**Dowex TAN1**	
	TOC(mg/L)	UV_{254} (cm^{-1})	TOC(mg/L)	UV_{254} (cm^{-1})
OL8 - 1k leachate	531.5	10.46	531.5	10.46
New Resin	230.80	1.70	223.9	1.77
1st Regeneration	227.10	1.70	227.1	1.73
2nd Regeneration	233.50	1.81	223	1.7608
3rd Regeneration	240.20	1.91	-	-
4th Regeneration	242.50	1.93	-	-
5th Regeneration	230.40	1.95	-	-

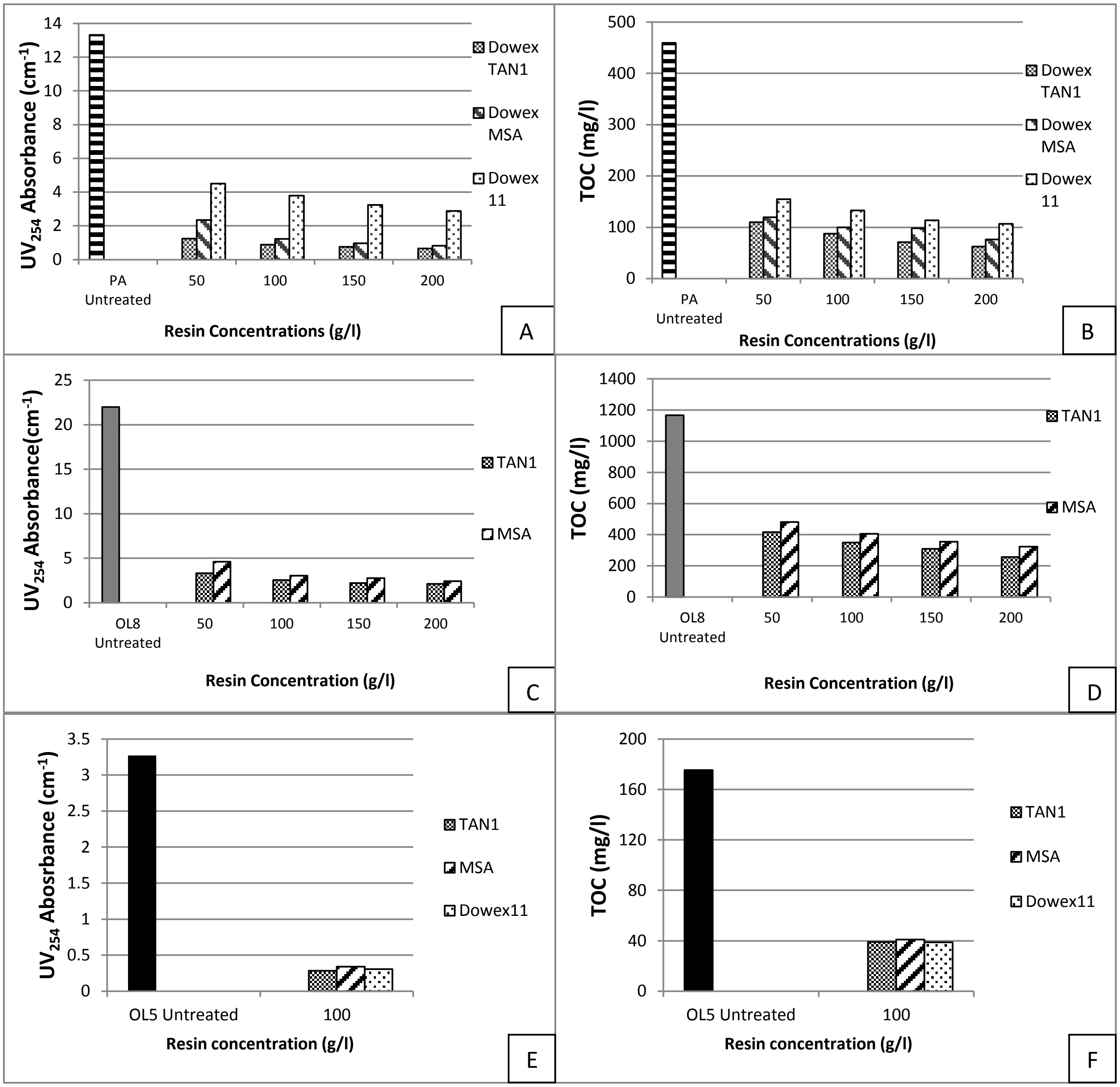

Figure 4- 1: Comparison of anion exchange resins on removal of UV quenching substances and organic matter for various leachates

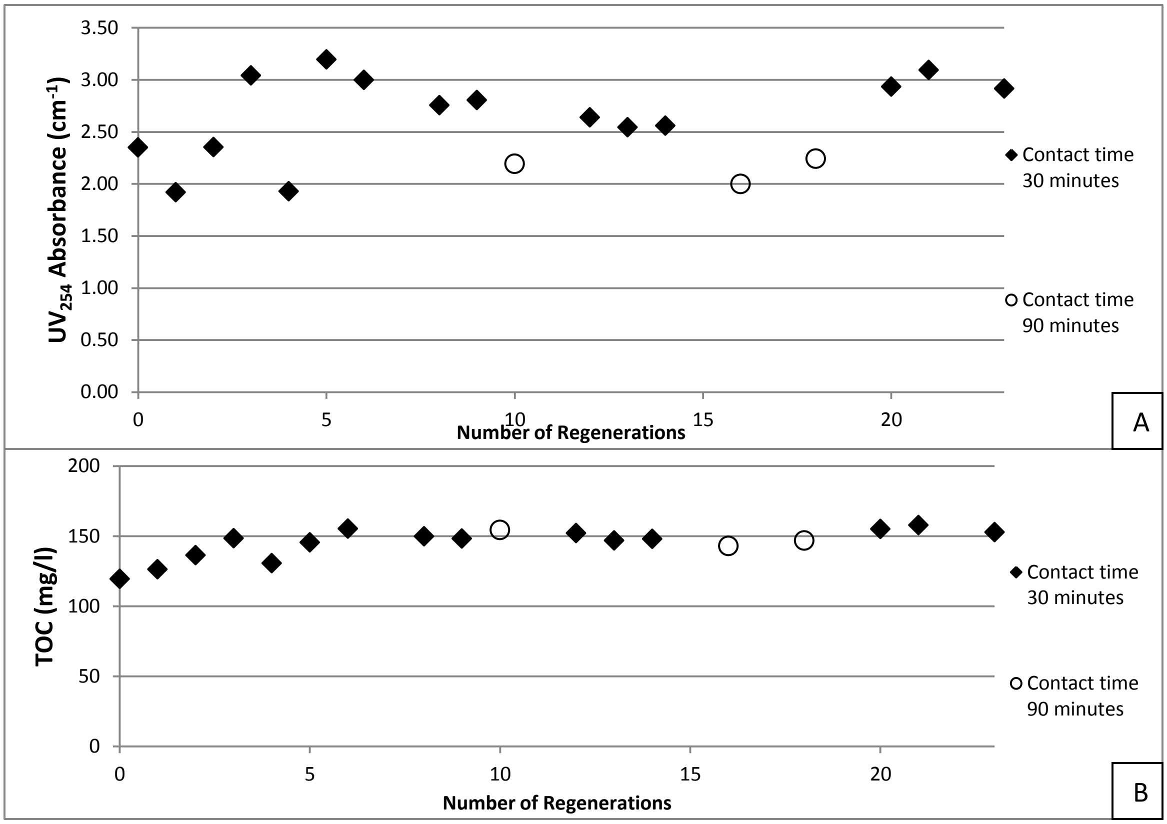

Figure 4- 2: Effect of regeneration on (A) UV_{254} values and (B) TOC at 50 g/L Dowex MSA for PA leachate

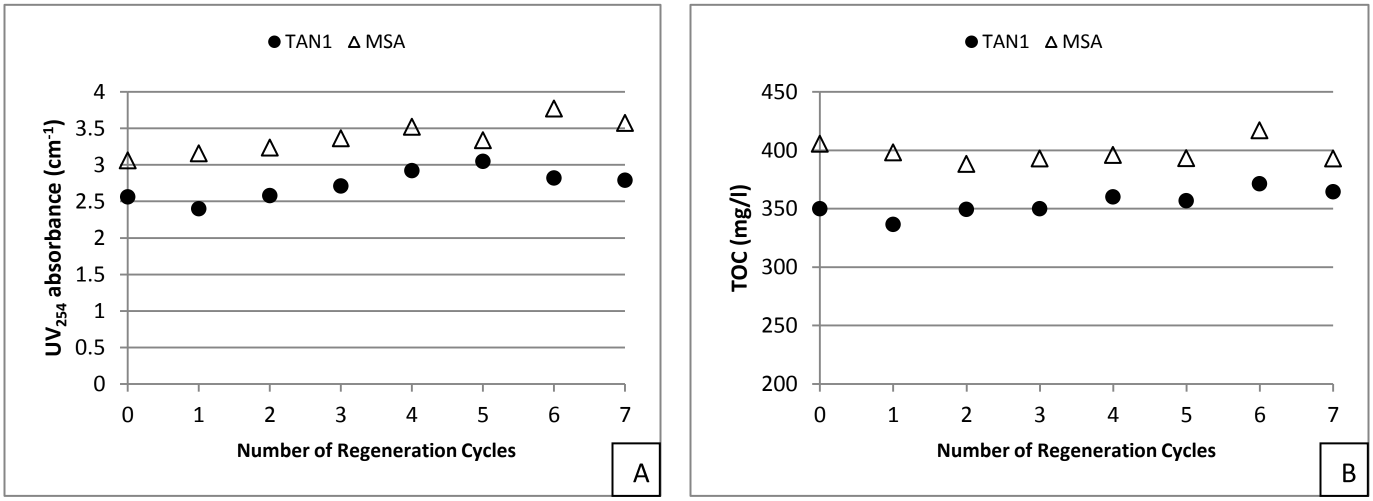

Figure 4- 3: Effect of Regeneration on (A) UV_{254} and (B) TOC at 100 g/L Dowex MSA and Dowex TAN1 for OL8 leachate

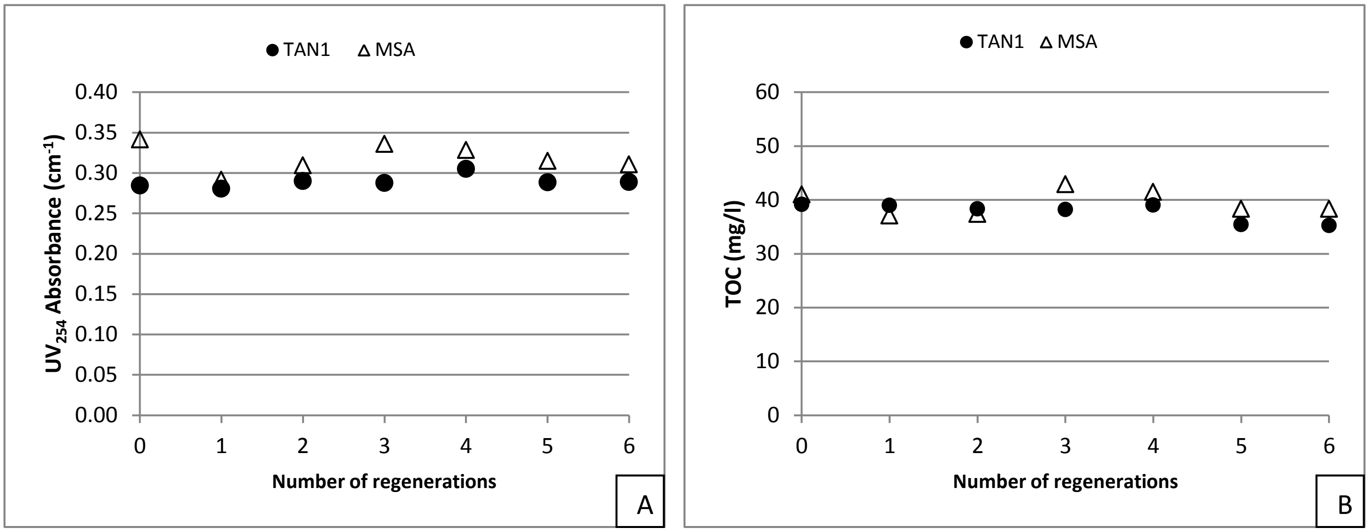

Figure 4- 4: Effect of regeneration on (A) UV_{254} and (B) TOC at 100 g/L Dowex MSA and Dowex TAN1 for OL5 leachate

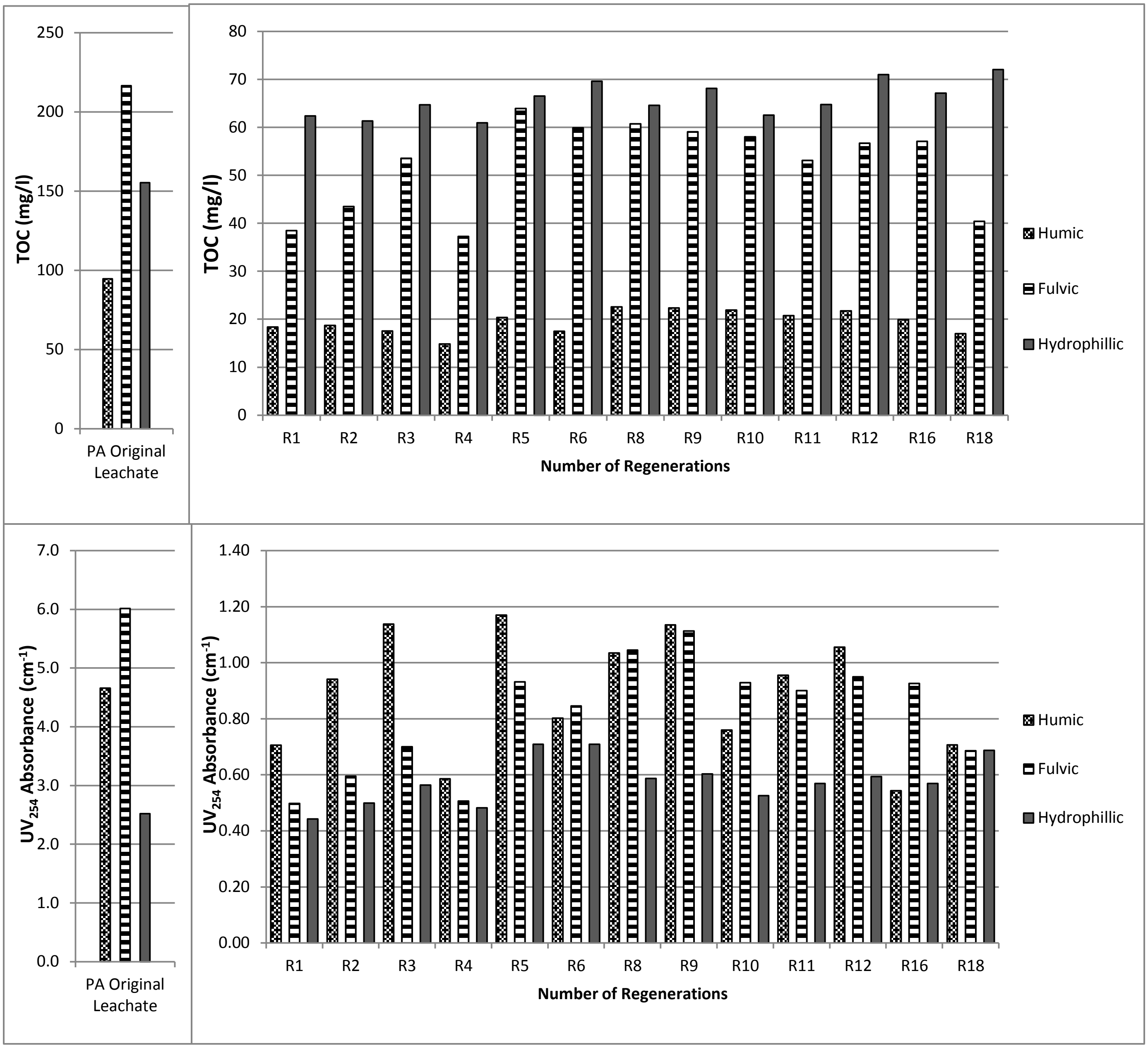

Figure 4- 5: Characterization of treated leachate samples for multiple regeneration cycles with Dowex MSA at 50 g/L

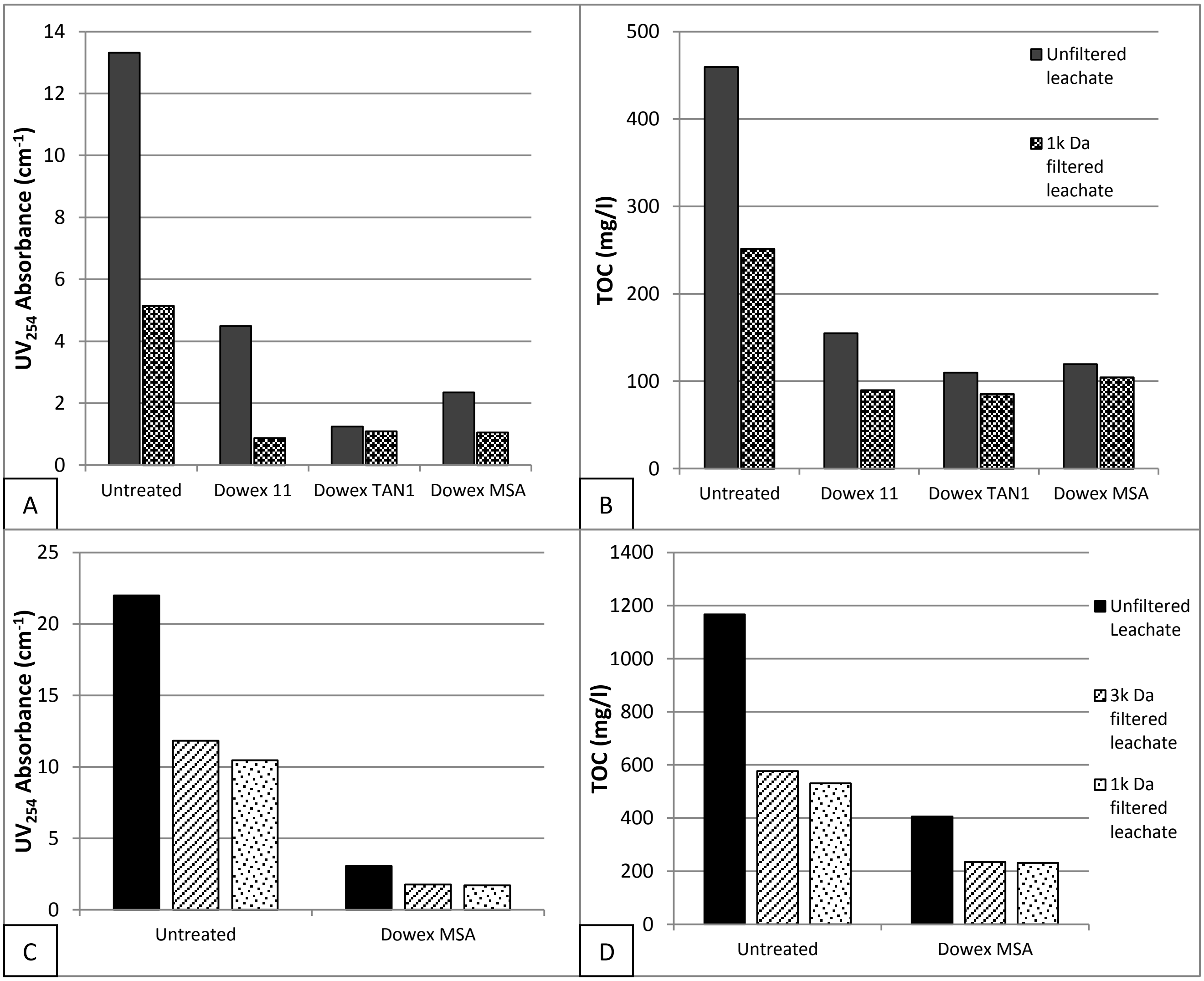

Figure 4- 6: (A) – UV_{254} absorbance and (B) TOC for PA leachate before and after membrane filtration for different resins, (C) UV_{254} absorbance and (D) TOC for OL8 leachate before and after membrane filtration for Dowex MSA

Chapter 5. Evaluation of Anion Exchange Resins in removing organic nitrogen from landfill leachates

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5.1 Abstract

Organic nitrogen is increasingly becoming a cause of concern because of its adverse environmental impacts such as eutrophication and potential for nitrogenous disinfectant by products formation. Landfill leachates contain large amounts of organic nitrogen and these could be a source of organic nitrogen in wastewater treatment plants. In this study, anion exchange resins, Dowex TAN1 and MSA were evaluated for their ability to remove organic nitrogen from leachates. Two leachate samples with different stabilization stages (young and old) from a Kentucky landfill and a biologically treated leachate from Pennsylvania landfill were utilized for this study. Both TAN1 and MSA performed similarly and were found to remove more than 50% organic nitrogen at a batch resin dose of 200 g/L. Regenerations conducted with the resins showed slight variability in the removal data. Fractionation of PA leachate into humic acid (HA), fulvic acid (FA) and hydrophilic (Hpi) fractions showed around 80% removal of bio-refractory Hpi fraction using anion exchange. Also, the organic nitrogen associated with HA fraction constituted the smallest fraction and had the greatest difficulty in its removal using anion exchange. Membrane filtration using 1000 and 3000 Da Molecular weight cutoff (MWCO) was performed on the leachate samples. For biologically treated leachate, almost all the organic nitrogen was < 1000 Da suggesting that this range of membrane filtration may not be useful for this leachate. But for young leachate substantial removal was observed after membrane filtration which further enhanced the performance of anion exchange resins.

Keywords: Landfill leachate, organic nitrogen, anion exchange resin, hydrophilic, membrane filtration,

5.2 Introduction

Landfilling is the most common method for disposal of municipal solid waste in throughout the world (Renou et al., 2008). But the decomposing solid waste in combination with percolating rainwater generates a highly polluted stream of wastewater referred to as leachate (Kurniawan et al., 2006). The leachate, if unchecked, seeps into the groundwater and pollutes it and therefore to prevent the seepage, modern landfills are installed with liners and leachate collection systems.

The general composition of leachate may include large amounts of organic matter, ammonia – nitrogen, some amount of chlorinated organics, inorganic salts, and heavy metals (Li et al., 2009). The presence of these potentially toxic compounds in leachates presents problems in their direct disposal to natural water bodies. It is therefore, imperative to treat landfill leachates before discharging them to natural waters. The leachate can be discharged to the surface waters (Anglada et al., 2009) after complete treatment but this is not very economical. Cost effective treatment options generally include discharging pre-treated leachate into municipal sewers where it can be treated in wastewater treatment plants (WWTPs). In the absence of sewers in close proximity to the landfill, leachates are frequently collected and transported to the WWTPs.

However, the considerable difference between characteristics of wastewater and leachate creates problems in the downstream treatment processes at WWTPs (Zhao et al., 2012). Lately, the presence of bio-refractory compounds in leachates has been a cause of concern (Vilar et al., 2011) because they can easily pass the biological treatment processes in the WWTPs and increase the organic matter in the effluent (Zhao et al., 2012).

In recent years, regulatory agencies have proposed stricter discharge limits on the total nitrogen in the effluent from WWTPs. The reason behind this is to prevent the problem of eutrophication in surface water bodies receiving the effluent from WWTPs. Organic nitrogen has been identified as a significant component of total nitrogen in wastewater effluents. The use of nitrification – denitrification systems at many WWTPs have been found to increase the organic nitrogen concentration in the effluent (Pehlivanoglu-Mantas and Sedlak, 2008). Organic nitrogen fractions as high as 80% of total nitrogen have been reported (Qasim et al., 1999).

Organic nitrogen can be a source of potentially carcinogenic nitrogenous disinfection by products (N-DBP’s) thereby adversely affecting the reuse of the effluent wastewater. It may also be responsible for eutrophication (Pehlivanoglu and Sedlak, 2004), posing a problem in the disposal of effluent wastewater to the surface water-bodies.

Landfill leachates generally contain large amounts of organic nitrogen (40-200 mg/l-N). Generally, the leachate may contain high amounts of other nitrogen sources such as ammonia nitrogen which can be easily removed through nitrification-denitrification. But the organic nitrogen is more bio-refractory than the organic carbon (Zhao et al., 2012) and cannot be removed effectively by the biological processes alone. Hence, leachate can be a major source of organic nitrogen in WWTPs (Zhao et al., 2012) which may not be removed completely in the WWTPs. Also, with tightening total nitrogen (TN) discharge limits (3-6 mg/l-N), most municipalities are asking for sewer input of around 30-50 g/l-N for total nitrogen. The presence of recalcitrant organic nitrogen makes it difficult for authorities to meet this limit and therefore, it is essential to pre-treat leachates before discharging them to WWTPs. Very limited literature is available on the available methods for removal of organic nitrogen from wastewater and leachate. Efforts have been made to identify the composition of organic nitrogen but most of the wastewater derived organic nitrogen (70%) still remains unknown (Pehlivanoglu and Sedlak, 2008). Hydrophobicity based studies have revealed the bulk of organic nitrogen to be hydrophilic in nature (Zhao et al., 2013). Various size distribution studies have been conducted and it has been found that bulk of organic nitrogen have molecular weight less than 1000 Da (Parkin and McCarty, 1981; Zhao et al., 2012; Pehlivanoglu and Sedlak, 2008). Therefore, membrane filtration might be utilized but it may not be entirely efficient due to fouling problems caused by organic matter (Kweon and Lawler, 2005).

In this study, two anion exchange resins were used for the treatment of landfill leachate for the removal of organic nitrogen. Two leachate samples at different stabilization stages and one biologically treated leachate were used to evaluate if leachate properties affect the removal of organic nitrogen. The initial study consisted of comparing the performance of resins for removing organic nitrogen from the leachates. Thereafter, the regeneration performance of the resin was evaluated to assess the efficacy of an ion exchange mechanism. Hydrophobicity based analysis was also conducted to identify the fraction (humic acid, fulvic acid and hydrophilic fraction) best removed by the resin. In addition, combined membrane filtration and anion exchange resins for removal of organic nitrogen have been evaluated to provide insight into adopting a viable method for organic nitrogen removal.

5.3 Materials and Methods

5.3.1 Leachate Sampling

The leachate samples that have been used in this study were collected from landfills located in Pennsylvania (PA) and Kentucky. The PA landfill has an on-site leachate treatment plant which performs nitrification/denitrification system and consists of a sequencing batch reactor activated sludge system. More details about the PA landfill leachate system can be found in Zhao et al.,(2012).

The Kentucky landfill has 8 separate individual units designated from Unit 1 to 8. Leachate samples for this study were taken from Unit 5 and Unit 8 whose average age are 16 and 2.5 years respectivley. No input has been made to Unit 5(OL5) in over a decade whereas Unit 8(OL8) is an active permitted landfill. The leachate from these units are stored underground onsite without any treatment under anaerobic conditions.

Based on their age and treatment methods, OL8 has been characterized as young leachate, OL5 as old leachate and PA leachate as biologically treated leachate.The leachates were shipped from landfills and stored in the Virginia tech at 4^{o}C to prevent any microbial activity from affecting the samples. Before any sampling for experimental purpose, the leachate containers were shaken vigourously to suspend the settled particles.

5.3.2 Resin Properties

Treatment of leachates was investigated using three different anion exchange resins manufactured by the Dow Chemical Company, Dowex MSA and Dowex TAN1. These resins were selected because they are strong base anion resin and have excellent organic removal capability as well as rapid exchange capacity. They can be operated in both the Cl^- and OH^- form and over a pH range of 0 – 14. The properties of these resins are listed in Pathak et al. (2013)

5.3.3 Experimental Process

Pretreatment

The leachate samples were microfiltered through a 1.5µm glass microfiber filters(42.5mm, Whatman 934-AH Glass Microfiber filters, GE Healthcare Biosciences Corp., Piscataway, NJ) to remove the suspended particles. The microfiltration was performed using 300 mL filtration cells (GELMAN, Ann Arber, MI) operating with a vaccuum pump.

Batch Experiments

The batch experiments were carried out to investigate the ion exchange equilibrium by using varying resin concentrations and 100 ml of leachate in 250 ml beakers. The beakers were stirred constantly during the experiments using a magnetic stir bar. Initial tests consisted of performing the kinetic studies to determine the optimal contact time needed by the resins. For these studies, an aliquot of sample was taken at specified intervals of 1, 5, 10, 20, 30, and 60 minutes and analyzed. Multiple regenerations of resin were also carried out and their treatment performance was evaluated to assess the loss in the removal capacity of the resin.

Fractionation

Characterization of leachate samples before and after treatment into Humic acid (HA), Fulvic acid (FA) and Hydrophillic (Hpi) components was done based on their hydrophobicity by passing them through DAX-8 non-ionic resin (Supelite DAX-8 resin, Sigma-Aldrich, St. Louis, MO) in accordance with the methods proposed by Thurman and Malcolm (1981) and Leenheer (1981).

The cleaned resin slurry (approximately 4 mL) was packed in 1.0 cm X 10 cm borosilicate glass column (Thomas Scientific, Swedesboro, NJ). The humic acid was precipitated and collected on 0.45 µm cellulose nitrate membrane (47 mm, Sartorius Stedim Biotech, France) by acidifying the leachate samples to pH 2 by adding concentrated HCL. The collected humic acid was redissolved in 0.1N NaOH solution and was used for further analysis. The supernatant consisting of Fulvic and Hydrophillic components was passed through DAX-8 resin column at a flow rate of 15 bed volumes per hour. Fulvic acids were retained on the resin column and the unabsorbed Hydrophillic fraction that passed through the resin column. The Fulvic acids retained on the DAX-8 resin were eluted by backwashing the resin column with 0.1N NaOH solution and the resultant eluent characterized as FA solution was used for further analysis.

Membrane Filtration

The apparatus for membrane filtration of the leachate samples consisted of a 200 mL stirred ultrafiltration cells (Amicon model # 8200), a nitrogen gas tank maintained at 120 kPa pressure and membrane discs (Millipore, Billerica, MA) with diameters of 63.5 mm. In this study, the molecular weight cutoffs (MWCO) for the membrane discs used were 1000 Da and 3000 Da(PLAC and PLBC, Millipore, Billerica, MA).

5.3.4 Chemical Analysis

All chemicals used in this experiment were of analytical grade. All the glassware used in this experiment were first detergent washed with water, rinsed, soaked in 10% nitric acid, rinsed with deionized (DI) water and baked at 450^{o} C for 4 h. The pH of samples was measured using a pH meter (Model No. 910, Accumet, Cambridge, MA) with a pH probe (Model No. 13-620-287, Accumet, Petalinga Jaya, Malaysia).

Estimation of organic nitrogen was done by subtracting the inorganic nitrogen from the total nitrogen (Westgate and Park, 2010). The inorganic nitrogen fraction is composed of nitrate, nitrite and ammonia nitrogen. There was a high concentration of ammonia present in the leachate from the Kentucky landfill and this was interfering with the determination of organic nitrogen. Hence, these leachate samples were subjected to ammonia stripping to remove the ammonia nitrogen before the determination of organic nitrogen.

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 exhausted resins were regenerated with 5% NaCl solution (regenerant brine). The regeneration experiments were conducted in batch mode by mixing the resins with regenerant brine for 180 minutes (Nyugen et al., 2011). The resins were washed with deionized water (DI) prior to regeneration with regenerant brine to remove the traces of leachate that might be present on the resin and again after the regeneration to remove the traces of regenerant brine.

5.4 Results

5.4.1 Kinetic removal of organic nitrogen

Figure 5-1 shows the removal of organic nitrogen with time for PA leachate treated with 100 g/L of MSA and TAN1. It can be observed for both MSA and TAN1 that 20 minutes contact time is sufficient to achieve equilibrium organic nitrogen removal. For MSA, the bulk of the removal (47%) was observed in the initial 1 minute of contact time whereas TAN1 was a little slower and the bulk of removal (47%) for TAN1 occured after 5 minutes of contact time. A similar contact time, 20 minutes, was found to be sufficient for the removal of UV_{254} absorbance and total organic carbon (Pathak et al., 2013). All the experiments were conducted with 30 minutes of contact time unless specifically mentioned.

5.4.2 Impact of resin dosage on organic nitrogen removal

Figure 5-2 shows the performance of resins in removing organic nitrogen from the PA , OL8 and OL5 leachate samples.There is an observable difference between the untreated organic nitrogen values of the three untreated leachate samples. PA leachate has undergone prior biological treatment on-site whereas OL8 leachate is from a newer landfill and has not undergone any treatment (young leachate). OL5 leachate is from an inactive landfill which has been closed for more than 16 years (stabilized leachate). The difference between OL8 and OL5 is that the former has a high organic matter constituent that can undergo bio-degradation, but OL5 has a high percentage of non-biodegradable organics remaining after long term landfilling.

Figure 5-2(A) shows the organic nitrogen removal for the PA leachate at different resin dosages. It can be seen that both MSA and TAN1 perform almost identically. At 50 g/L resin dose, both TAN1 and MSA decreased the organic nitrogen value from 48 mg/L – N to 19 mg/L – N, a 60% reduction in organic nitrogen. At 200 g/L, they decreased the organic nitrogen to 13 mg/L – N, a 72 % reduction.

Figure 5-2(B) shows PA leachate subjected to sequential resin treatment by MSA and TAN1. The leachate was first treated with either MSA or TAN1 and then the treated leachate was subjected to the other resin. Here 50 g/L MSA + TAN1 indicates that the leachate was first treated with 50 g/L MSA and then the treated leachate was again subjected to 50 g/L TAN1. It was observed that both resin arrangements produced nearly identical results suggesting that both TAN1 and MSA perform in nearly identical manner in removing organic nitrogen. At a 200 g/L sequential resin dose, both MSA + TAN1 and TAN1 + MSA achieved around 80% removal bringing the organic nitrogen in the effluent to 8 and 10 mg/L-N. This shows that though the increasing the resin dosage does not proportionally & significantly improve the organic nitrogen removal from the leachates, it is still possible to effect good removal using the anion exchange resins.

Figure 5-2(C) shows the organic nitrogen removal for the OL8 leachate. It was found that at 50 g/L, MSA and TAN1 decreased the organic nitrogen from 148 mg/L – N to around 82 mg/L- N (45% removal)and 84 mg/L – N (43% removal), respectively. After the treatment with 200 g/L ,the organic nitrogen of the effluent was around 72 mg/L – N(51% removal) for MSA and 67 mg/L –N (55% removal) for TAN1.

Figure 5-2(D) shows the removal of organic nitrogen for OL5. Since it has undergone long term landfilling, only a resin dose of 100 g/L was tested. MSA brought down the organic nitrogen from 30 mg/L – N to 19 mg/L – N (37% removal) whereas TAN1 achieved almost 47% removal, decreasing the organic nitrogen to 16 mg/L – N.

It was observed that removal of around 50% was observed in all the cases suggesting the significant presence of anionic character in the organic nitrogen in the leachates. Moreover, looking at OL8 and OL5 untreated values, even after long term landfilling, a siginificant amount of organic nitrogen was present indicating its recalcitrant nature. This is important as this clearly suggests that biological processes in their entirety would not work for the removal of organic nitrogen and that physical-chemical processes need to be explored.

It also appears that both TAN1 and MSA behave in an almost identical manner which was further confirmed by the sequential resin treatment.

5.4.3 Effect of regeneration

As observed earlier, a very high resin dosage is required to effect significant organic nitrogen removal. The ion exchange resins are expensive (Grote and Schumacher), so to be economically viable, these resins must be regenerated and used again many times. Therefore, the regeneration potential of the resins was investigated.

Multiple regenerations were performed with both MSA and TAN1 at the resin dosage of 50 g/L for PA leachate. Initially 6 regenerations were performed with both the resins but it was observed that the TAN1 resin beads were physically breaking down and deteriorating during stirring in the batch experiments. Since the behavior of both resins seemed identical, further regenerations were carried out with MSA only. Figure 3 shows the regeneration performance of MSA at 50 g/L resin dose.

It can be seen that after the first regeneration, the organic nitrogen values in the effluent started going up showing an increasing trend but after the 12th regeneration the values were nearly similar to the one obtained after the use of new resin. Also it should be noted that after observing that the organic nitrogen values in the effluent were increasing, the contact time between the resin and leachate was increased from 30 minutes to 90 minutes after 10th, 16th and 18th regeneration to assess the effect of contact time on removal efficiency as the regenerations progress. It was observed that after 10th regeneration, no favorable result was obtained i.e. the organic nitrogen value was not similar to the one obtained by the new resin. The organic nitrogen values after 16th and 18th regeneration were similar to the performance of the new resin. But, the value after 23rd regeneration when the contact time was again 30 minutes was similar to the performance of the new resin suggesting that increasing the contact time had no favorable effect on removal performance of the resin. There was some variability observed in the organic nitrogen data with the value lying in the range of 19-25 mg/L – N for the number of regeneration cycles. But after 12th regeneration, the deterioration stopped with the regenerated resin performing similar to the new resin.

5.4.4 Distribution of organic nitrogen among the hydrophobic and hydrophilic fractions

Figure 5-4 shows the distribution of organic nitrogen into humic acid (HA), fulvic acid (FA) and hydrophilic fraction (Hpi) for the PA leachate sample before and after treatment with MSA resin. The distribution of organic nitrogen in different fractions is: HA – 5.7 mg/L – N (12.5%) , FA – 8.79 mg/L – N (19.3%) and Hpi – 31 mg/L – N (68.2%). It can be observed that the Hpi fraction constitutes the bulk of organic nitrogen in the untreated leachate sample followed by the FA and the HA fraction. This is in agreement with Zhao et al., (2013) where it was reported that Hpi was the biggest fraction of organic nitrogen in the leachate samples examined. From Figure 5-4, it can be seen that at resin concentration of 50 g/L, the Hpi fraction decreases from 31 mg/L –N to 9.8 mg/L – N or 68% removal of the Hpi fraction. At the resin concentration of 200 g/L, the Hpi fraction reduces to 6 mg/L – N (80% removal). Zhao et al., (2013) also found that the organic nitrogen in the Hpi fraction becomes increasingly recalcitrant with age, suggesting that removal of this fraction by biological means is difficult but the significant removal observed using ion exchange indicates towards the possibility of using anion exchange for removing the recalcitrant Hpi fraction.

It can also be observed that although Hpi is the biggest fraction, the FA and HA fraction together account for roughly 30% of the organic nitrogen in the PA leachate. With the tightening regulations and increasing concern over the disadvantages associated with organic nitrogen, removal of these two fractions is also of considerable importance. It can be observed that the FA fraction decreases from 8.79 mg/L – N to 3.5 mg/L – N (60% removal) at 50 g/L resin dose and 2.16 mg/L – N (75% removal) at 200 g/L. For HA fraction, the results are very different. At 50 g/L, the organic nitrogen in the HA fraction decreased from 5.7 mg/L – N to 5.35 mg/L – N and at 200 g/L to 4.3 mg/L – N. This suggests that although good removal of bio-refractory Hpi and FA fraction is possible by anion exchange, removal of the HA fraction is problematic.

5.4.5 Effect of combined membrane filtration and ion exchange

Typically the HA fractions comprises of high molecular weight organic substances which might be adversely affecting the removal of organic nitrogen. To study if membrane filtration improves the performance of resins in removing organic nitrogen, the leachate samples were filtered through 3000 and 1000 Da membranes to remove the bulk of HA and some FA fractions. Figure 5 shows the effect of membrane filtration on the removal of organic nitrogen from PA (figure 5(A)) and OL8 (figure 5(B)) leachate. It can be seen from figure 5(A) for PA leachate that there was almost no removal of organic nitrogen after passing the leachate through both 3000 and 1000 Da membranes. But, for the OL8 leachate as shown in figure 5(B), there is substantial decrease in organic nitrogen values after filtering the leachate through 3000 Da (40% removal) and 1000 Da (42% removal) membranes. This could be attributed to the fact that PA leachate has undergone prior biological treatment. Thus, higher MW associated fractions of organic nitrogen could have been removed from the PA leachate during the prior biological treatment leaving the recalcitrant residue. This also confirms that the recalcitrant fraction is less that 1000Da which is in agreement with the results of (Zhao et al., 2012) and (Zhao et al., 2013). (Pehlivanoglu-Mantas and Sedlak, 2008) also reported for municipal wastewater that organic nitrogen fraction with molecular weight less than 1000Da accounted for 67 ± 24%. But there is a substantial presence of higher MW fractions of organic nitrogen (around 40%) in raw untreated OL8 leachate which is easily removed through membrane filtration. Also there was no observable difference between the 3000 and 1000 Da membranes which again suggests the presence of higher MW associated organic nitrogen in OL8 leachate.

For OL8, the 1000 Da membrane filtered leachate was subjected to 100 g/L MSA and TAN1. It was observed that the overall removal of organic nitrogen was 67% for MSA and 62% for TAN1. Comparing this with the performance of resin on bulk leachate (not membrane filtered), it can be seen that there is substantial improvement (17% increase for TAN1 and 27% increase for MSA at the 100 g/L resin dose) in the performance of resin in removing organic nitrogen.

Thus membrane filtration with 1000 or 3000 Da for removal of organic nitrogen is suitable for leachates which have not been subjected to any prior biological treatment.

5.5 Summary & Conclusions

Dowex MSA and Dowex TAN1 were evaluated for the removal of organic nitrogen from three different leachate samples. Following observations were made

1) Significant removal of organic nitrogen was observed indicating the highly anionic character of organic nitrogen in leachates. In case of PA leachate, removal as high as 80% was observed at sequential resin dose of 200 g/L for MSA +TAN1. Substantial amount of organic nitrogen was present in OL5 subjected to long term landfilling which confirms the bio-refractory nature of organic nitrogen.
2) Increasing the resin dose did not proportionally increase the organic nitrogen removal but the 23 regeneration cycles showed their ability to be effectively regenerated for organic nitrogen removal. This suggests that anion exchange resin can be a viable alternative even if higher dosage of resin is needed to effect certain removal.
3) Fractionation of PA leachate showed that the Hpi fraction constituted the bulk of organic nitrogen but despite its bio-refractory nature, around 80% removal was observed. On the other hand, the HA fraction which constituted the smallest fraction had difficulty getting removed by anion exchange resins.
4) Membrane filtration (using 1000 and 3000 Da membranes) significantly improved the performance of young OL8 leachate but was found to be inadequate in case of

biologically treated PA leachate. This indicates the suitability of membrane filtration only for the untreated leachates though that might lead to the fouling of membranes.

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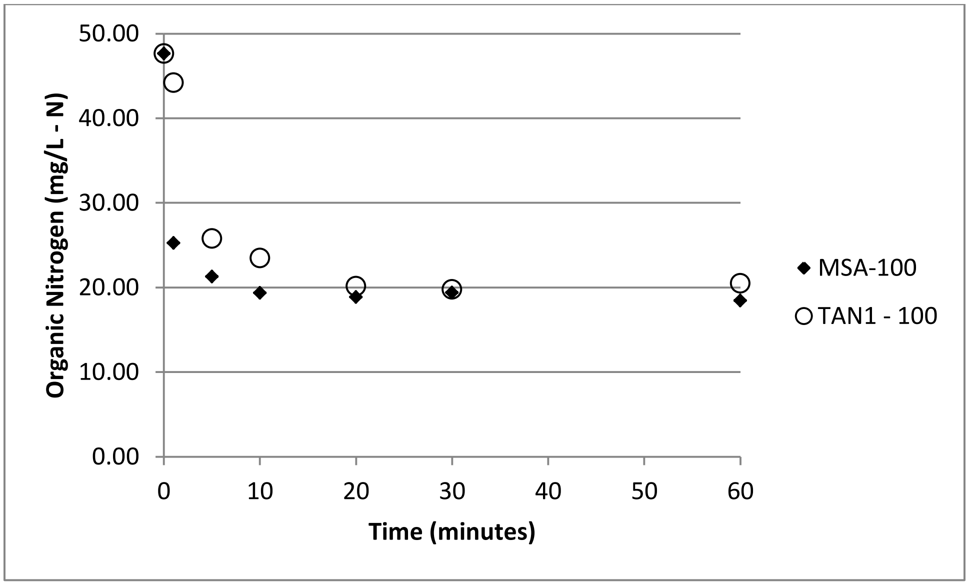

Figure 5- 1: Effect of contact time on organic nitrogen removal for MSA and TAN1 at 100 g/L resin concentration

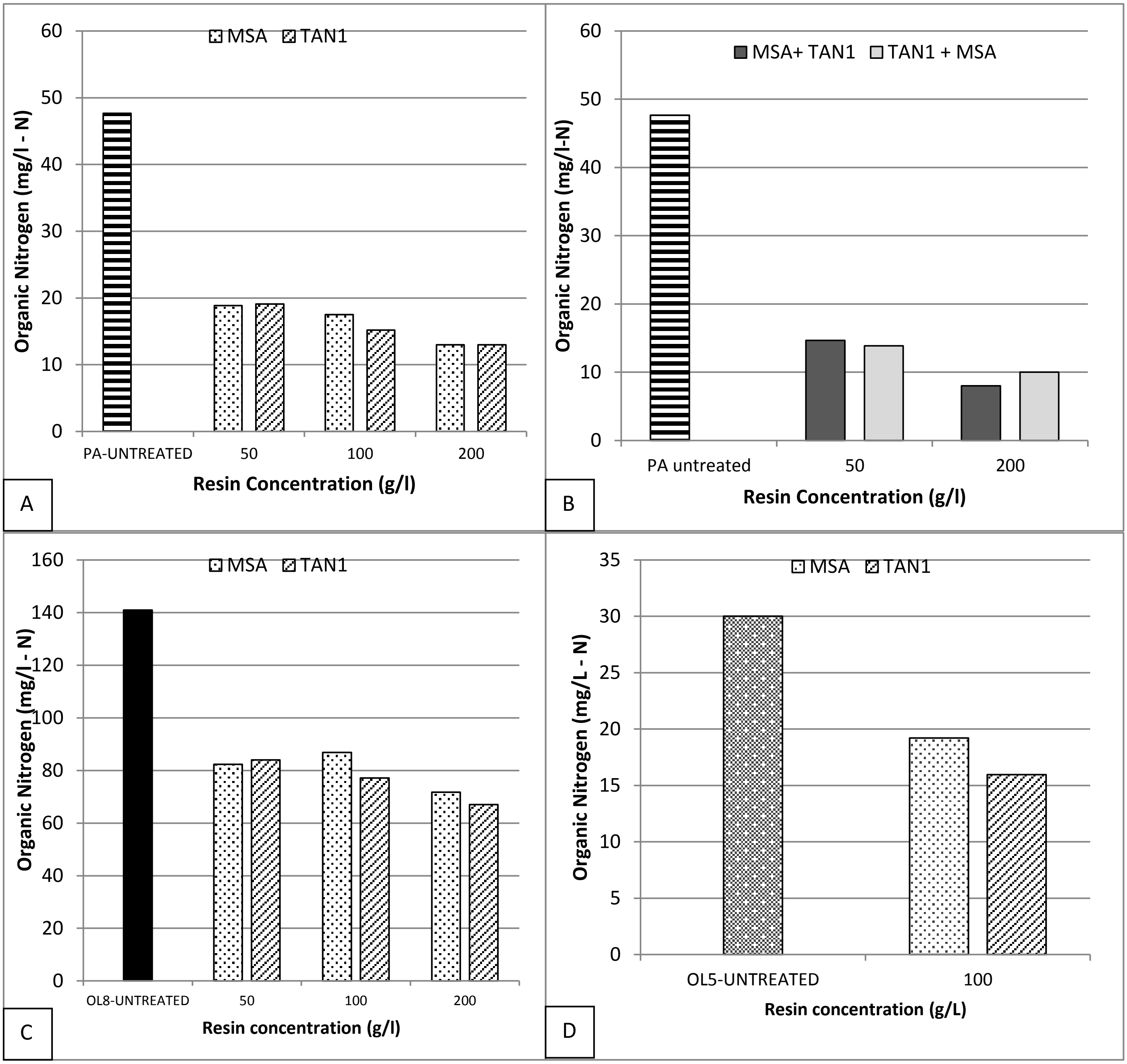

Figure 5- 2: Effect of resin concentration on organic nitrogen removal for PA, OL8 and OL5 leachate

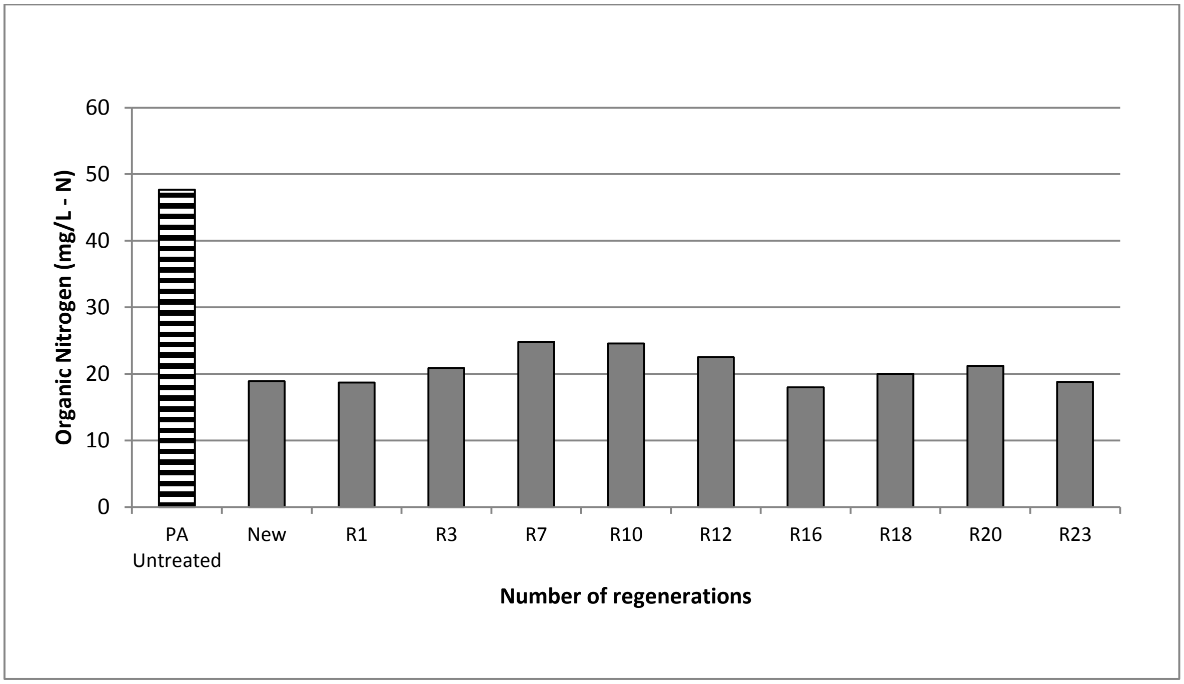

Figure 5- 3: Regeneration performance of MSA at resin dose of 50g/L for PA leachate

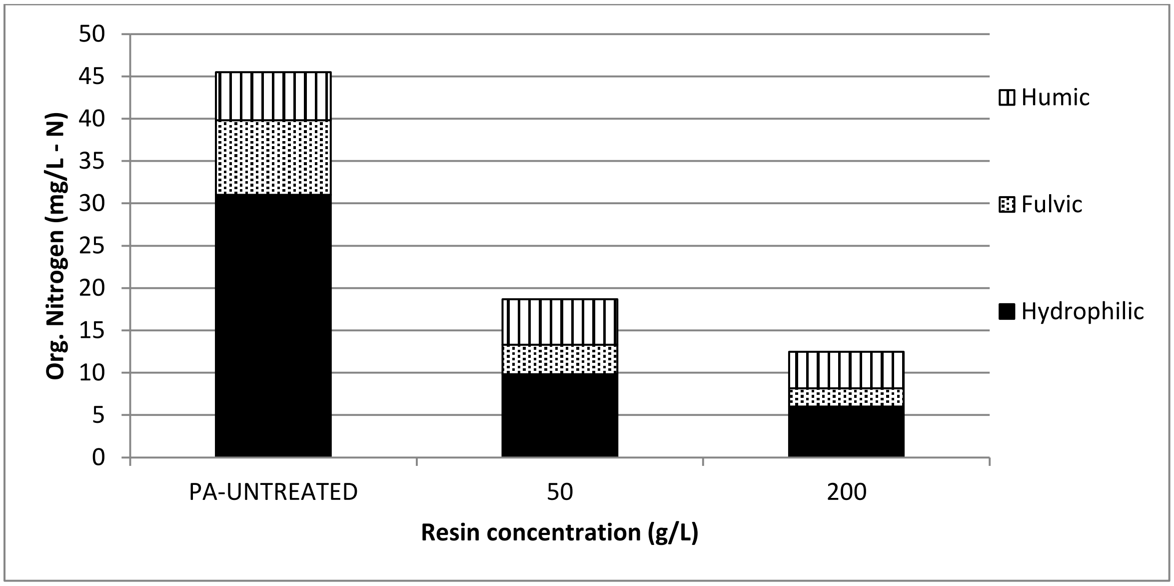

Figure 5- 4: Distribution of both treated and untreated leachate sample on the basis of hydrophobicity into HA, FA and Hpi fractions for PA leachate using MSA after first regeneration at 50 g/L and 200 g/L

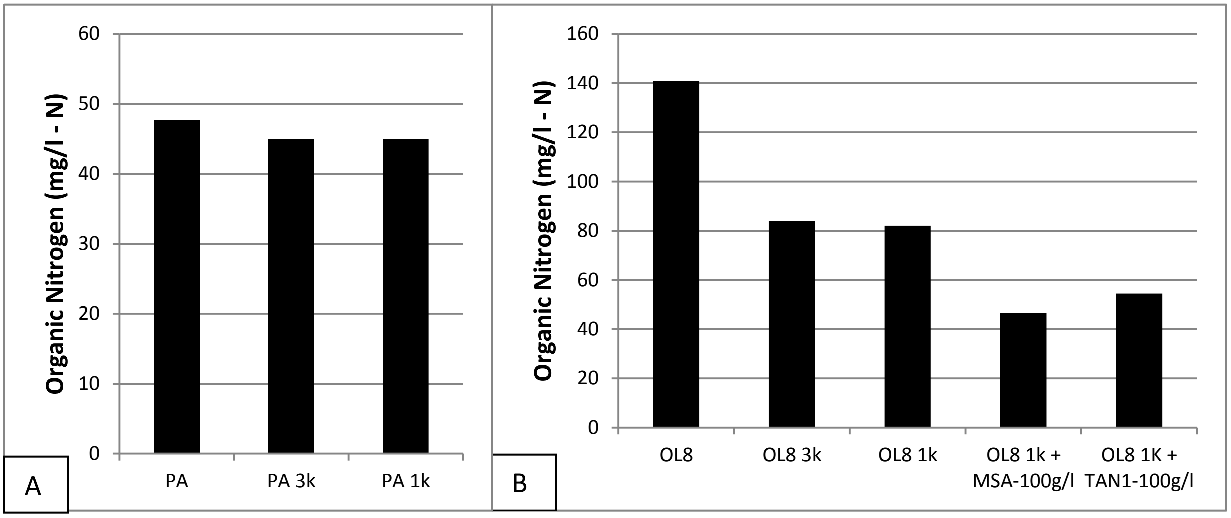

Figure 5- 5: Effect of membrane filtration on organic nitrogen removal for (A) PA leachate and (B) OL8 leachate