CHARACTERISTICS AND TREATMENT OF LANDFILL LEACHATE AND OPTIMIZATION OF LEACHATE OXIDATION WITH FENTON'S REAGENT

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ABSTRACT

The purpose of this study was to characterize the leachate from a landfill in Pennsylvania that had been pretreated by activated sludge and propose the most efficient treatment for this effluent. These samples had been pretreated in a sequencing batch reactor that also was operated to remove nitrogen by nitrification/denitrification. The SBR samples were found to have low BOD, high COD, high TOC and a very low BOD/COD ratio. These SBR decant samples have poor UV transmittance and hence quench UV light. Five treatment methods were evaluated, coagulation, ultrafiltration, combined coagulation/ultrafiltration, combined ultrafiltration/oxidation and combined filtration/fentons. These processes were tested for their ability to remove BOD and TOC and also to evaluate the improvement in UV transmittance. It was found that coagulation; Ultrafiltration and Ultrafiltration combined with coagulation do not work in improving the transmittance properties though there is a significant BOD and TOC removal with these processes. Ultrafiltration combined with oxidation was found to work the best in terms of TOC removal. In this study, four oxidants, $KMnO_4$, H_2O_2, NaOCl and Fenton's reagent were used. It was observed that Fenton's reagent was capable of removing 90% TOC at a dose of 1g/L each of iron salt and hydrogen peroxide at a pH of 4.5. Since Fentons reagent was found to be the most effective method, hence, efforts were made to optimize the oxidation process with Fenton's. The two parameters which were studied were the initial pH and the chemical dosage. The initial pH was varied from a value of 2.5 to 6.5. The range of iron salt and peroxide dose used was from 0.05 to 0.1 g/L

Additional studies were conducted using samples filtered through a 0.45 μm filter and oxidized with Fenton's reagent. The Fenton's process for oxidation of filtrates from the 0.45μm filter was also optimized with respect to pH and chemical dosage to determine the most economical operating conditions. The maximum transmittance of 57% was obtained for an iron dose of 0.075 g/L and a peroxide dose of 0.075 g/L at a pH of 4.5. This is in comparison to the transmittance of unoxidized 1K ultrafiltrate which was found to be 21.5%. There was a significant difference in the performance of 1K and 0.45μm filtrates in terms of TOC removal and percentage transmittance. The oxidation process for improving the UV transmittance of leachate can therefore be economically optimized depending upon the desired efficiency by varying the operational parameters.

To my parents, sister and loving boyfriend

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(I) *CHARACTERISTICS AND TREATMENT OF LANDFILL LEACHATE*

Abstract

The purpose of this study was to characterize the leachate from a landfill in Pennsylvania that had been pretreated by activated sludge and propose the most efficient treatment for this effluent. These samples had been pretreated in a sequencing batch reactor that also was operated to remove nitrogen by nitrification/denitrification. The SBR samples were found to have low BOD, high COD, high TOC and a very low BOD/COD ratio. These SBR decant samples have poor UV transmittance and hence quench UV light. Five treatment methods were evaluated, coagulation, ultrafiltration, combined coagulation/ultrafiltration, combined ultrafiltration/oxidation and combined filtration/fentons. These processes were tested for their ability to remove BOD and TOC and also to evaluate the improvement in UV transmittance. It was found that coagulation works well for BOD and TOC removal, but does not help in improving the UV transmittance. The maximum BOD and TOC removal obtained using coagulation as a treatment method was 50%. Ultrafiltration works better in BOD removal and also in improving the UV transmittance, but it does not work very well for TOC removal. The maximum transmittance obtained was 20% for a 1K ultrafiltrate. Ultrafiltration combined with coagulation works better than ultrafiltration alone in terms of TOC removal but the results were similar for UV transmittance. Ultrafiltration combined with oxidation was found to work the best in terms of TOC removal. In this study, four oxidants, $KMnO_4$, H_2O_2, NaOCl and Fenton's reagent were used. It was observed that Fenton's reagent was capable of removing 90% TOC at a dose of 1g/L each of iron salt and hydrogen peroxide at a pH of 4.5.

1 Literature Review

1.1 Introduction

Landfills are the most popular methods used worldwide for the disposal of municipal solid wastes (MSW). Approximately 95% of the total MSW collected worldwide is disposed of in landfills landfills (Diamadopoulos, 1994). The other alternatives such as recycling, composting and incineration have also been used, but these methods are more expensive and less widely used.

Leachate is produced by the degradation of the organic fraction of the waste in the landfill combined with the percolation of rainwater (Kjeldsen *et al*., 2002). Landfill leachate can be a potential source of ground and surface waters contamination if it percolates through soils and subsoils, thereby causing extensive pollution of streams, creeks and water wells. Hence, it is essential to ensure proper collection, treatment and safe disposal of landfill leachate (Mott *et al*., 1987).

Landfill leachate is generally characterized by a high strength of pollutants, such as organics, ammonium, inorganic salts and heavy metals (Horan *et al*., 1997). The properties of leachate exhibit temporal and site specific variations depending on the type of deposited wastes, the quality of refuse, hydrogeological factors and mainly the age of landfill (Ehrig, 1984; Crawford *et al*., 1985). The biodegradability of the leachate decreases as the age of landfill increases. In general, young leachate has high biological oxygen demand (BOD) and even higher chemical oxygen demand (COD) (Kjeldsen *et al*., 2002). Such leachate can be treated by biological processes. In fact, the characteristics of biologically pretreated young leachate are similar to that of mature leachate in terms of COD, BOD, pH and alkalinity (Alvarez-Vazquez *et al*., 2004; Wang *et al*., 2004).

Leachate from an aged landfill therefore has lower biodegradability and is comparatively stable as compared to the leachate from a new landfill. Therefore, biological treatment can be expected to be less effective for the treatment of most old landfill leachates (Medez *et al*., 1989). The BOD of aged leachate is primarily caused by refractory organics which mainly consists of dissolved organic matter (DOM) (Trebouet *et al*., 2001; Wang *et al*., 2003; Rivas *et al*., 2004). The components of refractory organics include humic substances (HS), which include humic acids (HA) and fulvic acids (FA) (Chian, 1977; Kjeldsen *et al*., 2002; Nanny *et al*., 2002). HS are refractory anionic macromolecules of moderate (1 kDa MW-FA) to high (10 kDa MW-HA) molecular weight (MW) (Xu *et al.,* 2006).

For the treatment of biologically stable leachate, physicochemical treatment processes are often needed (Ozturk *et al.,* 2003). These processes include electrochemical oxidation (Moraes *et al.,* 2005), coagulation–flocculation (Amonkrane *et al.,* 1997, O'Melia *et al., 1999,* Wang *et al., 2002,* Tatsi *et al.,* 2003), membranes (Osturk *et al.,* 2003, Martinnen *et al., 2002)*, combinations of coagulation, flocculation and chemical oxidation (Rivas *et al.,* 2004), advanced oxidation (Lopes de Morais *et al.,* 2005), ozonation (Monje *et al.,* 2004*,* Bilaa *et al.,* 2005, Poznyak *et al.,* 2004), combination of ozonation and Fenton's reagent. Many researchers have studied the performance of these methods. Table 1-1 shows the results of a review conducted by Kurniawan *et al*., 2005 which show the relative performance and application of various physicochemical treatment methods. However, because of the variation in leachate characteristics, the success of individual methods remains leachate specific.

Table 1-1 Summary of application of physico-chemical treatments for stabilized landfill leachates			
Type of treatment	**Type of removal**	**Remarks**	**References**
Coagulation-flocculation	Heavy metals and suspended solids	High sludge production and subsequent disposal may be a problem	(O'Melia *et al., 1999*)
Chemical precipitation	Heavy metals and NH_3-N	Requires further disposal due to sludge generation	(Charerntanyarak *et al.*, 1999)
Ammonium stripping	Ammoniacal Nitrogen	Requires other equipments for air pollution control	(Ali *et al.*, 2004)
Microfiltration	Suspended Solids	Used after metal precipitation	(Visvanathan *et al.*, 1994)
Ultrafiltration	High molecular weight compounds	Costly and limited applicability due to membrane fouling	(Saffaj *et al.*, 2004, Syzdek *et al.*, 1984)
Nanofiltration	Sulphate salts and hardness ions, like Ca (II) and Mg (II)	Costly and requires lower pressure than reverse osmosis	(Alborzfar *et al.*, 1998)
Reverse Osmosis	Organic and Inorganic compounds	Costly and expensive pretreatment is required prior to RO	(Cornellison *et al.*, 2001)
Activated Carbon Adsorption	Organic compounds	Carbon fouling can be a problem and GAC adsorption is costly	[Kargı *et al.*, 2003)

Ion exchange	Dissolved compounds, cations/anions	Used as a polishing step after biological treatments and treatment cost is high	(Fettig *et al.*, 1999)

1.2 Coagulation of leachate

Coagulation is one of the important processes in the treatment of water and also industrial wastewater. Several researchers have studied the use of coagulation for the treatment of leachate. Coagulation–flocculation can be used as both a pretreatment method for fresh leachate or as a post-treatment technique for partially stabilized leachate (Tatsi *et al*., 2003). Coagulants that have been commonly used are Aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate (Ehrig 1984; Amokrane *et al*., 1997). Many researchers have worked on optimizing the performance of this process in terms of type of coagulant, dose of coagulant, pH etc. Iron salts have proven to be more efficient than aluminum salts, resulting in considerable chemical oxygen demand (COD) reductions (up to 56%), whereas this value in case of alum and lime was comparatively lower (39 or 18%), respectively (Diamadopoulos, 1994). It was also found that greater COD reduction was obtained in the case of partially stabilized leachate (>75%) as compared to fresh leachate where the reduction was 25-38% (Tatsi *et al.*, 2003).

1.3 Ultrafiltration of leachate

Microfiltration, ultrafiltration and reverse osmosis are the membrane processes that have been historically applied for the treatment of landfill leachate (Chian *et al.,* 1976; Syzdek *et al.,* 1984; Slater *et al.,* 1983; Krug *et al.,* 1988; Bilstad *et al.,* 1992; Parveau, 1993). There have been attempts to characterize raw leachate using membrane fractionation before treatment (Park *et al*., 2001) and also after treatment (Bae *et al*., 1999; Gourdon *et al.,* 1989).

There have been studies in which ultrafiltration has been combined with other physicochemical as well as biological processes (Pirbazari *et al.,* 1996). In their work, Yoon *et al*., 1998, fractionated the aerobic lagoon effluents with 1000 MWCO and 500 MWCO membranes. The fractions were then coagulated followed by oxidation with Fentons reagent. The TOC removal efficiency was then investigated. In another study, Wang *et al*., 2006 investigated the molecular size distribution of an aged raw landfill leachate before and after oxidation with O_3 only and O_3/H_2O_2. They found that the fractionation of aged raw landfill leachate resulted in the fractionation of metals with humic substances. They could relate the metals to the molecular size distribution. Samples of size 0.45 μm–10,000 Da and 10,000–5000 Da were rich in Co, Cr, Cu, Fe, Ni, Pb, Sb, Sn, Ti and Zn while the sample of .45 μm–10,000 Da were enriched with Ag, Al, As, Cd , Hg and Mo. Similarly, V was predominant in the sample of 5000–1000 Da; and samples of size <1000 Da were enriched with Bi. Membrane fractionation was also helpful in defining color removal efficiently for each fraction. From this study, it appears that most of the metals are not soluble ions but are associated with various organic materials.

They could also define the fractions for which addition of H_2O_2 had a significant effect on the corresponding COD reduction. Hence, they could define the size range of the organics that cause BOD, COD and color. They determined that the organic compounds with molecular weight less than 10,000 Da were the major COD and BOD_5 contributors, while the organic compounds with molecular weight larger than 1000 Da made the major color contribution. In another study, Li *et al*., 2009 analyzed the behavior of organic matter and heavy metals in raw and treated leachates using ultrafiltration. They found that the organic matter in both raw and treated leachate existed as truly dissolved fractions. The percentage of the truly dissolved organic matter was higher in raw leachate from a new landfill as compared to the mature landfill which primarily contained biorefractory organics. However, after anaerobic treatment, new landfill leachate and raw leachate from a mature landfill had similar size fractions of organics. They also determined that the treatment processes were effective for the organic matter of size range 1-10 kDa.

1.4 Chemical oxidation

Advanced oxidation is one of the available treatment technologies that are used to oxidize the refractory organics in leachate into harmless substances and hence, make the leachate more biotreatable. Such oxidants have the capability to oxidize such organics into mineralized end products such as carbon dioxide and water (Perez *et al*., 2002; Gogate *et al.,*2004; Pera-Titus *et al*., 2003; Chidambara *et al.,*, 2005).

Chlorine, ozone, hydrogen peroxide, potassium permanganate and calcium hypochlorite are some of the oxidants which are generally used for drinking water treatment. But these oxidants were also later applied for treatment of leachate. (Chian *et al.*, 1976)

In recent years, advanced treatment processes (AOPs) have gained popularity as compared to the traditional oxidants. Such processes generate hydroxyl radical which is a very strong oxidant and is effective in degrading the refractory organics present in landfill leachate. Typical AOPs includes O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, H_2O_2/Fe(II), TiO_2/UV, and TiO_2/H_2O_2/UV (Huang *et al.,* 1993). It was found that Ozone in combination with H_2O_2 worked better than ozone alone (Wang *et al.,* 2006; Hagman *et al.,* 2008). In their study, Tizaoui et al. found that ozone efficacy was almost doubled when it was combined with hydrogen peroxide. However, he also found that the performance decreased with an increased dosage of H_2O_2.

The most widely used treatment technology in recent years has been Fenton's reagent. In this process, hydrogen peroxide is added with ferrous sulfate to break down the refractory organics. The oxidation is brought about by hydroxyl radicals that are produced during the reaction between peroxide and ferrous ion and serves as a strong oxidant. The mechanism of Fenton's reagent can be found elsewhere (Harber *et al.*,, 1934; Barb *et al.,* 1951). The oxidation process by Fenton's is generally composed of four stages (Bigda, 1995), pH adjustment, oxidation reaction, neutralization, coagulation and precipitation. The organics therefore get removed at two stages, oxidation and coagulation. Fenton's reagent can be used as a pretreatment or post treatment for landfill leachate. Papadopoulos *et al.,* 1994 used Fenton's reagent (100 ml, 30%, w/w H2O2 and 40 mg Fe2+ per liter leachate) to chemically oxidize leachate (initial COD range of 6500–8900 mg/L) after aerobic biological treatment and observed up to 33% COD reduction. Lau *et al.,* 2001 employed Fenton's (200 mg/L of H_2O_2 and 300 mg/L of ferrous ion) and coagulation to treat landfill leachate following UASB treatment and observed a 70% residual COD removal in the UASB effluent. Fenton's reagent is also used as a pretreatment step to increase the biotreatability of the leachate. Kim *et al.,* 2001 used coagulation and Fenton's oxidation to treat stabilized leachate and observed that the BOD_5/COD ratio improved from an initial range of 0.11–0.17 to 0.45. The efficiency of the oxidation process with Fenton's depends on number of operational parameters such as initial pH, absolute dosage of Fenton's reagent, Fe^{2+}/H_2O_2 molar ratio, reaction time, temperature, aeration etc (Zhang *et al.,* 2005; Deng, 2007; Deng *et al.,* 2006).

1.5 Objective

The objective of this present study was to determine the most viable method for the treatment of the landfill leachate from the landfill in Pennsylvania. This landfill discharges its leachate to the sewer system of a municipality, resulting in UV quenching so a viable method for reducing the UV quenching effect was investigated. More specifically, this study assessed the performance of five physico-chemical treatment methods in terms of relative BOD, TOC removal and also improvement in UV transmittance. The following methods were investigated:

1. Coagulation
2. Ultrafiltration
3. Coagulation + Ultrafiltration
4. Ultrafiltration + Oxidation
5. Filtration/ Ultrafiltration + Fentons

The influence of various operating parameters such as initial pH, dosage and molar ratio of oxidants was also investigated to determine the most economically efficient operating conditions.

2. Materials and Methods

2.1 Landfill leachate

The landfill leachate used for this study is treated in a sequencing batch reactor for removal of readily biodegradable organic matter and also for nitrogen removal by nitrification/denitrification. The SBR is periodically spiked with commercial dog food with the air shut off to remove nitrogen by denitrification. In addition to the SBR, at the time of the first collection of samples, a membrane bioreactor (MBR) was being tested so samples were also obtained from this system. The samples were tested for its UV UV transmittance using a spectrometer. It was found that the leachate quenches the ultraviolet light and hence zero transmittance was observed at 254 nm for all full-strength leachate. UV transmittance of raw leachate, MBR permeate and SBR decant at different dilution factors is shown in Figure 2-1. It was observed that pretreatment in a SBR and MBR did not improve the UV transmittance of the leachate compared to the raw leachate. The SBR effluent was further tested to determine its BOD, COD and TOC. The characteristics of the SBR Decant are shown in Table 2-1. It can be seen that the SBR effluent has a low BOD and high COD and TOC. Therefore, the biodegradability of SBR effluent is very low as indicated by the low BOD/COD ratio.

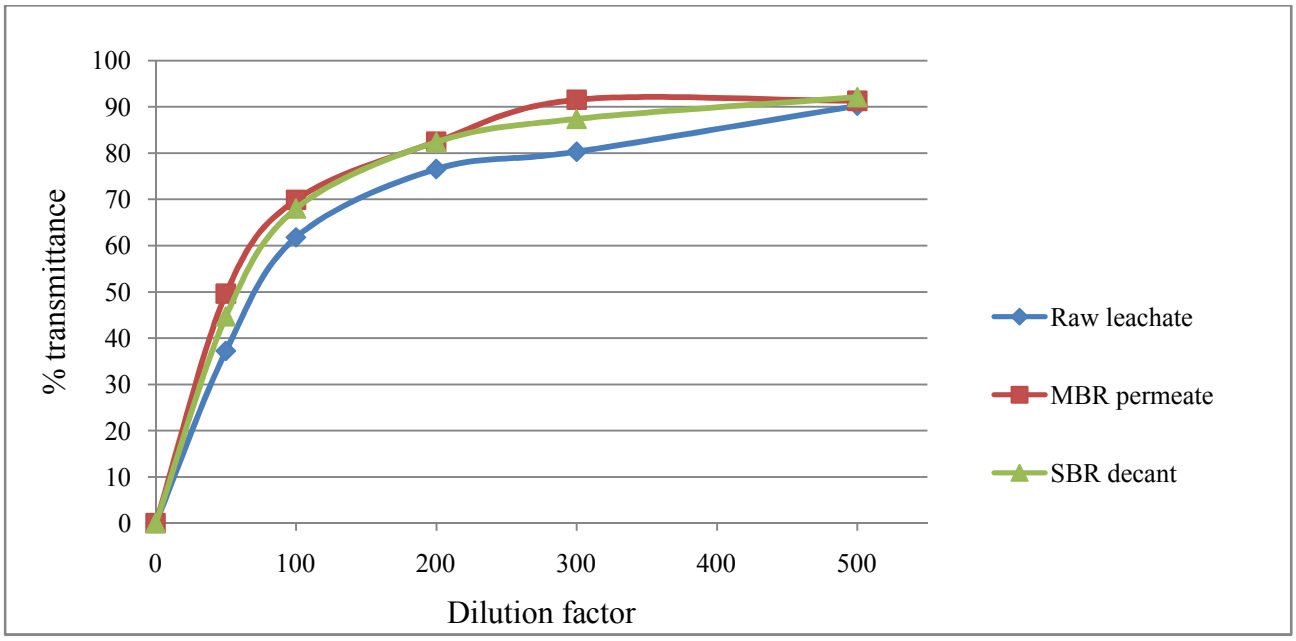

Fig 2-1 Spectrometer studies for raw leachate, MBR permeate and SBR decant

BOD	67.4 mg/L
COD	2129 mg/L
TOC	1491 mg/L
UV Transmittance	Zero

Table 2-1 Characteristics of SBR Decant

2.2 Treatment of SBR Decant

Biological treatment methods were thought to be ineffective for the treatment of leachate (low biodegradability due to low BOD/COD ratio). These methods are typically useful only for young leachate. The biodegradability of the leachate decreases as the leachate gets stabilized over a number of years. Hence physic-chemical treatment methods were adopted for this study. The methods studied were:

1. Coagulation

2. Ultrafiltration

3. Ultrafiltration followed by coagulation,

4. Ultrafiltration + Oxidation

5. Filtration/ ultrafiltration + Fenton's reagent

The effluent was tested for BOD and TOC removals and also UV transmittance. All these treatment methods and the results are described in details in the following sections.

2.2.1 Coagulation

The coagulants that are commonly used for water and wastewater treatment are aluminum sulfate (alum), ferrous sulfate, ferric chloride and ferric chloro-sulfate (Ehrig, 1984; Amokrane *et al.,* 1997). Studies conducted by various researchers show that ferric chloride works as a better coagulant than aluminum sulfate; hence it was used in this study. The experiment was performed with a conventional jar test apparatus that was comprised of six paddle stirrers and 1 liter beakers. A picture of the setup is shown in Fig 2-2. The coagulant Ferric chloride was put in different doses into the six 1L beakers that contained 200 mL of sample. Coagulant Doses of up to 1500 mg/L were used. The experimental process consisted of three stages, an initial flash mixing stage of 2.5 minutes at the rate 100 rpm, followed by a slow mixing stage of 17 minutes at 20 rpm. In the third stage, the beakers were allowed to settle for 30 minutes and the supernatant was collected thereafter. The supernatant was then tested for UV transmittance, BOD and TOC.

Fig 2-2 Coagulation Apparatus

2.2.2 ULTRAFILTRATION-

Ultrafiltration was carried out using the Amicon equipment. The membrane type used in this research was Millipore's Ultracel regenerated cellulose membranes of dia 63.5 mm and a filtration area of 28.7 cm^2. Each membrane is characterized by its Nominal Molecular Weight Limit (NMWL) also referred to as its molecular weight cut off. This represents its ability to retain molecules larger than those of a given size calibrated with globular macrosolutes or mixed dextrans. An ultrafiltration membrane's MWCO or NMWL is expressed in kilodaltons and abbreviated as K. For this study, five membrane sizes; 100K, 30K, 10K, 5K, 1K were used. According to Millipore's standard definition, an ultrafiltration membrane with a stated NMWL will retain (reject) at least 90% of a globular solute of that molecular weight in Daltons.

The membranes come pretreated with glycerin to prevent drying. Therefore, when using a new membrane, nanopure water was filtered through the membrane for at least 5 minutes before the actual sample was filtered. The membranes were operated at an air pressure of 55-60 psi. The filtrate for each sample was collected after wasting first 20 mL of filtrate. Reduced recoveries and decreased filtration rate served as an indication of need for membrane replacement. The filtrates obtained from different sized membranes were then tested for UV transmittance, BOD and TOC.

2.2.3 Ultrafiltration and Coagulation

In this treatment method, ultrafiltration was followed by coagulation. The SBR decant was filtered through membranes of 5 sizes; 100K, 30K, 10K, 5K and 1K. Ultrafiltration was carried out using the same procedure as described in Section 2.2.2. The filtrate was then coagulated using Ferric Chloride as a coagulant. The setup used for coagulant was same as described in Section 2.2.1. The coagulant dose was decided by doing a turbidity test. The ultrafiltrate from 100K was coagulated with different doses of coagulant ranging from 0 to 1200 mg/L. Based on the results of the turbidity tests, two coagulant doses, 450 mg/L and 1050 mg/L was used for further study. The supernatant was then tested for BOD, TOC removal and also UV transmittance.

2.2.4 Ultrafiltration and Oxidation

In this method, the filtrate from a 1K filter was oxidized using different oxidants. The 1K filtrate was used because it was a substantial portion of the overall UV. Four oxidants, $KMnO_4$, H_2O_2, NaOCl and Fenton's reagent were used for this study. Doses ranging from 1-12 g/L were adopted. It has been demonstrated through various studies that Fenton's reagent ($FeSO_4 + H_2O_2$) works best at an acidic pH. Therefore, the initial pH was adjusted to three different pH values, 2.5, 3.5 and 4.5 to observe the difference in removal with pH. For this study, the ratio of iron salt to hydrogen peroxide was kept as 1:1.

The oxidant was put in different doses in 10mL of sample and allowed to react for 2 hours. The samples were loaded onto a hand shaker before they were dosed with the oxidant. The effluent was then tested for percentage TOC removal.

2.3 Analytical Methods

1) Biochemical Oxygen Demand (BOD) - The five day BOD test was carried out in accordance with the method described in Standard Methods for the Examination of Water and Wastewater. Three hundred mL BOD bottles were used to determine the 5-day BOD. The test was carried out in a constant temperature room at 20^0C. For some samples, the oxygen depletion was too less to determine the five day BOD. These samples were therefore incubated for a period of 30 days so as to determine the ultimate BOD.

2) Total Organic Carbon (TOC) - The TOC test was carried out on Shimadzu's TOC-V series analyzer using NPOC analysis (non-purgeable organic carbon). The samples were diluted by a factor of 10 before the test was conducted. TOC standards of 10 ppm and 100 ppm were used to draw the calibration curve. A check standard of 10 ppm was used at the end of all samples for accuracy purposes.

3) UV Transmittance - The supernatant was tested for percentage transmittance at 254 nm using a UV spectrometer.

3 RESULTS AND DISCUSSION-

The results obtained for each treatment method are described under the respective headings. The effluents from each treatment method were tested for its BOD, TOC and UV transmittance

3.1Coagulation

i) Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC)-

The 5 day BOD could not be determined for the coagulated samples as the depletion of oxygen after 5 days was less than 2mg/L. Hence, ultimate BOD was determined for these samples. The results of this test are shown in Fig 3-1. It was observed that 50% removal of BOD_u is obtained with a dose of 1200 mg/L. This implies that the remaining biodegradable fraction of organics is too small to be removed by coagulation.

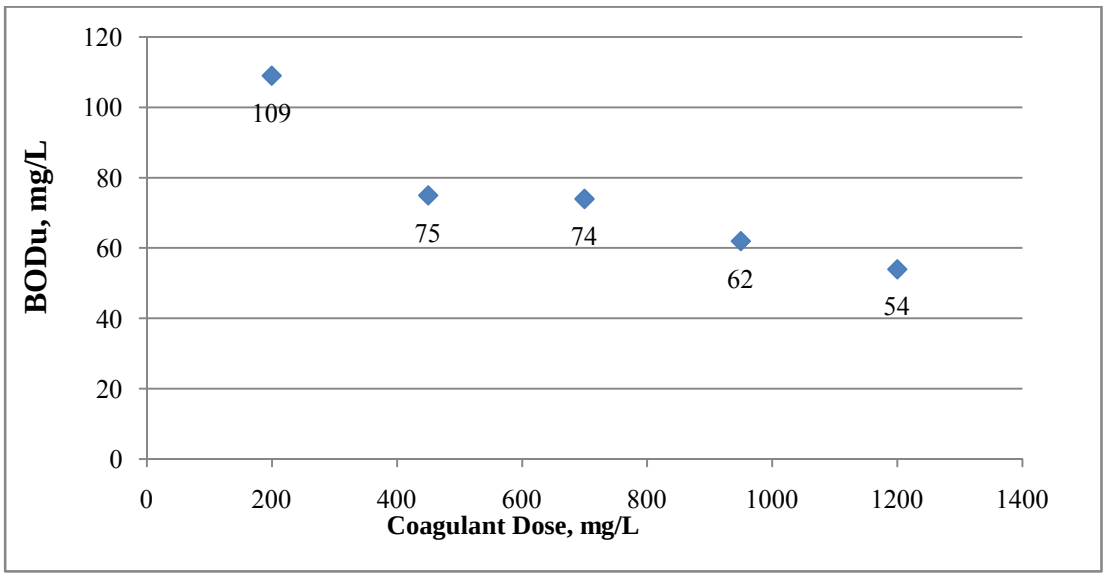

Fig 3-1 BOD vs Coagulant Dose for coagulated leachate samples

The results of the TOC test are shown in Fig 3-2. It was observed that 50% TOC removal was obtained with a ferric chloride dose of 1200 mg/L. This implies that remaining organics present in landfill leachate are too small to be removed by coagulation.

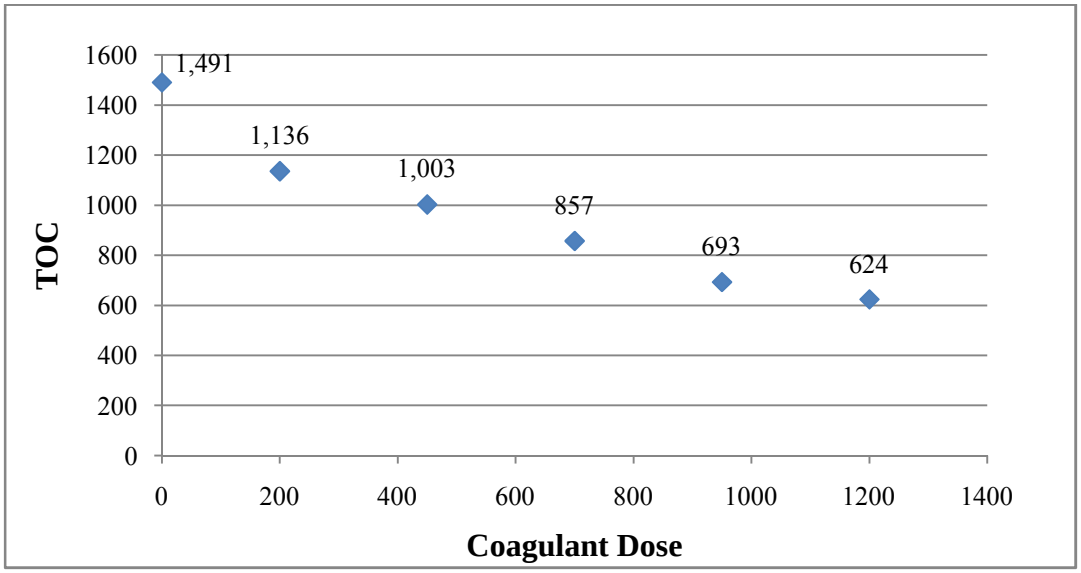

Fig 3-2 TOC vs Coagulant Dose for coagulated leachate samples

Fig 3-3 shows the variation of TOC with respect to BOD_u for the coagulated leachate samples. A linear relationship is observed between the two parameters. Fig 3-4 shows the ratio of BOD_u/TOC vs Coagulant Dose. The ratio shows a small decrease initially but then it levels out with increasing dosage. This implies that a small percentage of the biodegradable organics present in the leachate get removed with a coagulant dosage of 450 mg/L. But there is no removal with increasing dosages. Also, the very small BOD_u/TOC ratio indicates the presence of refractory organics which do not get removed even at the highest coagulant dose of 1200 mg/L. The inability of coagulation to remove these non biodegradable organics can be attributed to their extremely small size.

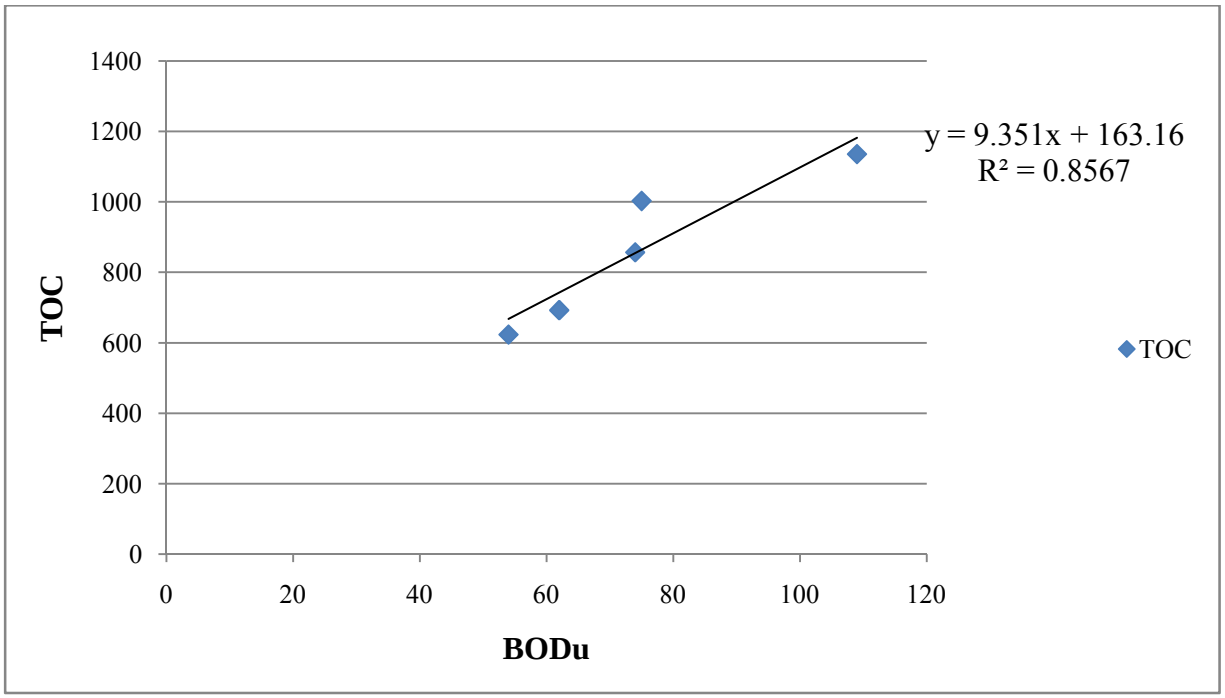

Fig 3-3 TOC vs BOD_u for coagulated leachate samples

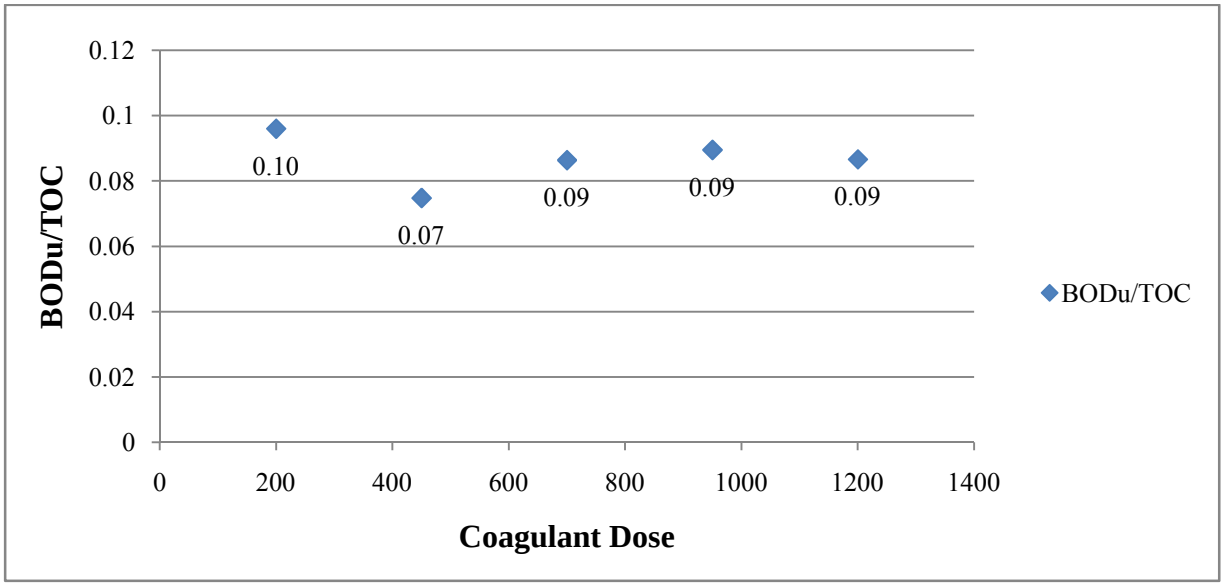

Fig 3-4 BOD_u/TOC vs Coagulant Dose for coagulated leachate samples

ii) UV transmittance

Zero transmittance was observed for the coagulated samples. Hence, dilution was adopted and dilution factors of 10 and 100 were used. The transmittance values for different doses of coagulant are shown in Fig 3-5. These values show that the UV transmittance is not affected by the coagulant dose. Also, a large dilution is required to achieve measurable improvement in UV transmittance. This could be attributed to that fact that large amount of refractory organics are still left in the samples even after coagulation.

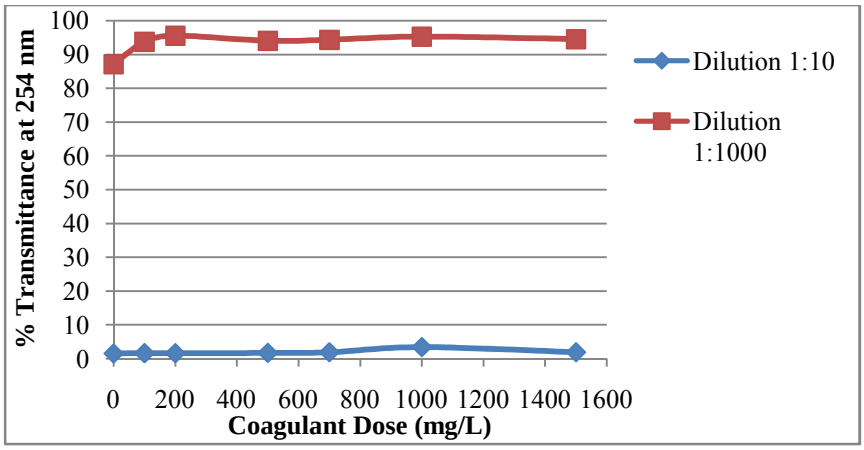

Fig 3-5 UV Transmittance of diluted supernatant vs Coagulant Dose for coagulated leachate samples.

3.2 Ultrafiltration

i) Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC)-

A range of dilution factors were used for accurate determination of BOD. The ultrafiltration was effective in removing approximately 95% BOD. The BOD of 5K and 1K ultrafiltrates was very low; hence a very high dilution factor had to be used to determine their BOD. However, these samples still showed a oxygen depletion of less than 2mg/L. According to the standard method, there should be a minimum oxygen depletion of 2 mg/L for the test to be considered accurate. However, for analysis purposes, the BOD of these samples were calculated using the depletion observed. The BOD values for ultrafiltrates are tabulated in Table 3-1. Fig 3-6 shows the TOC and BOD values with respect to the filtrates obtained from the ultrafiltration membranes. There is a sharp decrease in BOD when the leachate is filtered through the 30K filter. This shows that a considerable fraction of the biodegradable organics have a size greater than 30K. However, the BOD remains almost constant for the smaller size membranes. This implies that there aren't any biodegradable organics present in the leachate that lie in the size range of 5 kDa – 30 kDa. The TOC values show a gradual decrease up to filtration with 10K filter and a sharp decrease upto filtration with 1K filter. The maximum TOC removal was obtained for 1K filter and was approximately 35%.

Filter Size	Five day BOD (mg/L)
SBR	67.4
100 K	40.25
30 K	6.4
10 K	6.2
5 K	DO uptake < 2mg/L (~ 4.6 mg/L)
1 K	DO uptake < 2 mg/L (~ 3.1 mg/L)

Table 3-1 BOD of ultrafiltrates

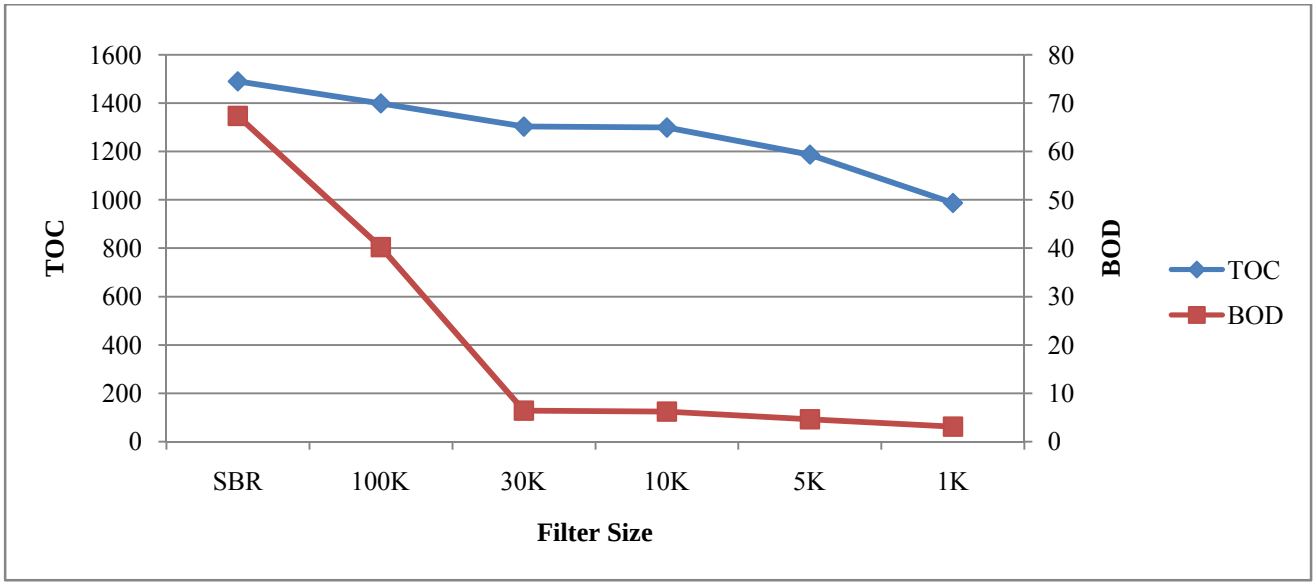

Fig 3-6 BOD and TOC vs Filter Size for ultrafiltrates

Fig 3-7 shows the BOD/TOC ratio vs the Filter Size. It shows a trend similar to that of BOD. The very low BOD/TOC ratio for organics of size less than 1K indicates that the refractory organics present in leachate are very small particles of size less than 1K Da. This conclusion reaffirms the conclusion drawn when coagulation was used as treatment method for leachate. A plot of BOD/TOC ratio vs BOD is shown in Fig 3-8. Linear relationship between the BOD/TOC ratios vs the BOD indicates that the biodegradability of the organics depends on the BOD of the leachate.

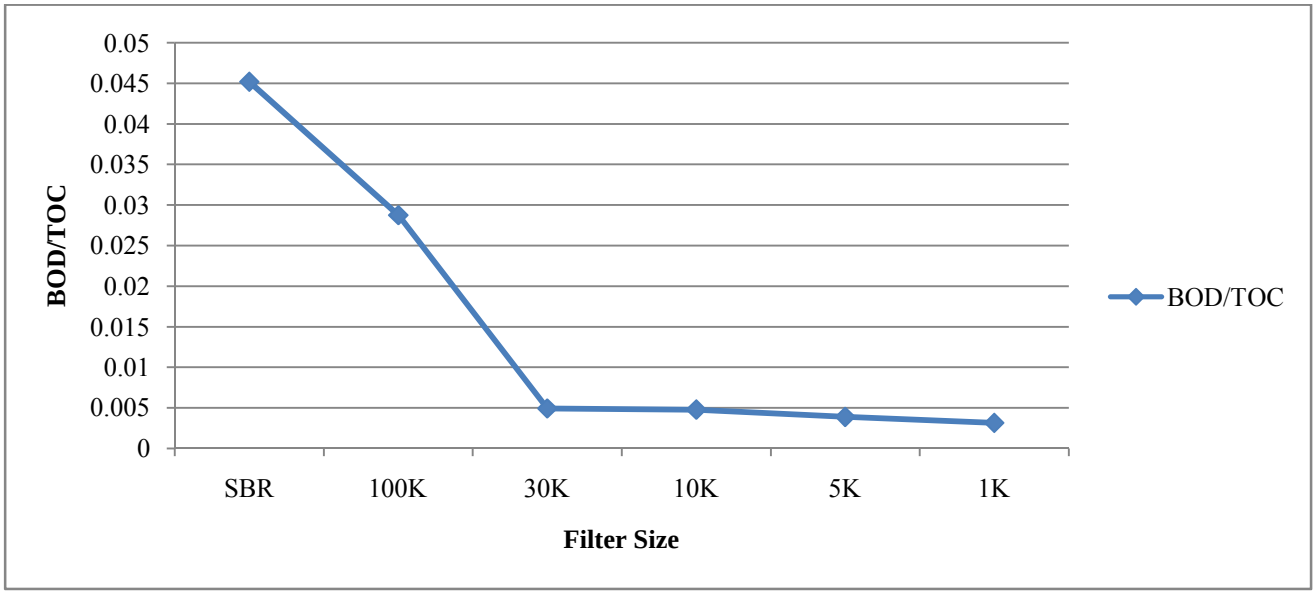

Fig 3-7 BOD/TOC vs Filter Size for ultrafiltrates

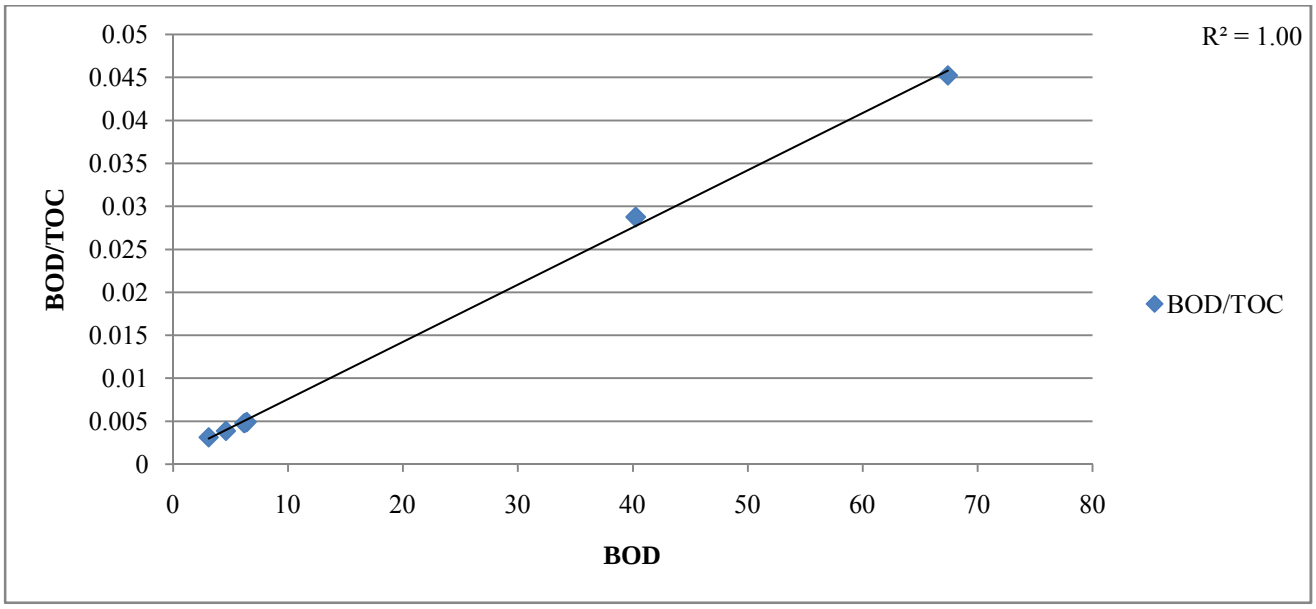

Fig 3-8 BOD/TOC vs BOD for ultrafiltrates

ii) UV transmittance-

Zero transmittance was observed for the raw ultrafiltrates. Hence, they were diluted by a factor of 10 and the results of the diluted ultrafiltrates are shown in Fig 3-9. The maximum transmittance was obtained for diluted ultrafiltrate from 1K filter. It was inferred from the UV transmittance of the ultrafiltrates that the particles which quench the UV light are very small in size.

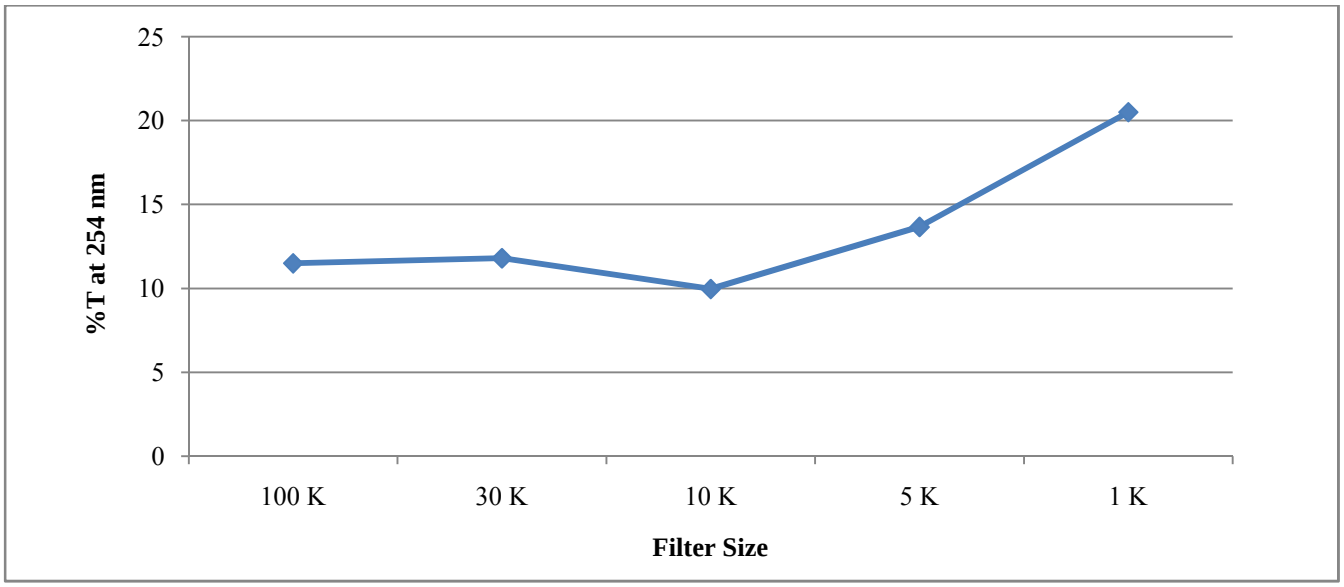

Fig 3-9 UV transmittance of diluted ultrafiltrates vs Filter Size

3.3 Ultrafiltration and Coagulation

i) Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC)-

The 5 day BOD could not be determined as the depletion of oxygen after 5 days was less than 2mg/L. Hence ultimate BOD was determined for coagulated ultrafiltrates. Fig 3-10 shows the ultimate BOD values versus the Filter Size. The BOD_u remains constant for filtrates of 30K, 10K and 5K membranes and then it decreases. This indicates that there aren't any biodegradable organics present in the size range of 1K to 30K. This reinforces the conclusion that there biodegradable organics of size less than 30K are absent in leachate drawn when ultrafiltration was used as the treatment method. The BOD values are very low to be removed by this treatment method. Also, this treatment method is ineffective in converting the refractory organics into biodegradable fractions.

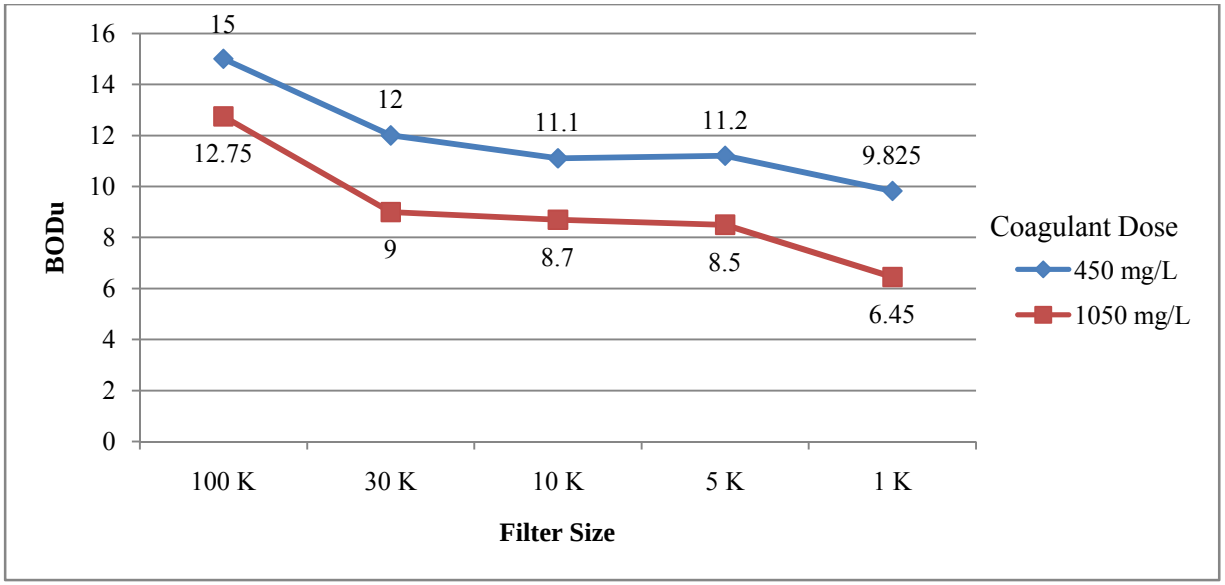

Fig 3-10 BOD_u vs Filter Size for Coagulated Ultrafiltrates

Fig 3-11 shows the TOC values versus Filter Size for coagulated ultrafiltrates. Coagulation of the ultrafiltrate removes a percentange of the organics and brings down the TOC value of 1400 mg/L for

raw filtrate to a value of 733 mg/L for coagulated ultrafiltrate i.e approximately 65% removal in TOC. But there wasn't much difference observed in TOC values of the different ultrafiltrates. The TOC values of coagulated ultrafiltrates remain similar for all filter sizes. This indicates that coagulation of the ultrafiltrate removes organics that are larger than 100 kDa but it is ineffective in removing organics smaller than 100kDa. Similar behavior is observed for the higher coagulant dose of 1050 mg/L. It is also interesting to note that an increase in the coagulant dose from 450 to 1050 mg/L does not bring a significant TOC removal. Hence, for economy purposes, a coagulant dose of 450mg/L is suggested if this treatment method is adopted.

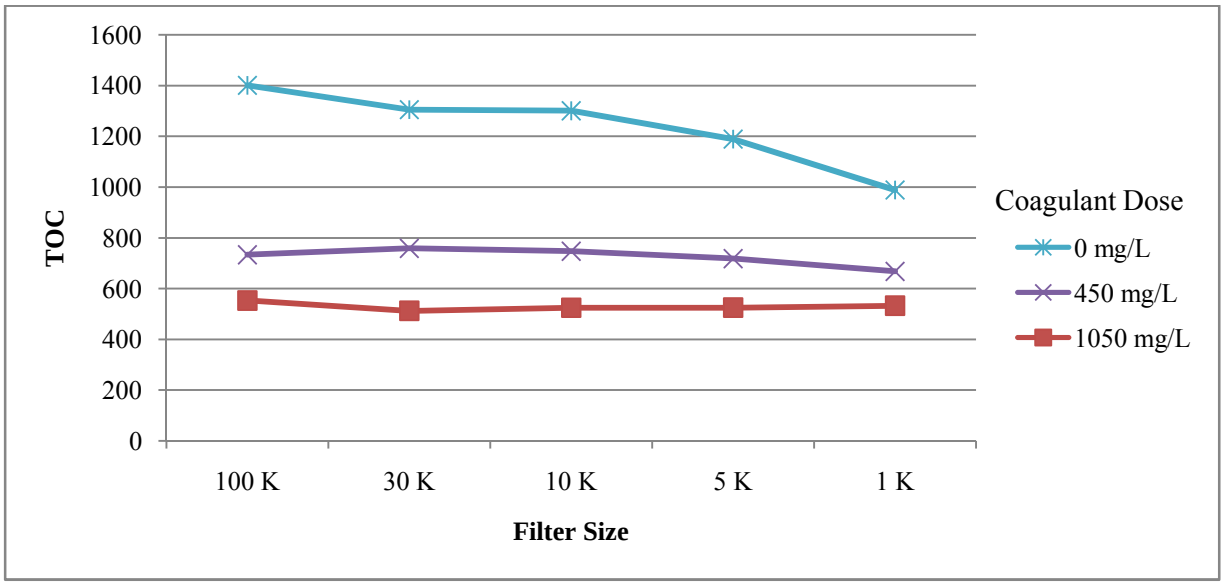

Fig 3-11 TOC versus filter size for coagulated ultrafiltrates

Fig 3-12 shows the relationship between BOD_u/TOC ratios versus the Filter Size. Fig 3-13 shows the relationship of BOD_u/TOC with BOD and Fig 3-14 shows its relationship with TOC. The constant BOD_u/TOC ratio for filtrates of 30 kDa, 10 kDa and 5 kDa membranes reaffirms the fact that there are

almost no biodegradable organics present in the size range of 1K -30K. Also, the very low BOD_u/TOC ratio indicates the presence of refractory organics of a size smaller than 1kDa

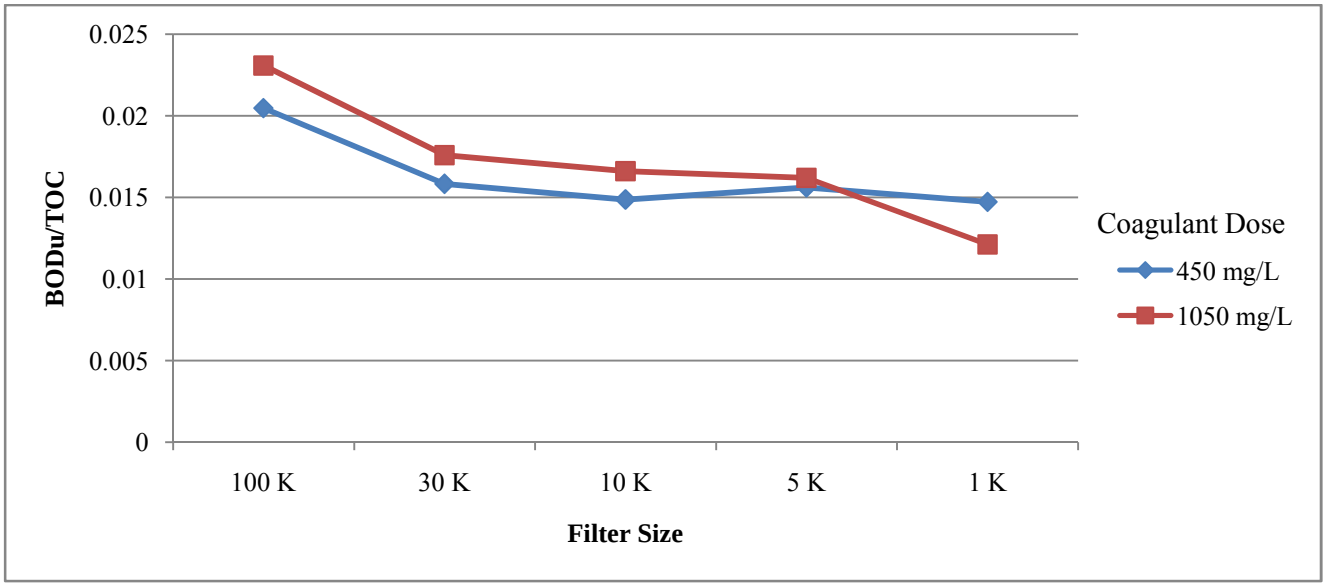

Fig 3-12 BOD_u/TOC vs Filter Size for coagulated ultrafiltrates

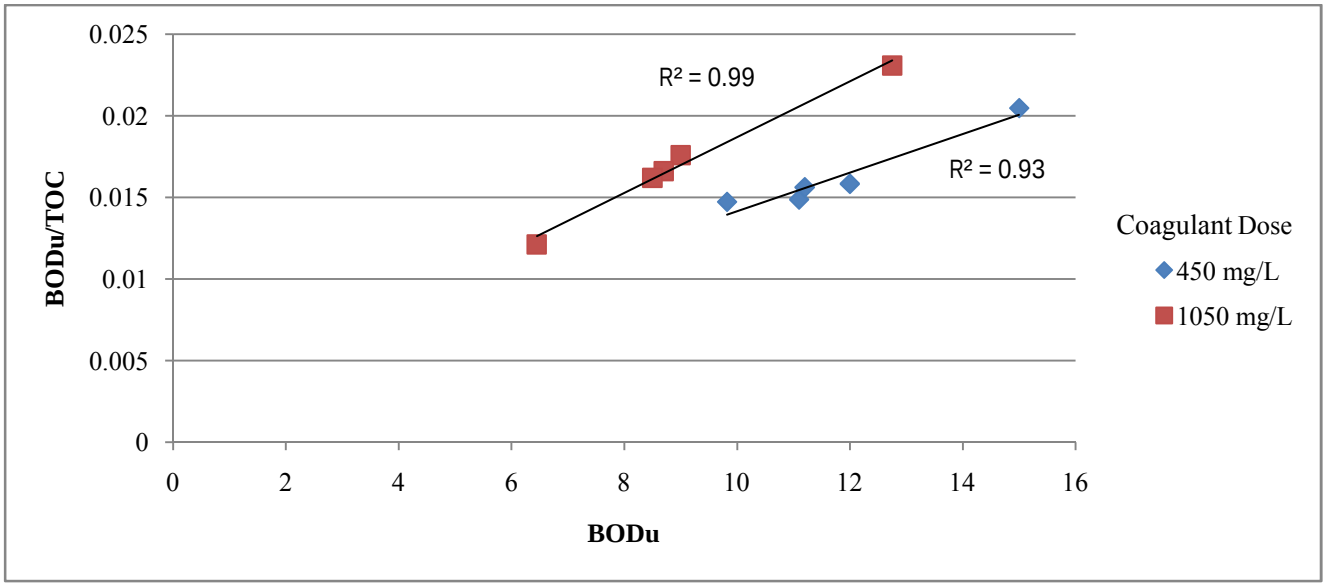

Fig 3-13 BOD_u/TOC vs BOD_u for coagulated ultrafiltrates

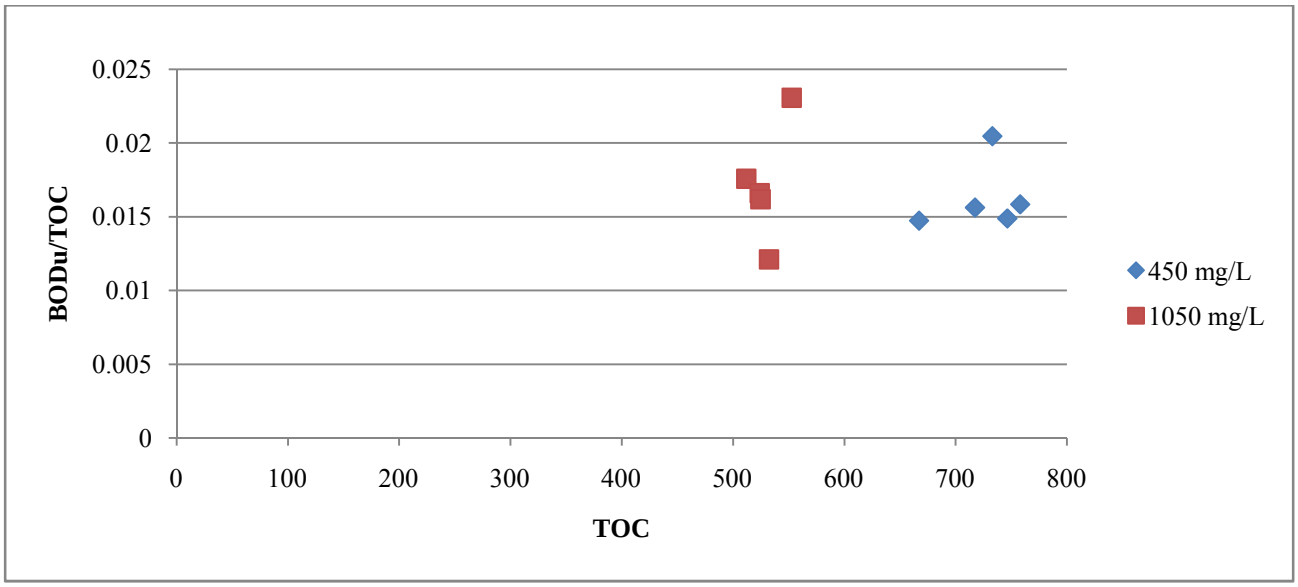

Fig 3-14 BOD_u/TOC vs TOC for coagulated ultrafiltrates

ii) UV transmittance-

The UV transmittance of coagulated ultrafiltrates was tested using the UV spectrometer. Zero transmittance was observed for these samples. Hence, they were diluted by a factor of 10 and the results of the diluted samples are shown in Fig 3-15. It can be observed that a higher coagulant dose does not bring about much improvement in UV transmittance. Hence, coagulant dose of 450 mg/L is as good as a higher dose of 1050 mg/L.

Also, coagulating the ultrafiltrates does not help in improving the UV transmittance of raw ultrafiltrates. The UV transmittance of raw ultrafiltrates and coagulated ultrafiltrates are similar to each other. The particles that quench the UV light are very small in size hence coagulation does not help in improving the UV transmittance.

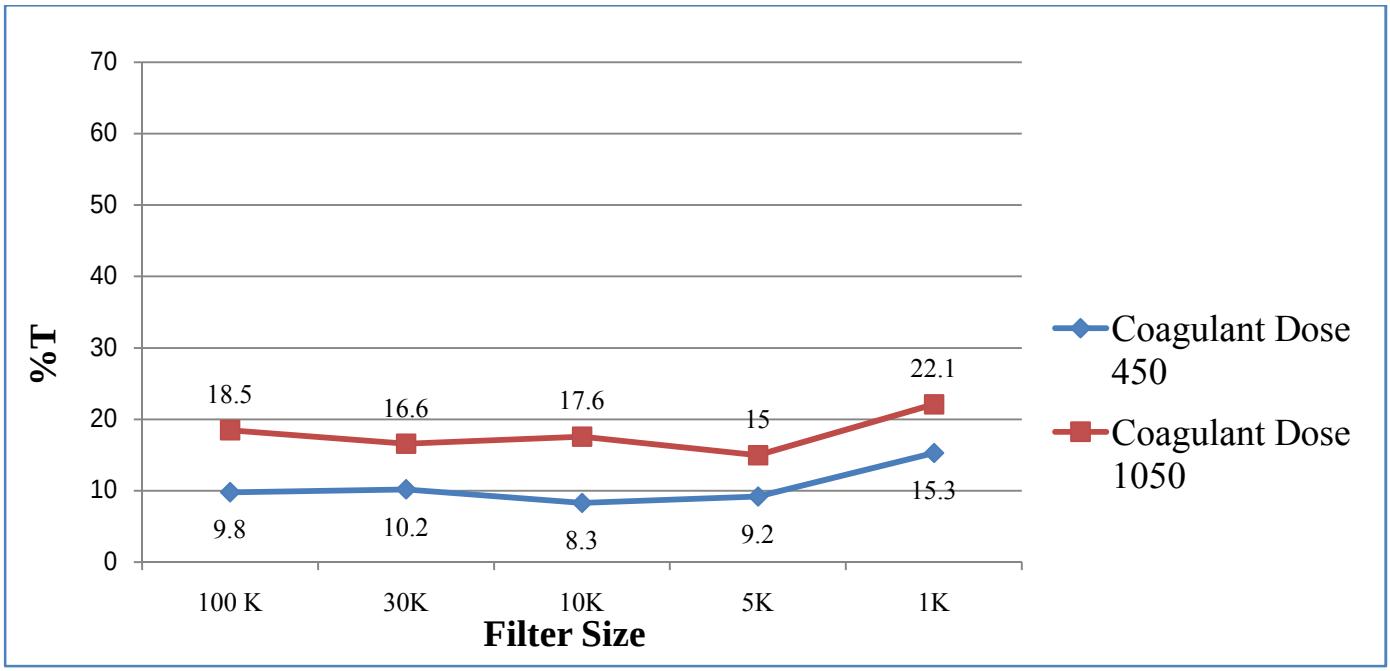

Fig 3-15 UV transmittance of coagulated ultrafiltrates (dilute by 1:10)

3.4 Ultrafiltration and Oxidation

i) TOC Removal

Oxidation is effective in bringing about large TOC removals. TOC values can serve as an indicator of presence of refractory organics as is evident from the data collected for other treatment methods. Also, it has been shown previously that the leachate samples under consideration have poor biodegradability. Therefore, reduction in TOC values indicates the removal of refractory organics. Fig 3-16 shows the TOC values versus the dose of the oxidant. The ultrafiltrate from a 1K filter was oxidized with different oxidants as mentioned in Section 2.2.4 and tested for TOC removal. It can be observed that Hydrogen Peroxide and Sodium Hypochlorite do not work. The maximum removal obtained for Sodium Hypochlorite hydrogen peroxide was 22% and 36% respectively. However, a very high dose of 12g/L had to be used to bring about this much removal. Potassium permanganate works really well in bringing down the TOC. Also, the TOC removal increases with increasing dose of the oxidant. The maximum removal obtained in this case was 75% for a dose of 12g/L. Fenton's reagent works the best out of all the oxidants. 90% TOC removal is obtained with the smallest dose of 1 g/L at a pH of 4.5. Also, acidic pH does not make any difference in the TOC removals. A higher pH of 4.5 is as good as a lower acidic pH of 2.5. These data indicate that oxidation with Fenton's reagent is the most viable method to remove a large percentage of the refractory organics which could not be removed by other treatment methods.

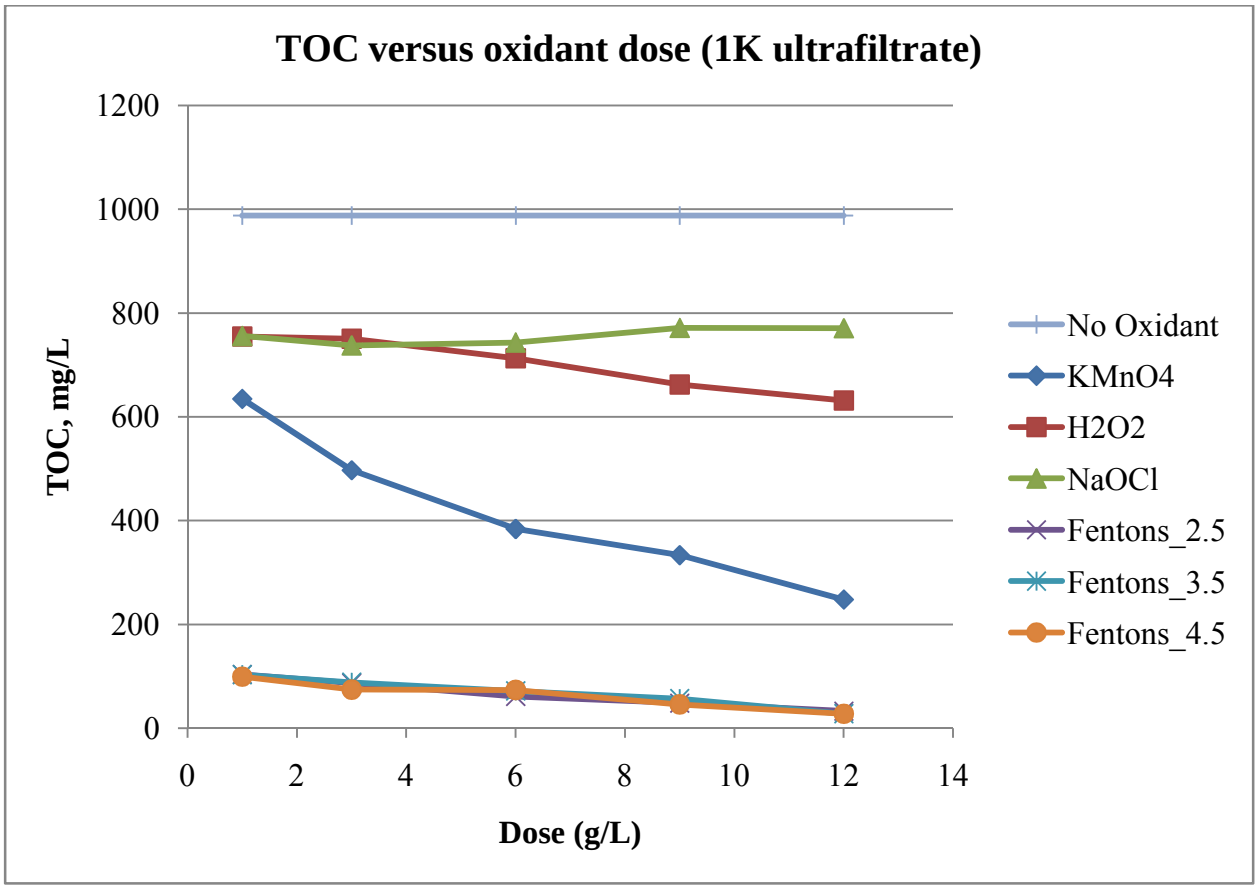

Fig 3-16 TOC vs Oxidant Dose for oxidized 1K ultrafiltrate

4.0 Conclusion-

The efficiency of different treatment methods for leachate were tested in this study. The leachate is characterized by a low BOD/COD ratio and high COD and TOC. Also, the leachate had poor UV transmittance and it quenches the UV light. Coagulation is not really effective in improving the UV transmittance. The maximum transmittance that could be obtained was approximately 2% and that too with a very high dose of 1200mg/L. Coagulation, however, is capable of bringing about 50% BOD and TOC removals.

Ultrafiltration works better than coagulation in improving the UV transmittance as 20% transmittance was obtained for the ultrafiltrate from a 1K filter. However, it is effective in BOD removal, 95% BOD removal was observed for filtrate from a 1K filter. Ultrafiltration combined with coagulation works better for TOC removal but not for BOD removal and UV transmittance as compared to ultrafiltration alone. Ultrafiltration combined with oxidation works the best in TOC removals. Fentons reagent was found capable of removing 90% TOC with a small dose of 1g/L at a pH of 4.5. It was also observed that pH did not make any difference in corresponding TOC removals.

(II) OPTIMIZATION OF LEACHATE OXIDATION WITH FENTON'S REAGENT

Abstract

Leachate samples were obtained from a landfill in Pennsylvania for this study. It was found through previous studies that these samples quench UV light due to the presence of very small sized refractory organics. It was also found that this leachate can be effectively treated by oxidizing the ultrafiltrate from a 1K ultrafilter with Fenton's reagent. In this study, efforts were made to optimize this oxidation with Fenton's. The two parameters which were studied were the initial pH and the chemical dosage. The initial pH was varied from a value of 2.5 to 6.5. The range of iron salt and peroxide dose used was from 0.05 to 0.1 g/L. Additional studies were conducted using samples filtered through a 0.45 μm filter and oxidized with Fenton's reagent. The Fenton's process for oxidation of filtrates from the 0.45μm filter was also optimized with respect to pH and chemical dosage to determine the most economical operating conditions. It was observed that the efficiency of TOC removal decreases with increasing pH for both 1K and 0.45 μm filtrates. However, the trend of percentage transmittance for the effluent from the oxidation of 1K ultrafiltrate depends on dose of the oxidant added. At some dosages, the percent transmittance increases with decreasing pH while it remains independent of pH at other chemical doses. The maximum transmittance of 57% was obtained for an iron dose of 0.075 g/L and a peroxide dose of 0.075 g/L at a pH of 4.5. This is in comparison to the transmittance of unoxidized 1K ultrafiltrate which was found to be 21.5%. For the 0.45 μm filtrate, the transmittance values were found to be independent of pH. For the oxidation of 1K ultrafiltrate, the TOC removal was found to be independent of iron and peroxide doses at pH values of 2.5, 3.5 and 4.5. In the case of the 0.45μm filtrate, the same trend is observed at pH values of 2.5 and 3.5. The transmittance properties of oxidized 1K ultrafiltrate improve with increasing peroxide dose at pH values of 3.5 and 4.5. But for iron dose, the maximum transmittance is observed at a dose of 0.075 g/L at all pH values. For the, 0.45 μm filtrate, the transmittance properties remained the same with increasing peroxide dose at an initial pH of 2.5 and 3.5. Also, there was a

significant difference in the performance of 1K and 0.45μm filtrates in terms of TOC removal and percentage transmittance. The oxidation process for improving the UV transmittance of leachate can therefore be economically optimized depending upon the desired efficiency by varying the operational parameters.

1 Introduction

1.1 Literature Review

Leachate is produced by the degradation of the organic fraction of the waste in the landfill combined with the percolation of rainwater (Kjeldsen *et al*., 2002). The biodegradability of the leachate decreases as the age of landfill increases. In general, young leachate has high biological oxygen demand (BOD) and even higher chemical oxygen demand (COD) (Kjeldsen *et al*., 2002). Leachate from an aged landfill therefore has lower biodegradability and is comparatively stable as compared to the leachate from a new landfill. The BOD of aged leachate is primarily caused by refractory organics which mainly consists of dissolved organic matter (DOM) (Trebouet *et al*., 2001; Wang *et al*., 2003; Rivas *et al*., 2004). For the treatment of biologically stable leachate, physicochemical treatment processes are often needed (Ozturk *et al.,* 2003). These processes include electrochemical oxidation (Moraes *et al.,* 2005), coagulation–flocculation (Amonkrane *et al.,* 1997, O'Melia *et al., 1999,* Wang *et al., 2002,* Tatsi *et al.,* 2003), membranes (Osturk *et al.,* 2003, Martinnen *et al., 2002),* combinations of coagulation, flocculation and chemical oxidation (Rivas *et al.,* 2004), advanced oxidation (Lopes de Morais *et al.,* 2005), ozonation (Monje *et al.,* 2004, Bilaa *et al.,* 2005, Poznyak *et al.,* 2004), combination of ozonation and Fenton's reagent.

The most widely used treatment technology in recent years has been the Fenton's reagent. In this process, hydrogen peroxide is added with ferrous sulfate which results in the catalytic generation of hydroxyl radicals (•OH) due to the chain reaction between peroxide and ferrous ion. The hydroxyl radical produced in this reaction serves as a strong oxidant. The oxidation of organic compounds (RH) by Fenton's reagent proceeds by the following chain reactions [Kang *et al.,* 2000, Neyens *et al.,* 2003]

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH$ (1)

$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^-$ (2)

$RH + \bullet OH \rightarrow H_2O + R\bullet$ (3)

$R\bullet + Fe^{3+} \rightarrow R^{+} + Fe^{2+}$ (4)

Fenton's reagent can be used as a pretreatment or post treatment for landfill leachate. In his study, Papadopoulos *et al.,* 1994 used Fenton's reagent (100 ml, 30%, w/w H2O2 and 40 mg Fe2+ per liter of leachate) to chemically oxidize leachate (initial COD range of 6500–8900 mg/L) after aerobic biological treatment and observed up to 33% COD reduction. Fenton's reagent is also used as a pretreatment step to increase the biotreatability of the leachate. Kim *et al,.* 2001 used coagulation and Fenton's oxidation to treat stabilized leachate and observed that the BOD_5/COD ratio improved from an initial range of 0.11–0.17 to 0.45. The efficiency of the oxidation process with Fenton's depends on number of operational parameters such as initial pH, absolute dosage of Fenton's reagent, Fe^{2+}/H_2O_2 molar ratio, reaction time, temperature, aeration etc (Zhang *et al.,* 2005; Deng, 2007; Deng *et al.,* 2006).

There has been little research on optimizing the Fentons process for treatment of leachate. Zhang *et al.,* 2005 tested the effect of these parameters on Fentons process using a batch reactor. He found that the oxidation of organic materials in the leachate was pH dependent and the most favorable pH lied in the range of 2-3. The optimum H_2O_2/Fe(II) molar ratio was 1.5, and efficiency of organic removal increased with increasing dosage at the optimum H_2O_2/Fe(II) molar ratio. He also observed better sludge settling characteristics with the addition of the proper polymer. Temperature was found to have a positive effect on organic removal.

In their study, Hermosilla *et al.,* 2009 determined the optimal conditions for the treatment of leachate by Fenton's and Photo- Fenton's process. He observed high COD removal rates at acidic pH of 2.5 and at room temperature. There wasn't any significant increase in the COD and TOC removals with application of UV light under the optimal conditions of conventional Fenton process. He observed that

the COD and TOC removals remained high and relatively independent of [Fe^{2+}] in the photo-Fenton process; but the ferrous iron concentration used can be reduced about 32 times obtaining the same results in terms of COD and TOC removals than when performing a conventional Fenton's treatment under optimal conditions. The production of iron sludge was reduced from 25% to 1% of the total final volume.

1.2 Objective-

The objective of this study was to optimize the oxidation of leachate using Fenton's reagent. The samples obtained for this study quench UV light and it was found from previous study that the particles that cause this are very small in size. Hence, samples were passed through a 0.45 μm filter and 1K filter before it was oxidized using Fenton's reagent. It has been proved through various studies that efficiency of Fenton's process depends on number of operating parameters. For this study, two parameters, pH and chemical dose, were studied in terms of the corresponding TOC removal and also improvement in transmittance properties.

2 Materials and Methods-

2.1 Landfill leachate

The landfill leachate used for this study is treated in a sequencing batch reactor for removal of readily biodegradable organic matter and also for nitrogen removal by nitrification/denitrification. The SBR is periodically spiked with commercial dog food with the air shut off to remove nitrogen by denitrification. In addition to the SBR, at the time of the first collection of samples, a membrane bioreactor (MBR) was being tested so samples were also obtained from this system. The samples were tested for its UV transmittance properties using a spectrometer. It was found that the leachate quenches the ultraviolet light and hence zero transmittance was observed at 254 nm for all full-strength leachate. Transmittance properties of raw leachate, MBR permeate and SBR decant at different dilution factors is shown in Figure 1. It was observed that pretreatment in a SBR and MBR did not improve the transmittance properties of the leachate compared to the raw leachate.

2.2 Experimental Procedure

The SBR decant was first filtered through a 0.45 μm filter (Nitrocellulose disc filters, Fischer Scientific). The filter was mounted on a disc and the sample was filtered through it using a vacuum pump. A picture of the filtration apparatus is shown in Fig 13. The filtrate was then oxidized with Fenton's reagent at different operating condition. For the first set of operating condition, the iron dose was kept constant at 0.05 g/L and two peroxide doses viz. 0.05 g/L and 0.0025 g/L were used. In the second set, the iron dose was increased to 0.075 g/L and two peroxide doses viz. 0.075g/L and 0.0375 g/L. In the third set a higher iron dose of 0.1g/L was combined with two peroxide doses i.e 0.1g/L and 0.05 g/L. For each set of doses, initial pH was varied from 2.5 to 6.5. The effluent from each set of doses was tested for TOC and transmittance properties.

Ultrafiltration was carried out using Amicon equipment. The membrane type used in this research was Millipore's Ultracel regenerated cellulose membranes of dia 63.5 mm and a filtration area of 28.7 cm^2.

Each membrane is characterized by its Nominal Molecular Weight Limit (NMWL) also referred to as its molecular weight cut off. This represents its ability to retain molecules larger than those of a given size calibrated with globular macrosolutes or mixed dextrans. An ultrafiltration membrane's MWCO or NMWL is expressed in kilodaltons and abbreviated as K.As mentioned above, membrane size of 1K was used for this experiment. According to Millipore's standard definition, an ultrafiltration membrane with a stated NMWL will retain (reject) at least 90% of a globular solute of that molecular weight in Daltons.

The membranes come pretreated with glycerin to prevent drying. Therefore, when using a new membrane, nanopure water was filtered through the membrane for at least 5 minutes before the actual sample was filtered. The membranes were operated at an air pressure of 55-60 psi. The filtrate for each sample was collected after wasting first 20 mL of filtrate. Reduced recoveries and decreased filtration rate served as an indication of need for membrane replacement.

For each set of operating conditions, the chemicals were put in 10mL of sample and allowed to react for 2 hours. The samples dosed with the oxidants were mounted on a hand shaker during the oxidation process.

2.3 Analytical Methods

1) Biochemical Oxygen Demand (BOD) - The five day BOD test was carried out in accordance with the method described in Standard Methods for the Examination of Water and Wastewater. Three hundred mL BOD bottles were used to determine the 5-day BOD. The test was carried out in a constant temperature room at 20^0C. For some samples, the oxygen depletion was too less to determine the five day BOD. These samples were therefore incubated for a period of 30 days so as to determine the ultimate BOD.

2) Total Organic Carbon (TOC) - The TOC test was carried out on Shimadzu's TOC-V series analyzer using NPOC analysis (non-purgeable organic carbon). The samples were diluted by a factor of 10 before the test was conducted. TOC standards of 10 ppm and 100 ppm were used to draw the calibration curve. A check standard of 10 ppm was used at the end of all samples for accuracy purposes.

3) UV Transmittance - The supernatant was tested for percentage transmittance at 254 nm using a UV spectrometer.

3 Results and Discussion-

3.1 *1 K Ultrafiltrate:*

a) TOC Removal Study

1) **Effect of pH:** The iron and peroxide dose were kept constant and the pH is varied from a value of 2.5 to a value of 6.5. The results are shown in Fig 3-1, 3-2 and 3-3. It was observed for all iron and peroxide doses that the pH does not affect the TOC removal efficiency for pH values in the range of 2.5-4.5. However, the efficiency decreases as the pH is increased above pH 4.5.
2) **Effect of peroxide dose:** It was observed that higher peroxide dose did not bring about greater TOC removals. Also, for lower pH values, the corresponding TOC removal remained the same with increasing peroxide doses. For higher pH values i.e 5.5 and 6.5 there is an optimum dose of peroxide beyond which there is less TOC removal.
3) **Effect of Iron Dose**- It was observed that at all pH values except pH 6.5, increasing iron does not bring about a significant increase in TOC removals. The corresponding TOC removal at a higher iron dose is similar to the removal at a lower iron dose**.** The plots showing the effect of iron dose on corresponding TOC removal can be found in Appendix A.

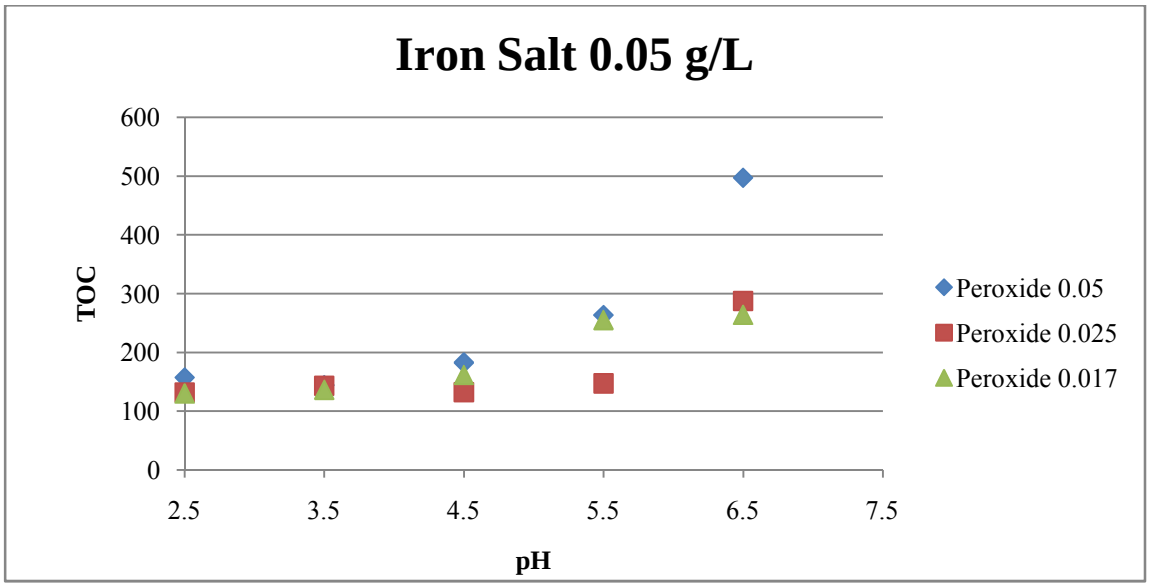

Fig 4-1 TOC vs pH for oxidized 1K ultrafiltrate for varying peroxide doses and at an iron dose of 0.05 g/L

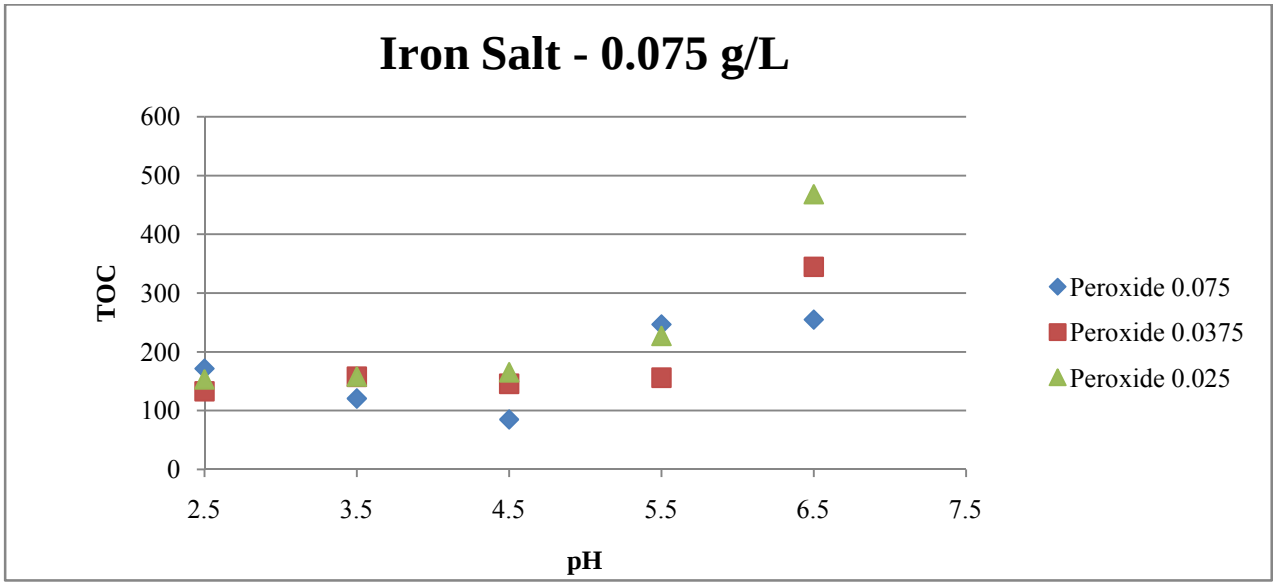

Fig 4-2 TOC vs pH for oxidized 1K ultrafiltrate for varying peroxide doses and at an iron dose of 0.075 g/L

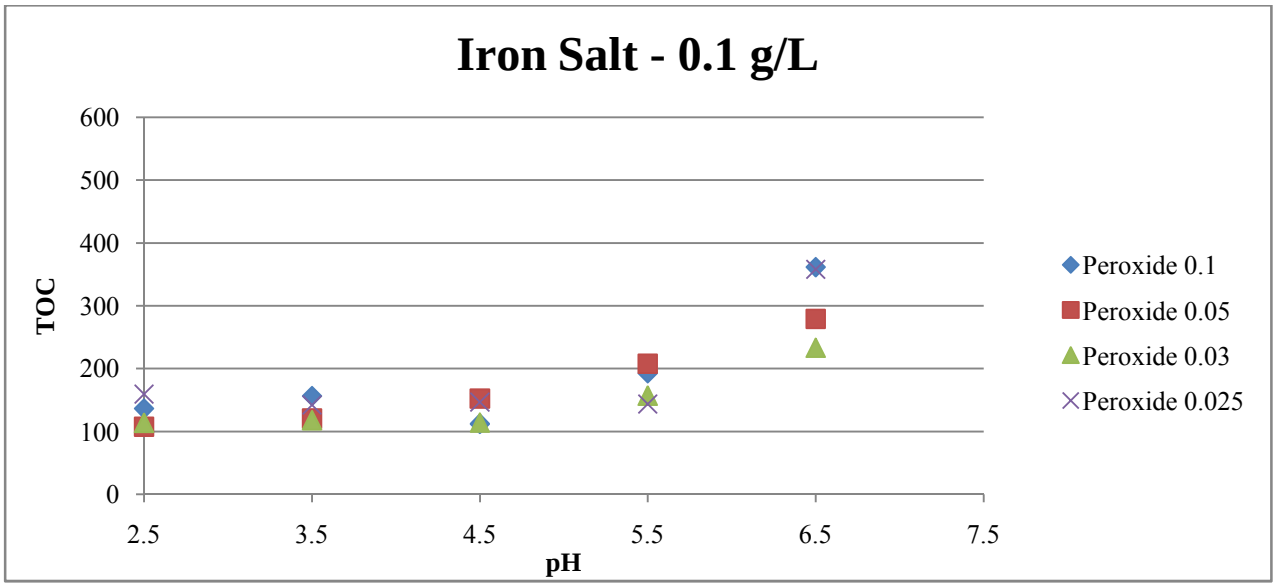

Fig 4-3 TOC vs pH for oxidized 1k ultrafiltrate for varying peroxide doses and at an iron dose of 0.1 g/L

b) UV transmission

Zero transmittance was observed for the untreated samples. Therefore, the samples were diluted by a factor of 10 before they were tested.

1) **Effect of pH** - It was observed that trend in transmittance properties varies depending on the chemical dose. For some dosages, higher transmittance is obtained at lower pH values. But for other dosages, pH does not make much difference to the transmittance properties. The results of this experiment are shown in Fig 3-4, 3-5 and 3-6. The maximum transmittance of 57% was obtained for an iron dose of 0.075 g/L and a peroxide dose of 0.075 g/L at a pH of 4.5.
2) **Peroxide Dose –** There is no particular trend with respect to transmittance properties with increasing peroxide dose at an initial pH of 2.5. For pH values 3.5 and 4.5, the transmittance increases with increasing peroxide dose.

3) **Iron dose –** The maximum transmittance at all pH is observed at an iron dose of 0.75 g/L. This value is the optimum iron dose, the percent transmittance decreases for any dose above this value or below this value. The plots showing the effect of iron dose on the transmittance properties can be found in Appendix B.

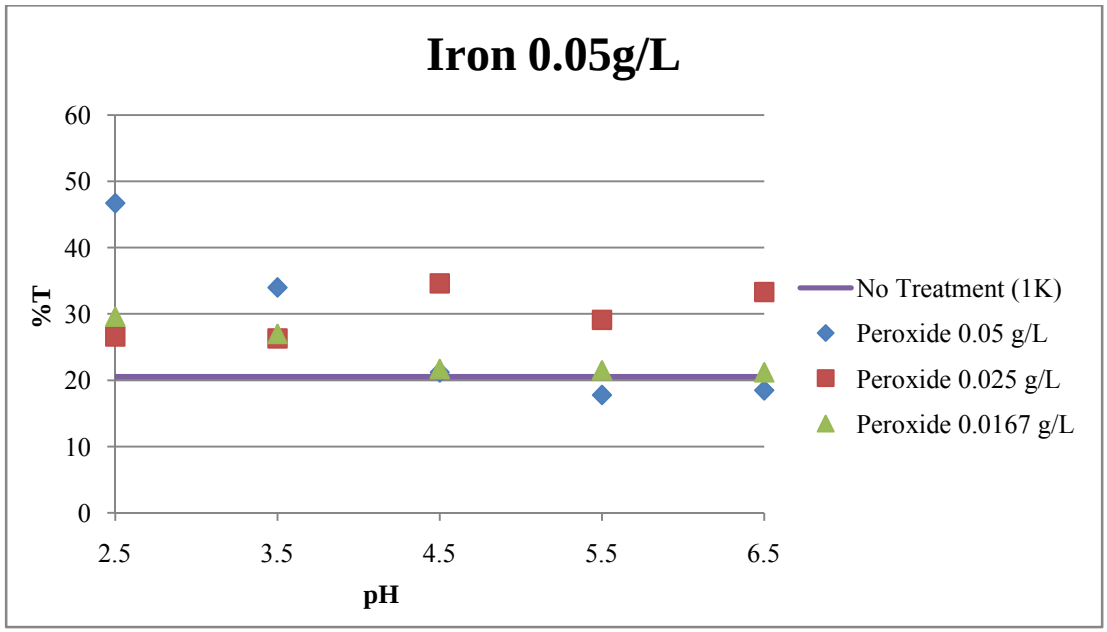

Fig 4-4 UV Transmittance vs pH for oxidized 1k ultrafiltrate for varying peroxide doses and at an iron dose of 0.05 g/L

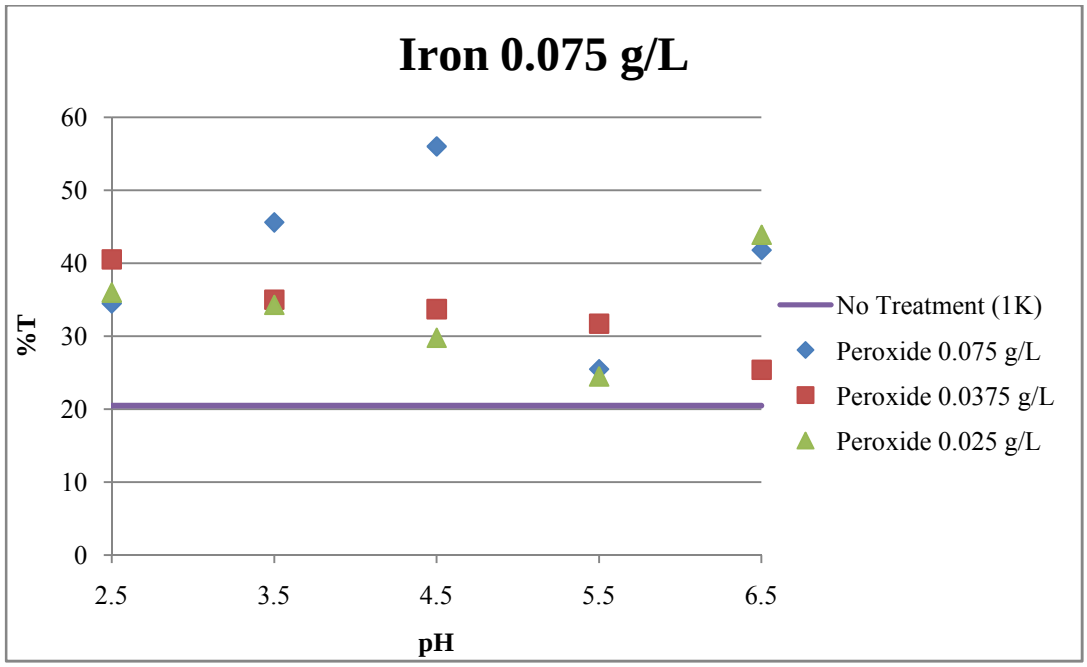

Fig 4-5 UV Transmittance vs pH for oxidized 1k ultrafiltrate for varying peroxide doses and at an iron dose of 0.075 g/L

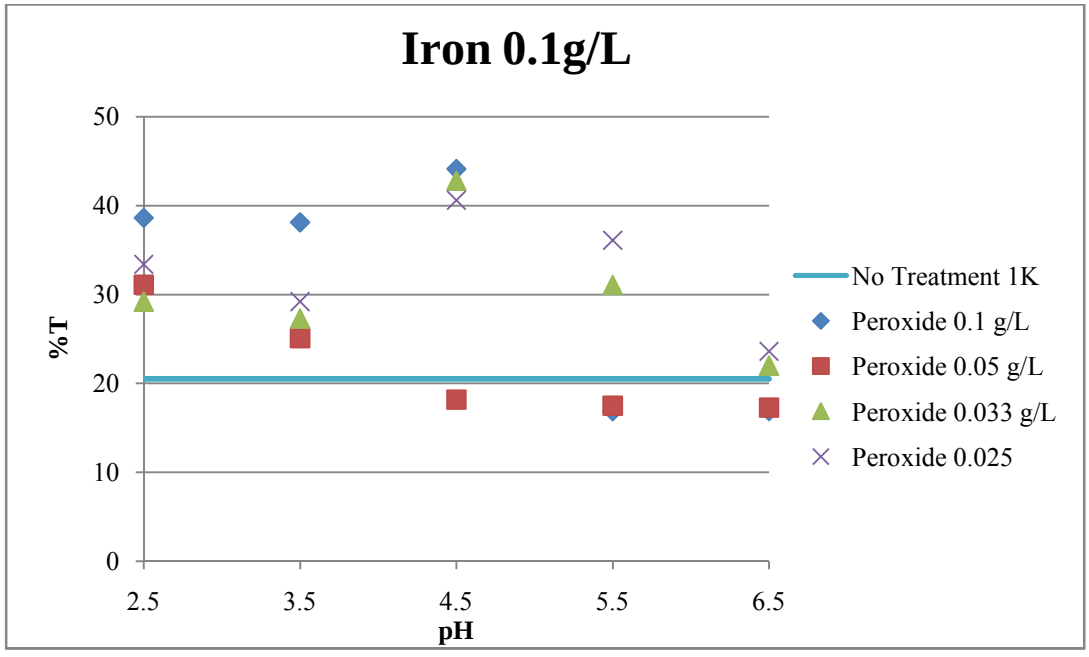

Fig 4-6 UV Transmittance vs pH for oxidized 1k ultrafiltrate for varying peroxide doses and at an iron dose of 0.1 g/L

3.2 *0.45 μm filtrate*

a) TOC Removal Study

1) **Effect of pH:** The iron and peroxide dose are kept constant and the pH is varied from a value of 2.5 to a value of 6.5. The results are shown in Fig 3-7, 3-8 and 3-9. It is observed for all iron and peroxide doses that the pH does not affect the TOC removal efficiency for pH values in the range of 2.5-5.5. However, the efficiency decreases when the initial pH is adjusted to 6.5.
2) **Effect of peroxide dose-** It was observed that the TOC removal remains same with increasing peroxide dose at lower initial pH of 2.5 and 3.5. No trend in corresponding TOC removal with respect to increasing peroxide dose is observed at pH 4.5 and 5.5. However, TOC removal increases with increasing peroxide dose at pH 6.5
3) **Effect of iron dose –** It was observed that an increase in the iron dose does not affect the corresponding TOC removal at pH of 2.5 and 3.5. No trend was observed at pH of 4.5 and 5.5. But at a pH value of 6.5, the TOC removal decreases with increasing iron dose. The plots showing the effect of iron dose on corresponding TOC removal can be found in Appendix C.

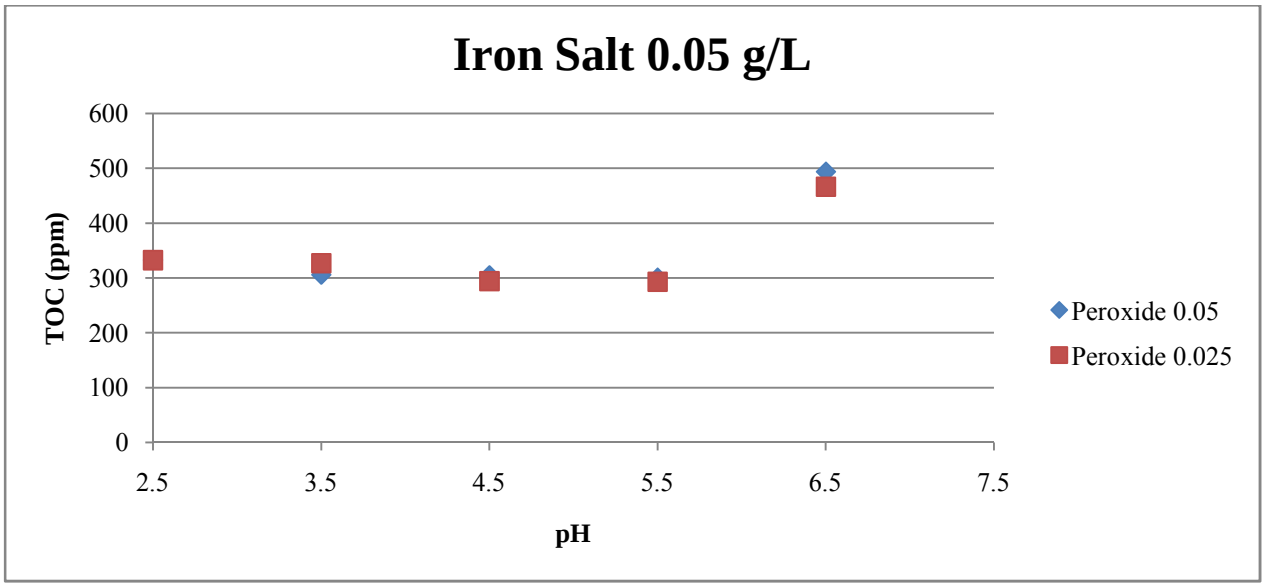

Fig 4-7 TOC vs pH for oxidized 0.45 µm filtrate for varying peroxide doses and at an iron dose of 0.05 g/L

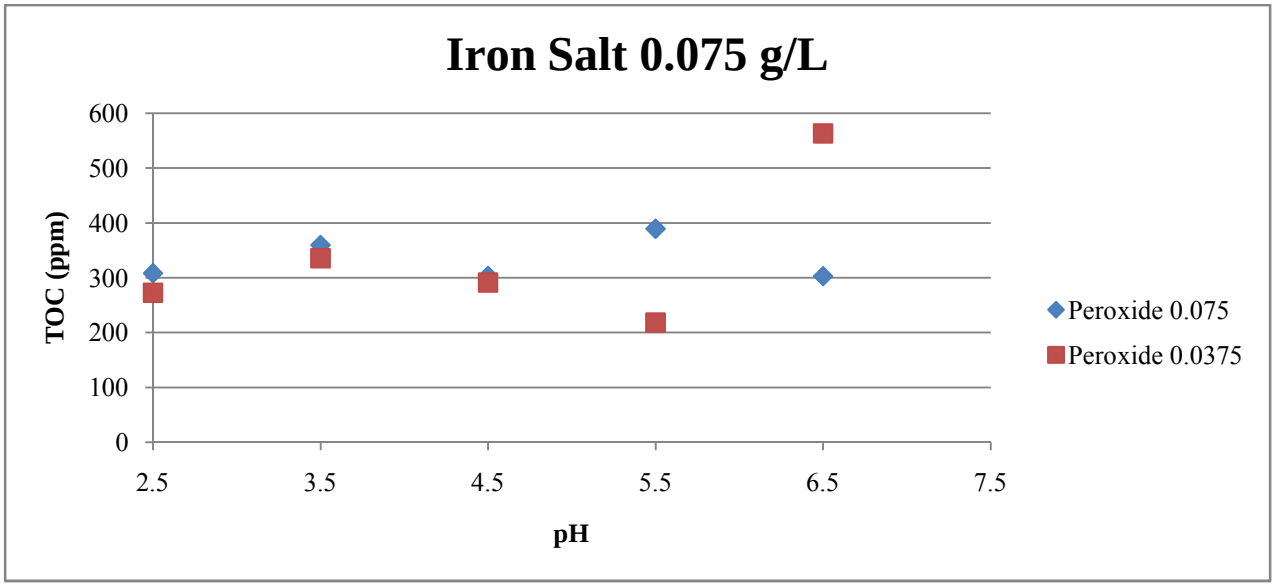

Fig 4-8 TOC vs pH for oxidized 0.45 µm filtrate for varying peroxide doses and at an iron dose of 0.075 g/L

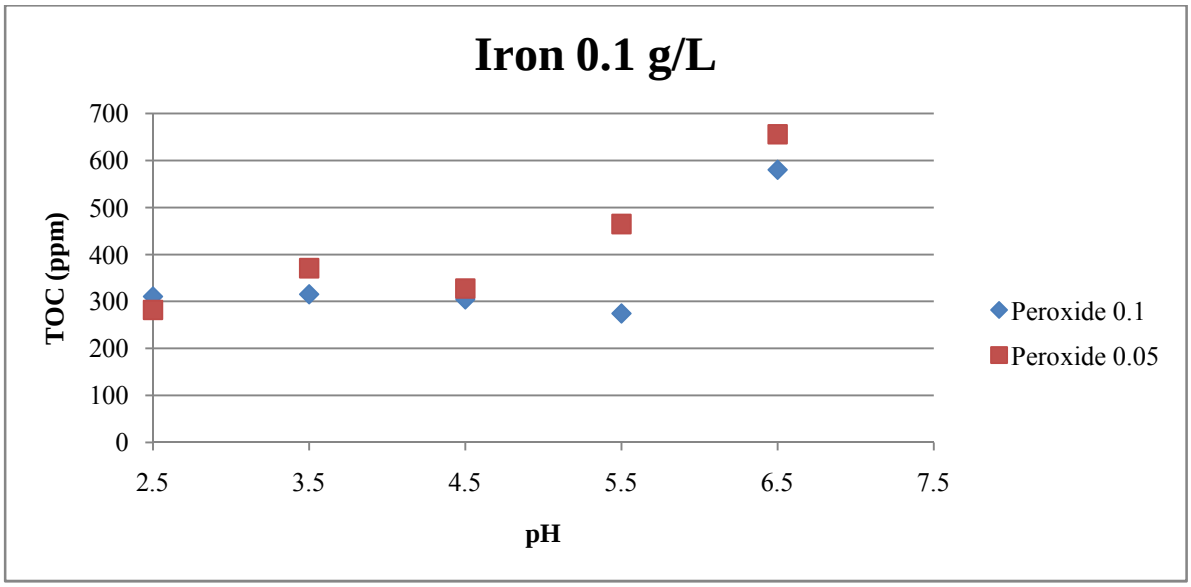

Fig 4-9 TOC vs pH for oxidized 0.45 μm filtrate for varying peroxide doses and at an iron dose of 0.1 g/L

b) UV Transmission

Zero transmittance was observed for untreated samples so the samples were diluted by a factor of 10 before they were tested.

1) **Effect of pH** - The value of initial pH does not make much difference to the transmittance values. The transmittance values at lower and higher pH values were found to be similar to each other. The results of this experiment are shown in Fig 3-10, 3-11 and 3-12. The maximum transmittance of 24% was obtained for an iron dose of 0.075 g/L and peroxide dose of 0.0375 g/l at a pH of 5.5.

2) **Effect of peroxide dose –** It was observed that the transmittance properties remain the same with increasing peroxide dose at an initial pH of 2.5 and 3.5. No trend was observed at an initial pH value of 4.5

3) **Effect of iron dose –** It was observed that the percentage transmittance increases with increasing iron dose at an initial pH of 2.5. The trend is however opposite for pH 3.5. No trend is however observed with respect to percentage transmittance with increasing iron dose at an initial pH of 4.5. The plots showing the effect of iron dose on the transmittance properties can be found in Appendix D

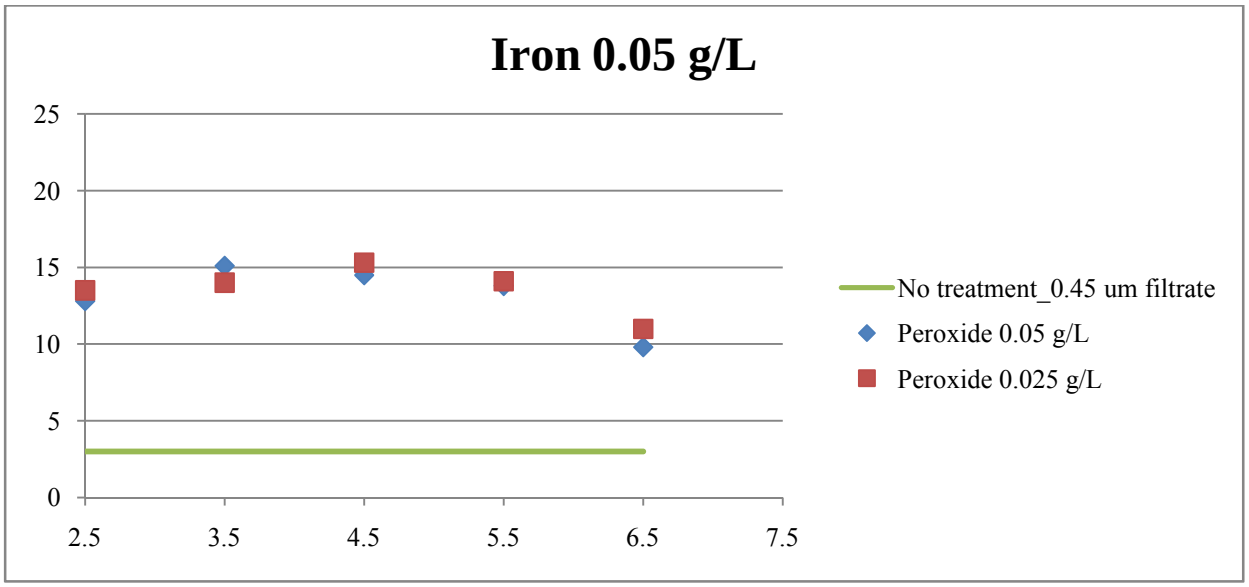

Fig 4-10 UV Transmittance vs pH for oxidized 0.45 µm filtrate for varying peroxide doses and at an iron dose of 0.05 g/L

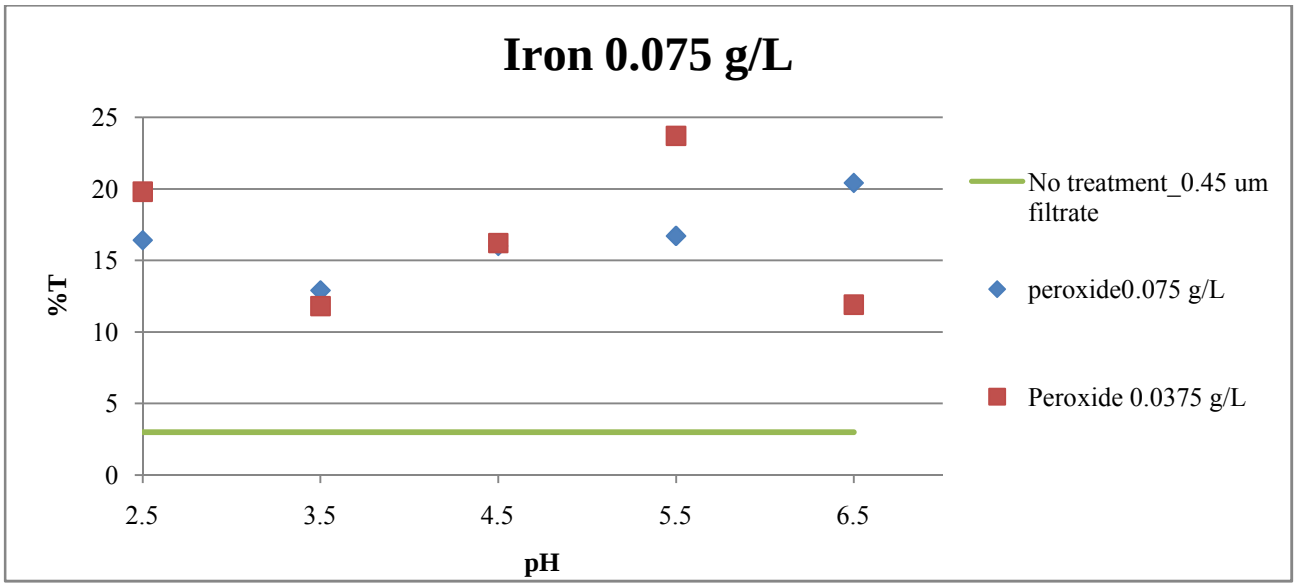

Fig 4-11 UV Transmittance vs pH for oxidized 0.45 µm filtrate for varying peroxide doses and at an iron dose of 0.075 g/L

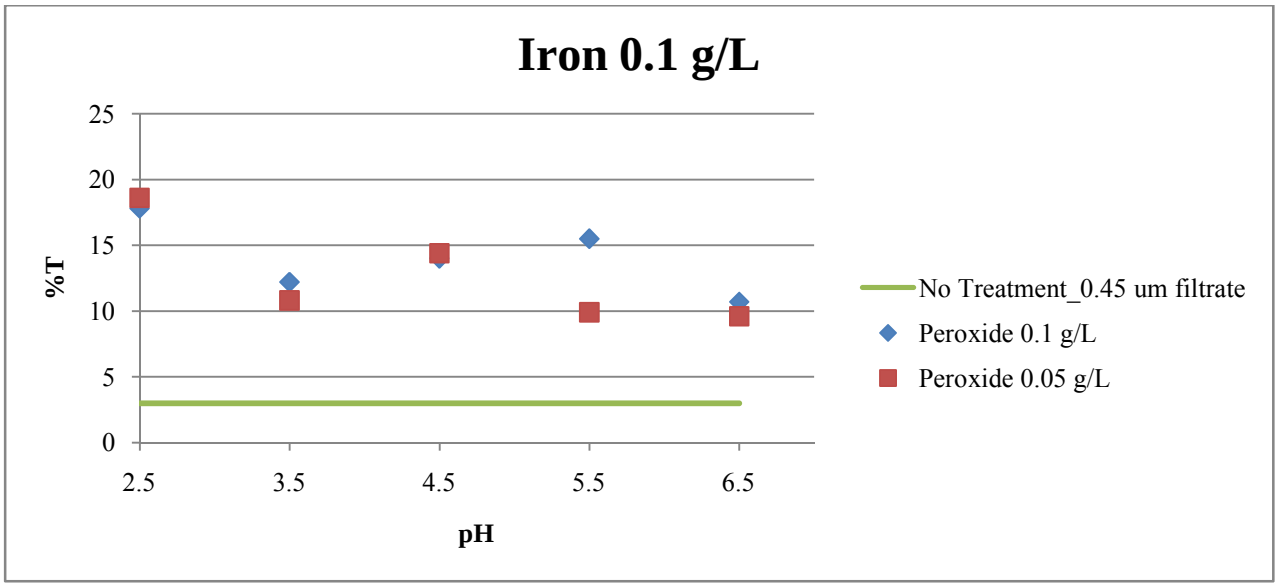

Fig 4-12 UV Transmittance vs pH for oxidized 0.45 µm filtrate for varying peroxide doses and at an iron dose of 0.1 g/L

Comparison of performance of 1K ultrafiltrate and 0.45 μm filtrate

The efficiency of TOC removal and also percentage transmittance is found to be higher in the case of the 1K ultrafiltrate. The maximum transmittance obtained for 1K ultrafiltrate was 58.9% while it was just 23.7% for the filtrate from a 0.45 μm filter. Additional studies are needed to determine if an increase in percentage transmittance for 0.45 μm filtrate can be obtained by varying the operational parameters such as increasing the dosages. However, increased dosages will result in increased sludge production. Therefore, the economy of using the 1K ultrafiltrate and 0.45 μm filtrate need to be calculated to determine the optimum process.

Appendix A

Effect of Iron Dose on TOC removal for oxidized 1K ultrafiltrate

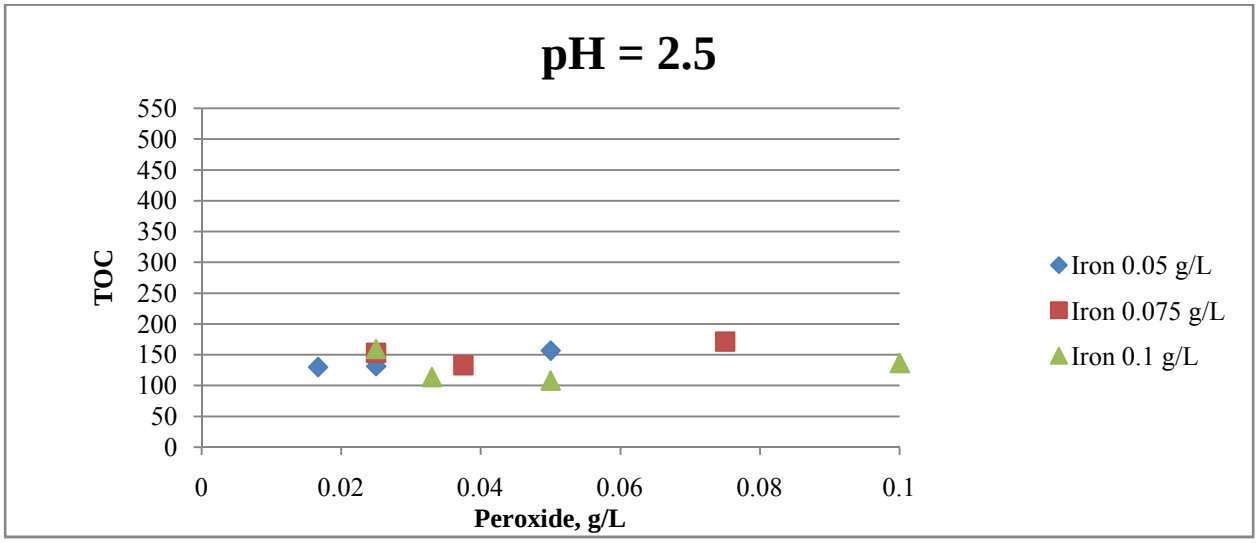

Fig A-1 TOC vs Peroxide dose for oxidized 1k ultrafiltrate at an initial pH of 2.5

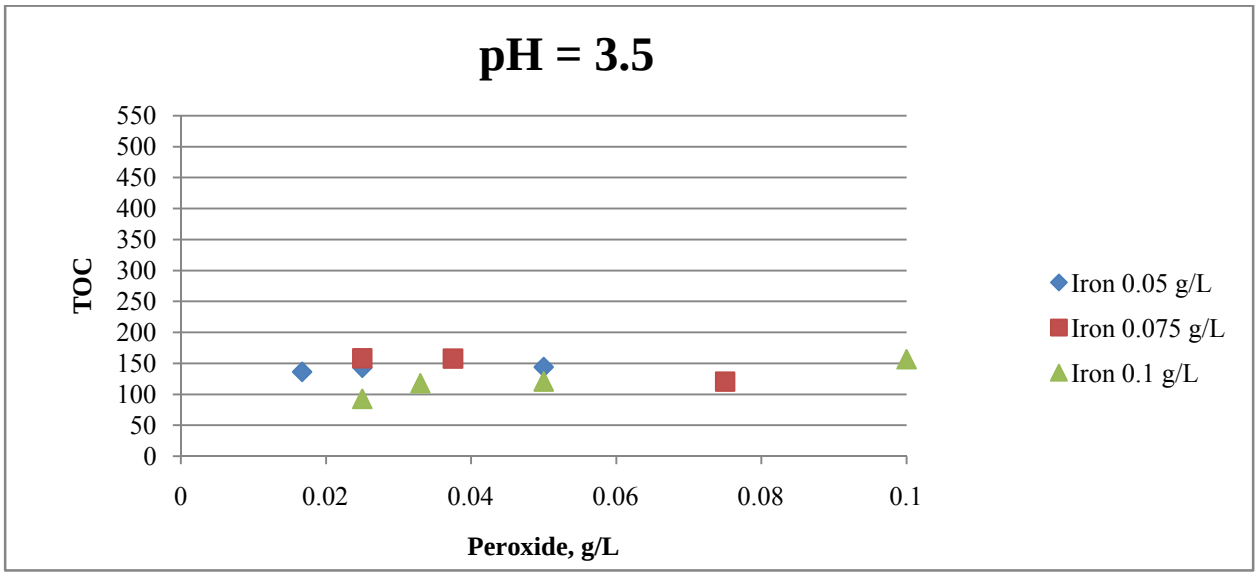

Fig A-2 TOC vs Peroxide dose for oxidized 1k ultrafiltrate at an initial pH of 3.5

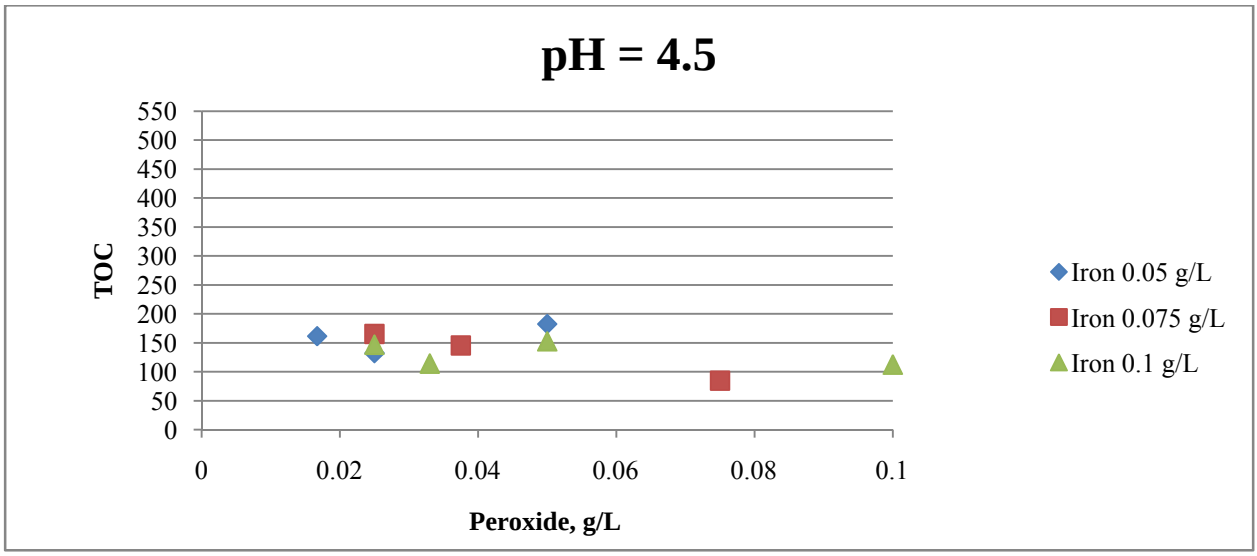

Fig A-3 TOC vs Peroxide dose for oxidized 1k ultrafiltrate at an initial pH of 4.5

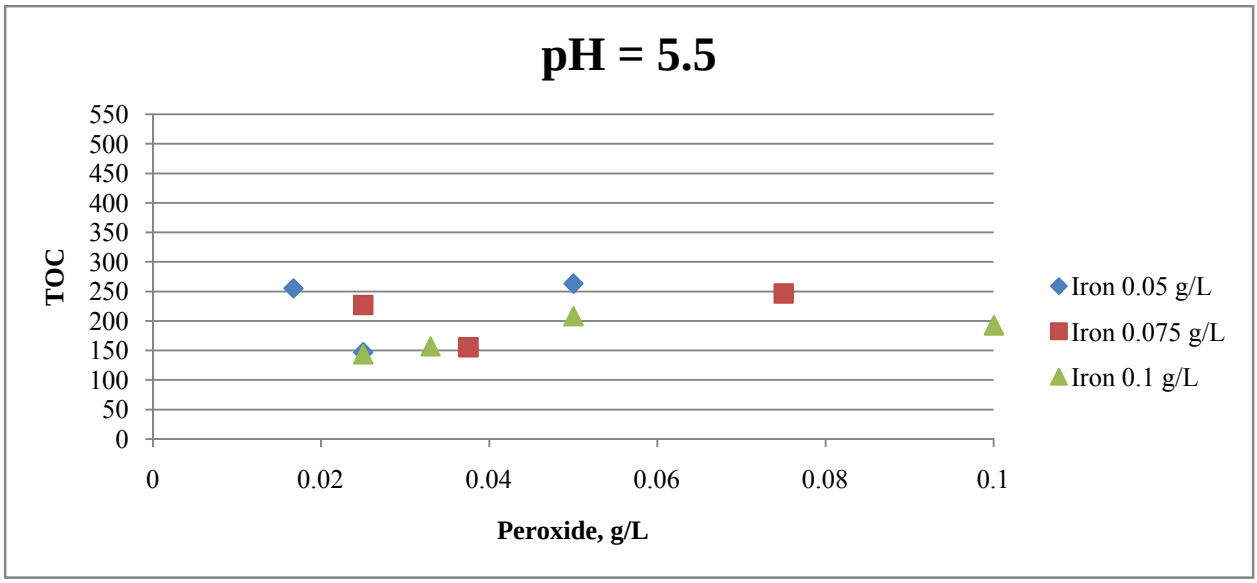

Fig A-4TOC vs Peroxide dose for oxidized 1K ultrafiltrate at an initial pH of 5.5

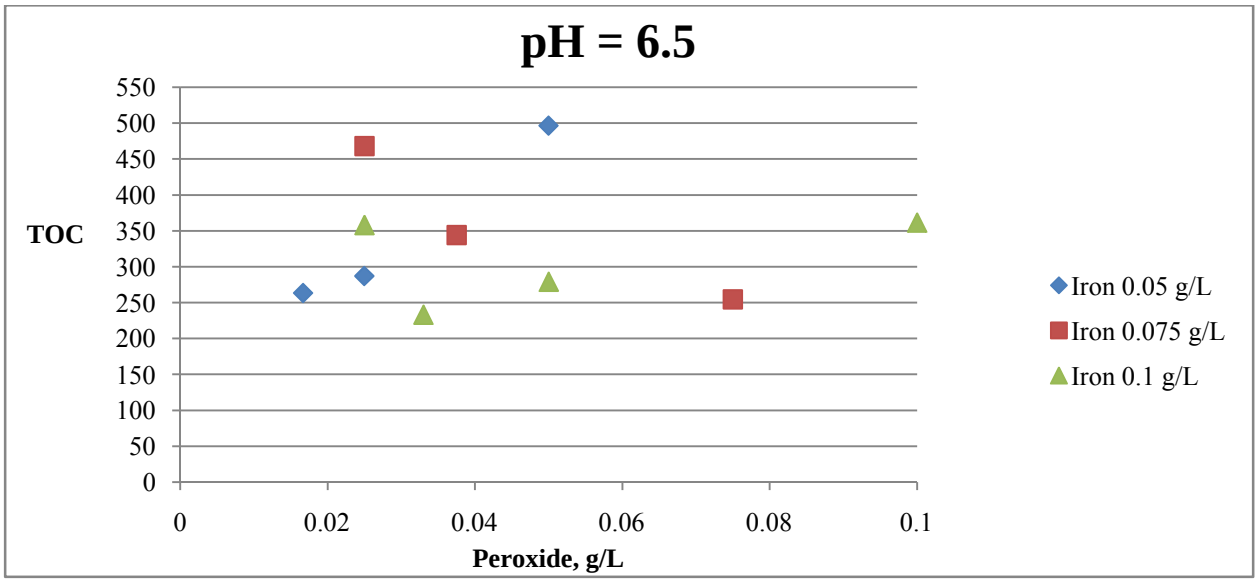

Fig A-5 TOC vs Peroxide dose for oxidized 1K ultrafiltrate at an initial pH of 6.5

Appendix B

Effect of iron dose on transmittance properties for oxidized 1K ultrafiltrates

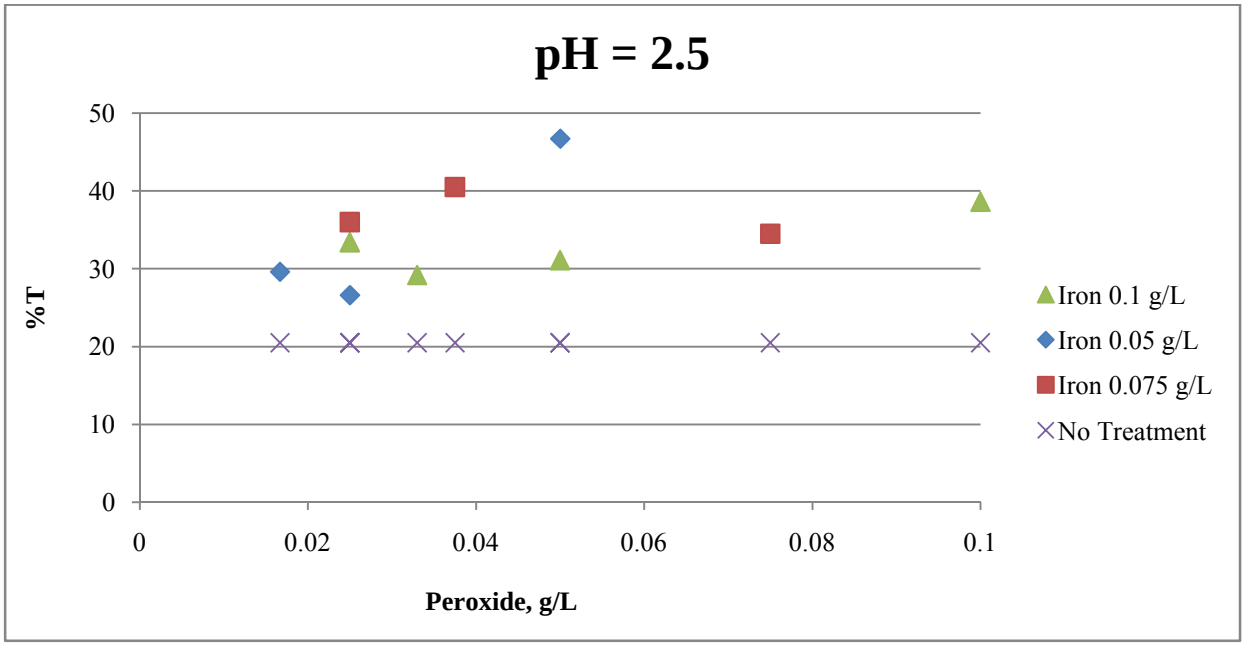

Fig B-1 Percent transmittance vs Peroxide dose for oxidized 1K ultrafiltrate at an initial pH of 2.5

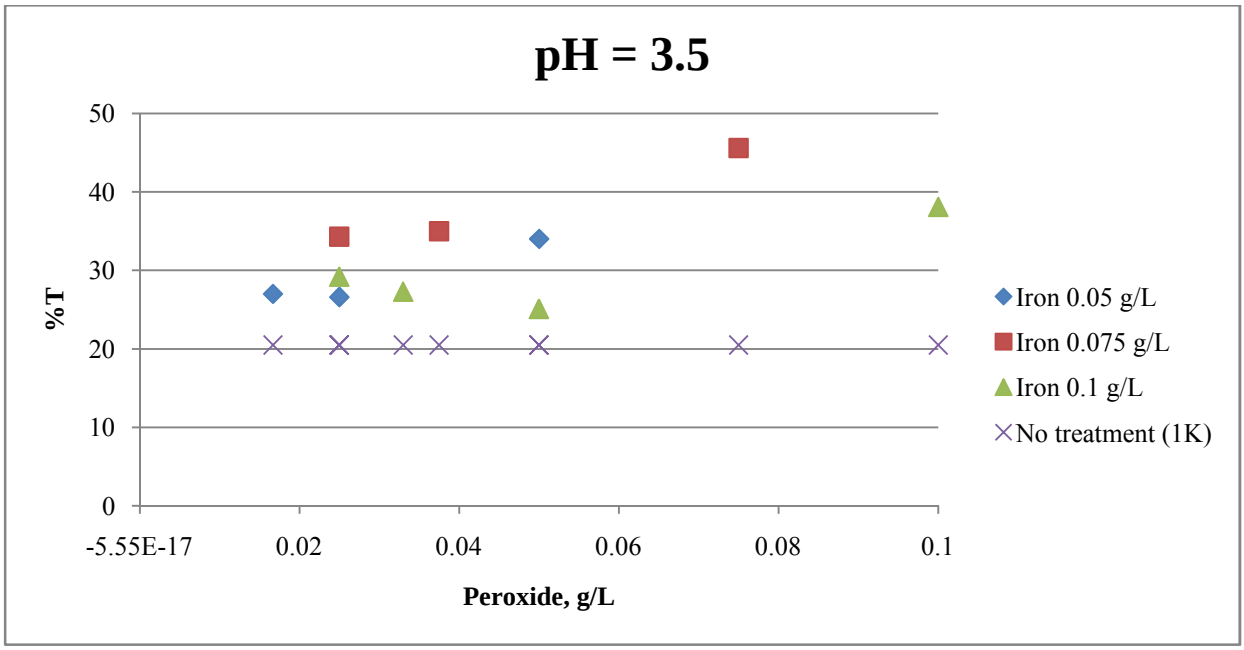

Fig B-2 Percent transmittance vs Peroxide dose for oxidized 1K ultrafiltrate at an initial pH of 3.5

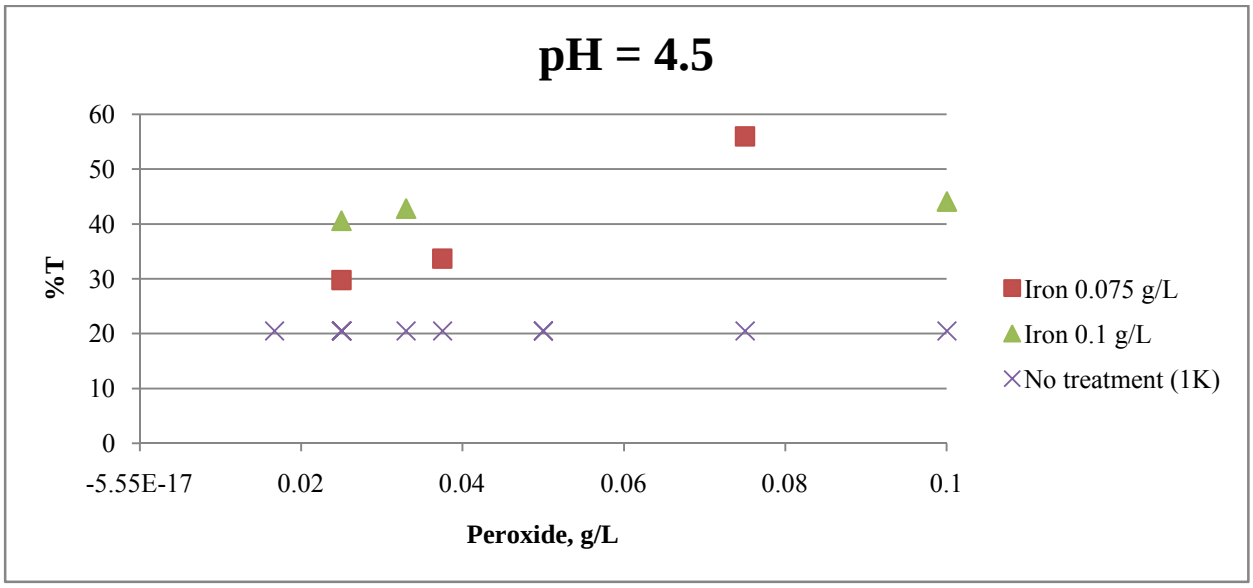

Fig B-3 Percent transmittance vs Peroxide dose for oxidized 1K ultrafiltrate at an initial pH of 4.

Appendix C

Effect of iron dose on corresponding TOC removal for 0.45 μm filtrate

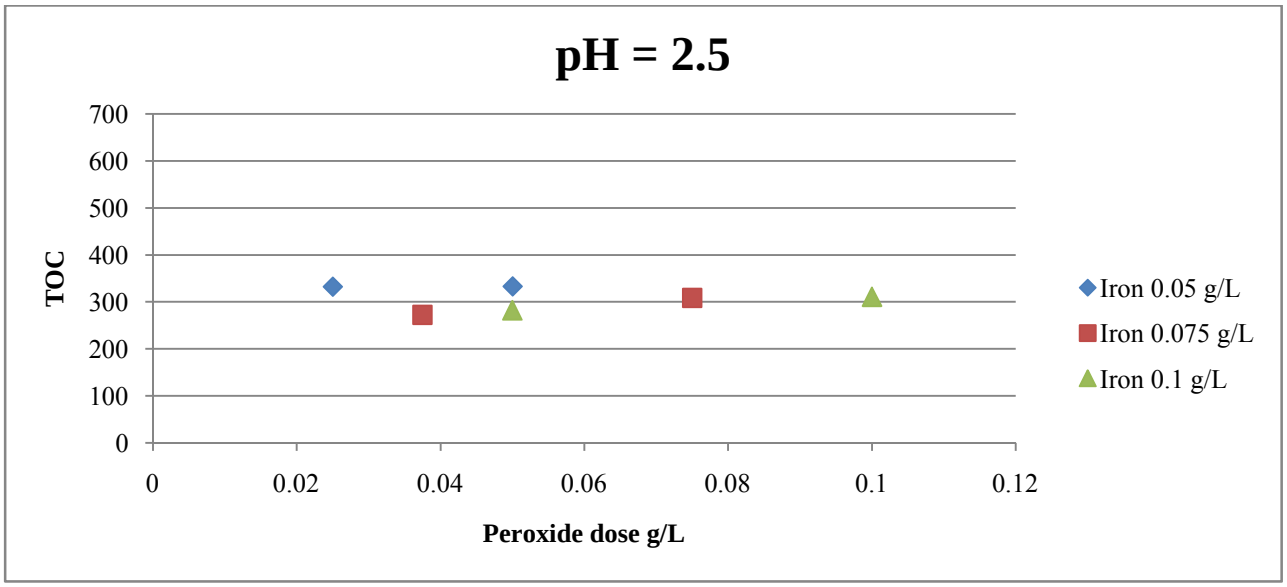

Fig C-1 TOC vs Peroxide Dose for oxidized 0.45μm filtrate at an initial pH of 2.5

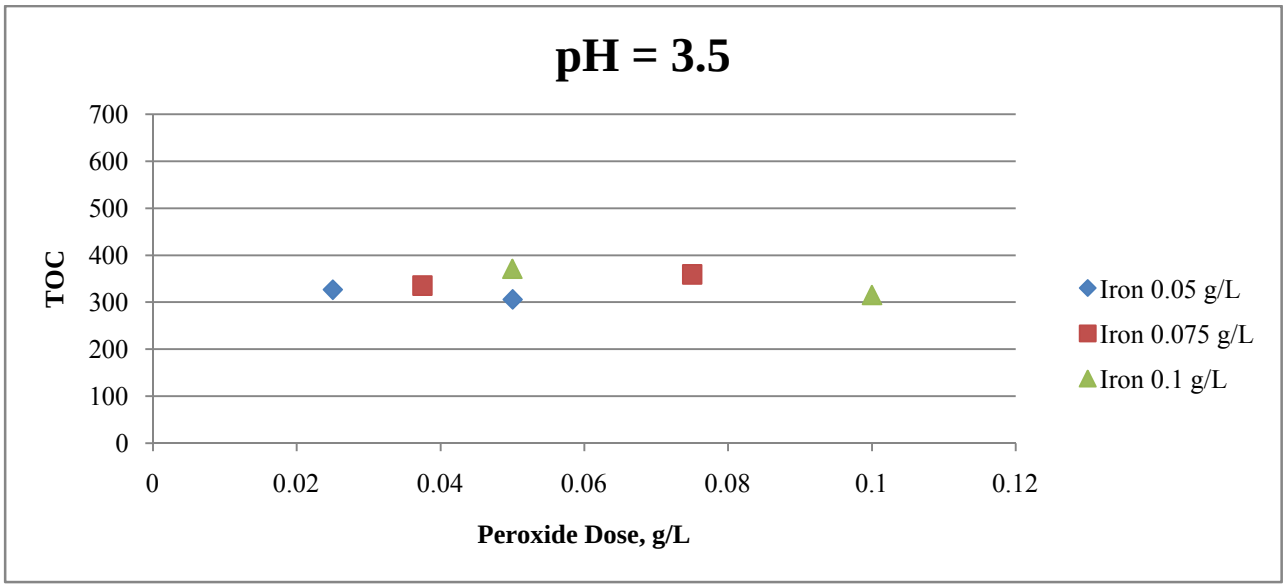

Fig C-2 TOC vs Peroxide Dose for oxidized 0.45μm filtrate at an initial pH of 3.5

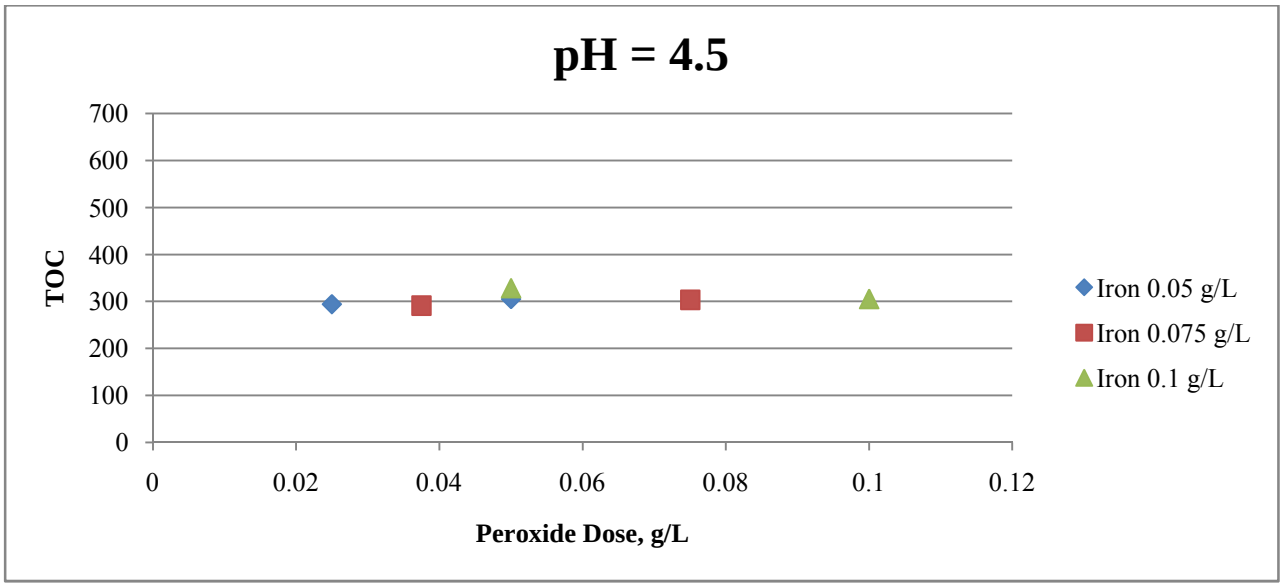

Fig C-3 TOC vs Peroxide Dose for oxidized 0.45µm filtrate at an initial pH of 4.5

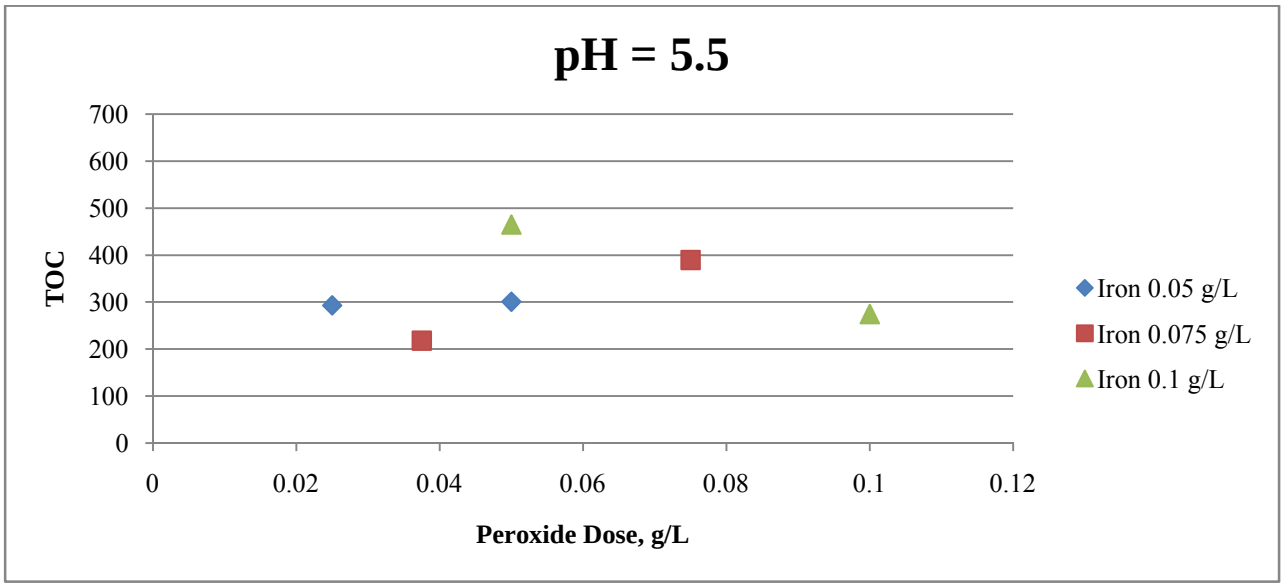

Fig C-4 TOC vs Peroxide Dose for oxidized 0.45µm filtrate at an initial pH of 5.5

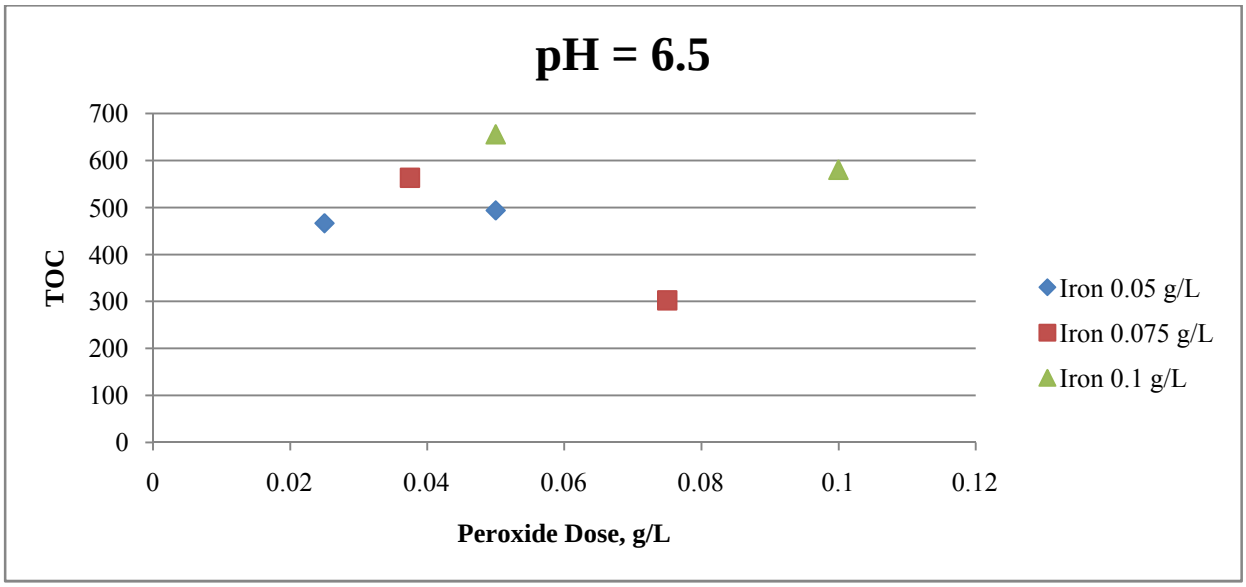

Fig C-5 TOC vs Peroxide Dose for oxidized 0.45µm filtrate at an initial pH of 6.5

Appendix D

Effect of iron dose on transmittance properties for oxidized filtrates

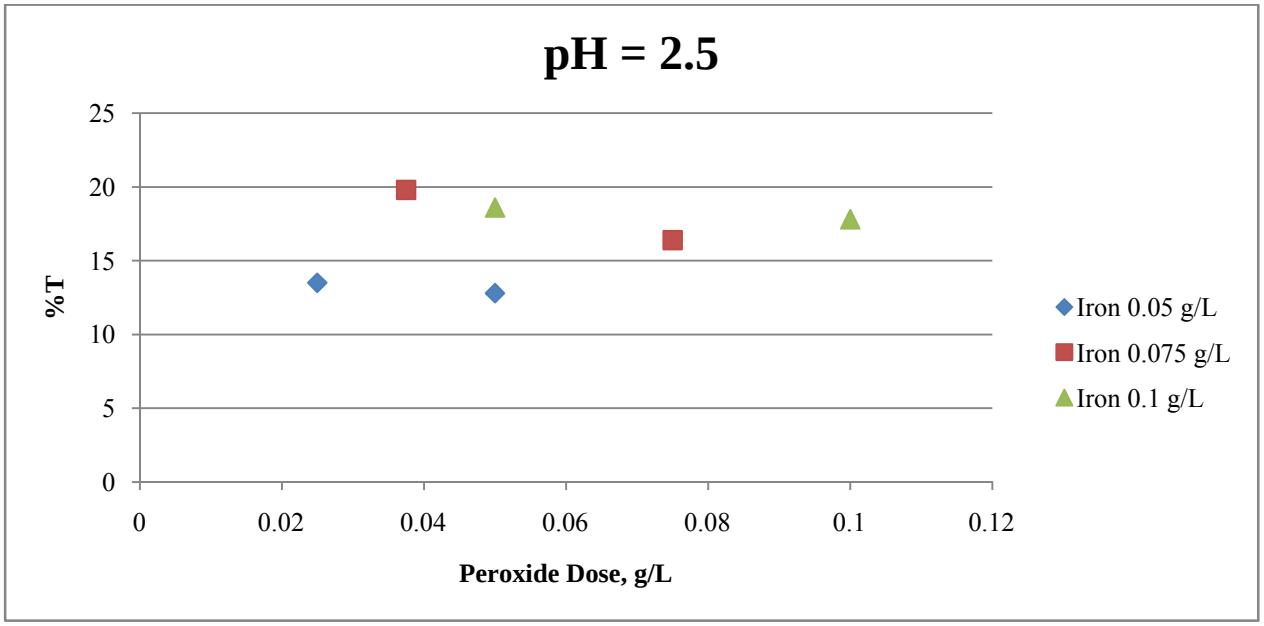

Fig D-1 Percent transmittance vs Peroxide dose for oxidized 0.45 µm filtrate at initial pH of 2.5

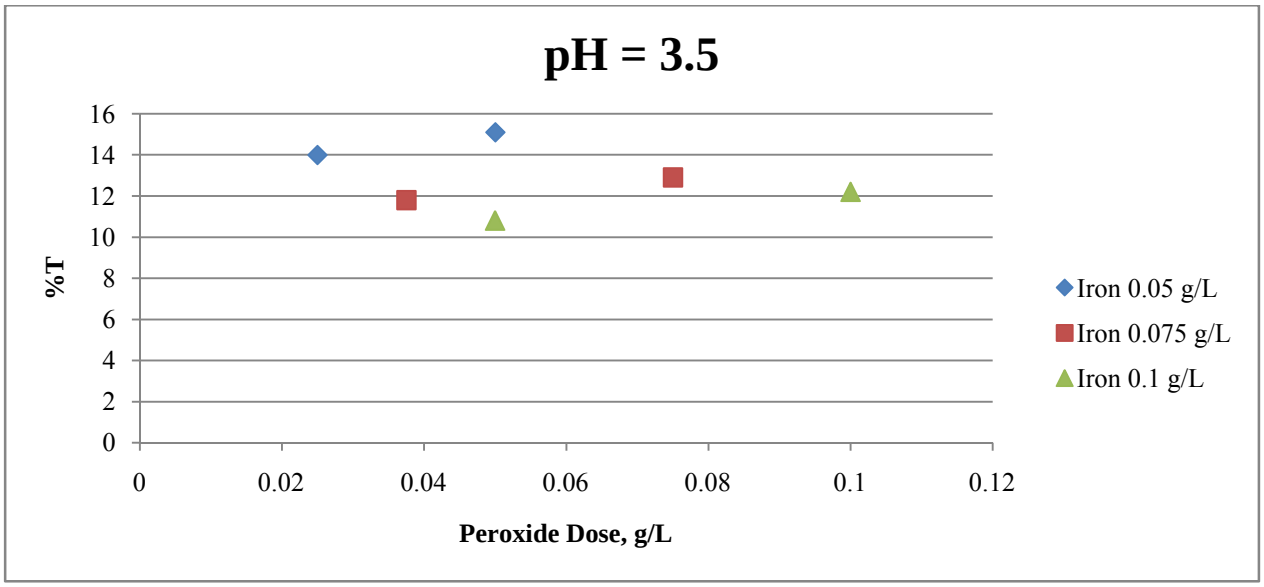

Fig D-2 Percent transmittance vs Peroxide dose for oxidized 0.45 µm filtrate at initial pH of 3.5

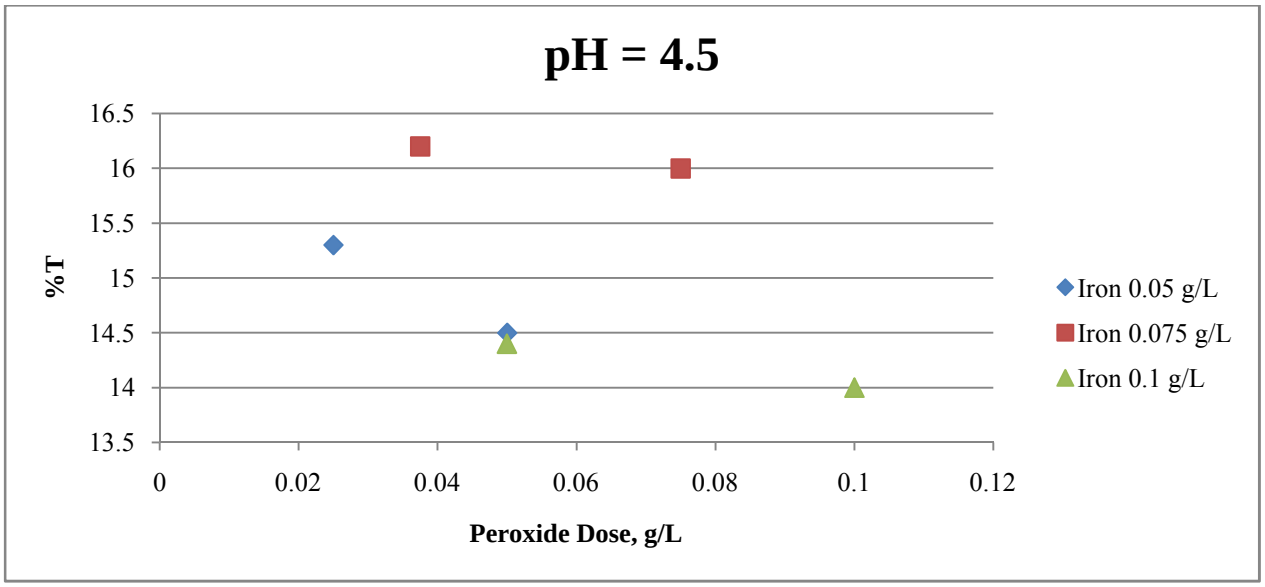

Fig D-3 Percent transmittance vs Peroxide dose for oxidized 0.45 μm filtrate at initial pH of 4.5

References-

1) Alborzfar M., G. Jonsson, C. Grøn, Removal of natural organic matter from two types of humic groundwater by nanofiltration, Water Res. 32 (10) (1998) 2983–2994.
2) Ali M.A.B., M. Rakib, S. Laborie, P.H. Viers, G. Durand, Coupling of bipolar membrane electrodialysis and ammonia stripping for direct treatment of wastewaters containing ammonium nitrate, J. Membr. Sci. 244 (1-2) (2004) 89–96.
3) Alvarez-Vazquez, H., B. Jefferson, S.J. Judd, Membrane bioreactors vs conventional biological treatment of landfill leachate: a brief review. J. Chem. Technol. Biot. 79 (2004), 1043–1049.
4) Amonkrane, A., C. Comel, J. Veron, Landfill leachates pretreatment by coagulation–flocculation, Water Res. 31 (11) (1997) 2775–2782.
5) Bae, B.U., E.S. Jung, Y.R. Kim, H.S. Shin, Treatment of landfill leachate using activated sludge process and electron-beam radiation. Water Res. 33 (11) (1999), 2669–2673.
6) Barb W. G., J.H. Baxendale, P. George and K.R. Hergrave, (1951) Reactions of ferrous and ferric ions with hydrogen peroxide. Part 1. The ferrous ion reaction, Trans. Faraday Soc. 47 (1951), 462 – 500.
7) Bigda, R.J., Consider Fenton's chemistry for wastewater treatment. Chem. Eng. Prog. **91** (2) (1995), 62–66.
8) Bila, D.M., A.F. Montalvao, A.C. Silvaa, M. Dezottia, Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement, Hazard. Mater. 117 (2-3) (2005) 235–242.
9) Bilstad, T. and M.V. Madland, Leachate minimization by reverse osmosis. *Wat. Sci. Technol.* 25 (3) (1992), 117-120.
10) Charerntanyarak L., Heavy metals removal by chemical coagulation and precipitation, Water Sci. Technol. 39 (10) (1999) 135–138.
11) Chian E.S.K and F.B. Dewalle, Sanitary landfill leachates and their treatment. J. Environ. Eng. Div. **102** (1976), 411–431
12) Chian, E. S. K. and Dewalle F. B., Sanitary landfill leachates and their treatment. J. Environ. Eng. Div. 102, (1976) 411-431.
13) Chian, E.S.K., Stability of organic matter in landfill leachates. Water Res. 11 (2) (1977), 225–232.

14) Chidambara, C.B., H.L. Quen, Advanced oxidation processes for wastewater treatment: optimization of UV/H2O2 process through a statistical technique. Chem. Eng. Sci. 60 (19) (2005), 5305–5311.

15) Cornelissen E.R., P. Sijbers, H. Berkmortel, J. Koning, A. De Wit, F. De Nil, J.F. Impe, Reuse of leachate wastewater using MEMBIOR technology and reverse osmosis, Membr. Technol. 2001 (136) (2001) 6-9.

16) Crawford, J.F., and P.G. Smith, Landfill Technology, Butterworths, London (1985), 84–85.

17) Deng Y., J.D. Englehardt, Treatment of landfill leachate by the Fenton process Wat. Res. 40 (20) (2006) 3683 – 3694

18) Deng Y., Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate, J. Haz. Mat. 146 (2007) 334–340.

19) Diamadopoulos, E., Characterization and treatment of recirculation-stabilized leachate. Wat. Res. 28 (12) (1994), 2439–2445.

20) Ehrig, H.J., Treatment of sanitary landfill leachate: biological treatment. Waste Manage. Res. 2, (1984), 131–152.

21) Fettig J., Removal of humic substances by adsorption/ion exchange, Water Sci. Technol. 40 (9) (1999) 173–182

22) Gogate, P.R., A.B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods. Advances in Environmental Research 8 (3-4) (2004), 553–597.

23) Gourdon, R., C. Comel, P. Vermande, J. Veron, Fractionation of the organic-matter of a landfill leachate before and after aerobic or anaerobic biological treatment. Water Res. 23 (2) (1989), 167–173.

24) Hagman M., E. Heander and J. la C. Jansen, Advanced oxidation of refractory organics leachate – potential methods and evaluation of biodegradability of the remaining substrate, Environmental Technology 29 (9) (2008), 941–946.

25) Harber F. and J.J. Weiss, The catalytic decomposition of hydrogen peroxide by iron salts. Proc. Roy. Soc. (London) A147 (861) (1934), 332-351.

26) Hermosilla D., M. Cortijo, C. P. Huang Optimizing the treatment of landfill leachate by conventional Fenton and photo-Fenton processes. Sci. of the Total Environment 407 (11) (2009) 3473–3481

27) Horan, N.J., H. Gohar, B. Hill, Application of a granular activated carbon-biological fluidised bed for the treatment of landfill leachates containing high concentrations of ammonia. Wat. Sci. and Tech. 36 (2) (1997), 369–375.

28) Huang C.P., C. Dong, Z. Tang, Advanced chemical oxidation: its present role and potential future in hazardous waste treatment, Waste Manage. 13 (1993) 361–377.

29) Kang Y.W., K.Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, Water Res. 34 (10) (2000) 2786–2790.

30) Kargi F., M.Y. Pamukoglu, Simultaneous adsorption and biological treatment of pre-treated landfill leachate by fed-batch operation, Process Biochem. 38 (10) (2003) 1413–1420.

31) Kim J.S., H.Y. Kim, C.H. Won, J.G. Kim, Treatment of leachate produced in stabilized landfills by coagulation and Fenton oxidation process, J. Chin. Inst. Chem. Eng. 32 (2001) 425–429.

32) Kjeldsen, P., M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review. Crit. Rev. Environ. Sci. Technol. 32, (2002) 297–336.

33) Krug T. A. and S. McDougall (1988) Preliminary assessment of a microfiltration/ Reverse osmosis process for the treatment of landfill leachate. Proc. Ind. Waste Conf. West Lafayett (Indiana) 43rd (1988), 583-590.

34) Kurniawan, T.A., W.H. Lo, G.Y.S. Chan, Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate, Hazard. Mater. 129 (1-3) (2006) 80–100.

35) Lau I.W.C, P. Wang, H.H.P. Fang, Organic removal of anaerobically treated leachate by Fenton coagulation, J. Environ. Eng., ASCE 127 (7) (2001) 666–669.

36) Li R., D. Yue , J. Liu, Y. Nie, Size fractionation of organic matter and heavy metals in raw and treated leachate Waste Management 29 (9) (2009) 2527–2533.

37) Lopes de Morais, J., P.P. Zamora, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, Hazard. Mater. 123 (1-3) (2005) 181–186.

38) Martinnen, S.K., R.H. Kettunen, K.M. Sormunen, R.M. Soimasuo, J.A. Rintala, Screening of physical-chemical methods for removal of organic material, nitrogen and toxicity from low strength landfill leachates, Chemosphere 46 (6) (2002) 851–858.

39) Medez, R., J.M. Lema, R. Blazquez, M. Pan and C. Forjan, Characterization, digestibility and anaerobic treatment of leachates from old and young landfills. Wat. Sci. Technol. 21 (1989), 145–155.

40) Monje, I.R., M.T. Orta de Velasquez, Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachate by coagulation–ozonation coupling processes, Water Res. 38 (9) (2004) 2359–2367.

41) Moraes, P.B., R. Bertazzoli, Electrodegradation of landfill leachate in a flow electrochemical reactor, Chemosphere 58 (1) (2005) 41–46.

42) Mott, H.V., K.E. Hartz, and D.R.Yonge, Metal precipitation in two landfill leachates, J. Environ. Engineering, ASCE, 113(3) (1987), 476–485.

43) N. Saffaj, H. Loukili, S.A. Younssi, A. Albizane, M. Bouhria, M. Persin, A. Larbot, Filtration of solution containing heavy metals and dyes by means of ultrafiltration membranes deposited on support made of Morrocan clay, Desalination 168 (2004) 301–306.

44) Nanny, M.A., N. Ratasuk, Characterization and comparison of hydrophobic neutral and hydrophobic acid dissolved organic carbon isolated from three municipal landfill leachates. Water Res. 36 (6) (2002), 1572–1584.

45) Neyens E., J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (1-3) (2003) 33–50.

46) O'Melia C.R., W.C. Becker, K.K. Au, Removal of humic substances by coagulation, Water Sci. Technol. 40 (1999) 47–54.

47) Ozturk, I., M. Altinbas, I. Koyuncu, O. Arikan, C. Gomec-Yangın Advanced physico-chemical treatment experiences on young municipal landfill leachates, Waste Manage. 23 (5) (2003) 441–446.

48) Papadopoulos A., D. Fatta, M. Loizidou, Treatment of stabilized landfill leachate by physico-chemical and bio-oxidation processes, J. Environ. Sci. Heal. A33 (4) (1998) 651–670.

49) Park, S., K. S. Choi, K.S. Joe, W.H. Kim, H.S. Kim, Variations of landfill leachate's properties in conjunction with the treatment process. Environ. Technol. 22 (6) (2001), 639–645.

50) Pera-Titus, M., V. Garcia-Molina, M.A. Banos, J. Gimenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review. Applied Catalysis B: Environmental 47 (4) (2003), 219–256.

51) Perez, M., F. Torrades, X. Domenech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents. Wat. Res. 36 (11) (2002), 2703–2710.

52) Pirbazari, M., V. Ravindran, B.N. Badriyha and S.H. Kim, Hybrid membrane filtration process for leachate Wat. Res. 30 (11) (1996), 2691-2706.

53) Rivas, F.J., F. Beltr´an, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachates: sequential coagulation–flocculation + chemical oxidation process, Hazard. Mater. 116 (1-2) (2004) 95–102.

54) Slater C. S., R.C. Ahlert and G. Uchri, Treatment of landfill leachates by reverse osmosis. Environ. Prog. 2 (4) (1983), 251-256.

55) Syzdek A. C. and Ahlert R. C., Separation of landfill leachate with polymeric ultrafiltration membranes, J.Haz. Mat. 9 (2) (1984) 209-220.

56) Tatsi, A., A.L. Zouboulis, K.A. Matiss, P. Samara, Coagulation–flocculation pretreatment of sanitary landfill leachates, Chemosphere 53 (7) (2003) 737–747.

57) Tizaoui C., L. Bouselmi, L. Mansouri, A. Ghrabi, Landfill leachate treatment with ozone and ozone/hydrogen peroxide systems. J. Haz. Mat. 140 (1-2) (2007), 316-324.

58) Trebouet, D., J.P. Schlumpf, P. Jaouen, F. Quemeneur, Stabilized landfill leachate treatment by combined physicochemical–nanofiltration processes. Water Res. 35 (12) (2001), 2935–2942.

59) Visvanathan C., S. Muttamara, S. Babel, Treatment of landfill leachate using cross-flow microfiltration and ozonation, Sep. Sci. Technol. 29 (3) (1994) 315–332.

60) Wang, F., D. W. Smith, M.G. El-Din, Aged raw landfill leachate: Membrane fractionation, O3 only and O3/H2O2 oxidation, and molecular size distribution analysis Water Res. 40 (3) (2006) 463 – 474

61) Wang, F., Gamal El-Din, M., Smith, D.W., 2004. Oxidation of aged raw landfill leachate with O3 only and O3/H2O2: treatment efficiency and molecular size distribution analysis. Ozone Sci. Eng. 26 (3) (2004), 287–298.

62) Wang, F., M. G. El-Din, D.W. Smith, Ozonation of biologically treated landfill leachate: treatment efficiency and molecular size distribution analysis. Environ. Technol. 25 (11) (2004), 1277–1283.

63) Wang, F., M.G. El-Din, D.W. Smith, Oxidation of aged raw landfill leachate with O3 only and O3/H2O2: treatment efficiency and molecular size – a review. J. Environ. Sci. 2 (2003), 413–427.

64) Wang, Z., Z. Zhang, Y. Lin, N. Deng, T. Tao, K. Zhuo, Landfill leachate treatment by a coagulation photooxidation process, Hazard. Mater. 95 (1-2) (2002) 153-159.

65) Xu Y.D., D.B. Yue, Y. Zhu, Y.F. Nie Fractionation of dissolved organic matter in mature landfill leachate and its recycling by ultrafiltration and evaporation combined processes, Chemosphere 64 (6) (2006) 903–911.

66) Yoon, J., S. Cho, Y. Cho, S. Kim, The characteristics of coagulation of Fenton reaction in the removal of landfill leachate organics. Water Sci. Technol. 38 (2) (1998), 209–214.

67) Zhang H., H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Haz. Mat. 125 (1-3) (2005) 166–174.