Evaluation of the Effects of Chemically Enhanced Primary Treatment on Landfill Leachate and Sewage Co-treatment in Publicly Owned Treatment Works

Harsh V. Patel[1,2], Brian Brazil[3], Helen H. Lou[4], Manoj K. Jha[1], Stephanie Luster-Teasley[1], Renzun Zhao[1]*

1. Department of Civil, Architectural and Environmental Engineering, North Carolina Agricultural and Technical State University, Greensboro, NC 27411 USA

2. Department of Computational Science and Engineering, North Carolina Agricultural and Technical State University, Greensboro, NC 27411 USA

3. Waste Management Inc., Gaithersburg, MD 20878 USA

4. Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710 USA

* Corresponding author. Phone: 336-285-3684; Fax: 336-334-7126; email: rzhao@ncat.edu

ABSTRACT

Co-treatment of landfill leachate and sewage in publicly owned treatment works (POTWs) is widely applied. In POTWs, Chemically Enhanced Primary Treatment (CEPT) has been broadly utilized to enhance the removal of solids, organic matter, and nutrients. However, landfill leachate is known for high UV absorbance and can interfere with the UV disinfection. This study aims to evaluate the effects of CEPT for leachate and sewage co-treatment, especially on UV quenching phenomenon. 54%-74% organic matter removal was achieved by ferric and aluminum coagulants. Ferric coagulant was found to perform better for organic matter removal than aluminum in most cases. Theoretical models are discussed to elucidate co-precipitation behaviors under various pH scenarios. Notably, ferric chloride coagulation increased the UV absorbance of treated leachate significantly by up to 10 times, while aluminum sulphate only slightly decreased it. It is exacerbated by the complexes formed by ferric and organic matter, which have characteristic light absorption in the UV range. The formation of such complexes is supported by the Fourier Transform Infra-Red (FTIR) spectroscopy. In addition, the volatile acids in leachate were found to play an important role in mediating pH through their buffering capacity.

Keywords: Landfill leachate; Chemically Enhanced Primary Treatment; UV Quenching Phenomenon; Dissolved Organic Carbon; Metal Complexation.

1. INTRODUCTION

In the USA, 50-60% of the municipal solid waste (MSW) is disposed of in landfills as it is the most economical and convenient method based on an US EPA survey (US EPA, 2017). In landfills, a large volume of leachate is generated continuously. Based on an survey by the Environmental Research and Education Foundation (EREF), approximately 27 billion liters of leachate was generated in 2017 in the U.S. (Bolyard, 2017). More than 60% of the landfill leachate is discharged to Publicly Owned Treatment Works (POTWs) in the U.S. as it is convenient and cost-effective (Aarts, 1994; Bolyard, 2017; Karidis, 2016). In a landfill, the cost of leachate management contributes the highest portion among all operation and maintenance. Hence, co-treatment with sewage in POTWs is the most common practice for leachate disposal (Zhao et al., 2013a).

Over the recent decade, POTWs have been switching from chlorination to other disinfection alternatives because chlorine disinfection has been found to produce secondary contamination due to production of Disinfectant By-Products (DBPs). UV disinfection is a promising method because it is highly effective, DBP free, chemical free, etc. However, landfill leachate that contains a high concentration of organic matter can interfere with the UV disinfection process, as the recalcitrant organic matter can strongly absorb the UV light (Iskander et al., 2018; Zhao et al., 2013b). Even after upfront biological treatment, the residual recalcitrant organic matter further interferes with the downstream UV disinfection in POTWs (Gupta et al., 2014a). Hence, POTWs are prudential on accepting landfill leachate (Karidis, 2016). In wastewater treatment practices, POTWs operating with a UV disinfection unit typically requires 60 – 65% transmittance at 254 nm wavelength to achieve the appropriate level of disinfection (Basu et al., 2007).

Chemically Enhanced Primary Treatment (CEPT) is a chemical treatment used in POTWs to enhance the removal of suspended solids, organic matter, and nutrients (such as phosphorus). In the CEPT process, chemical coagulants are typically added to the primary sedimentation basin. CEPT can help reduce the solids and organic loading rate on biological treatment, the treatment infrastructure requirement and overall capital cost (Chagnon and Harleman, 2005). CEPT process is also considered to be a cost-effective method for wastewater treatment in developing countries (Harleman and Murcott, 1999), as it is advantageous in saving footprint (Aiyuk et al., 2004), has low energy requirement (De Feo et al., 2008), and is easy to operate and maintain (Jordão and Volschan, 2004). The efficiency of CEPT in a primary treatment facility depends on the type and dose of coagulant, pH level, temperature and alkalinity (Jiang, 2015). Hence, CEPT, which is coagulation-flocculation in essence, can potentially remove the recalcitrant organic matter carried by landfill leachate and potentially have beneficial impacts on the UV disinfection during sewage-leachate co-treatment in POTWs. However, it has also been found that coagulant with metal salts can increase the UV absorbance due to the interaction between metal cations and organic matter or macromolecules such as humic acid. Such phenomenon has been reported in previous studies where interaction between ferric ion and organic macromolecules increases the UV absorbance (Doane and Horwáth, 2010; Maloney et al., 2005).

In this experimental study, the overall goal is to mimic the scenario that sewage and landfill leachate are co-treated in a POTW using CEPT methods in order to evaluate the overall treatment efficacy and beneficial effects of CEPT for the co-treatment, especially the effects on the UV quenching phenomenon. The objectives are: (a) to evaluate the overall organic matter removal performance of CEPT in co-treatment of landfill leachate and sewage; (b) to reveal the exacerbating effect of UV quenching by CEPT; and (c) to provide theoretical explanations for the effects of CEPT on UV quenching.

2. MATERIALS AND METHODS

2.1 Leachate Sample

Leachate samples were collected from landfill sites A and B in Virginia and Ohio, respectively. In each landfill site, leachate samples were collected from two different zones, denoted as normal leachate and concentrated leachate, respectively. Table 1 shows the characteristics of the raw leachate collected from the two different zones in each site. It was observed that the normal leachate and concentrated leachate are very different in terms of physical, chemical and biochemical characteristics. The normal leachate samples from both sites shared slightly alkaline pH, lower organic component concentrations, higher specific ultraviolet absorbance (SUVA) and lower iron, while both the concentrated leachate samples shared acidic pH, higher organic component concentrations, lower SUVA and higher iron.

Table 1: Characteristics of Raw Leachate Samples

	Site A		Site B	
Parameters	**Normal**	**Concentrated**	**Normal**	**Concentrated**
pH	7.8	5.5	8.6	5.4
Iron (mg/L)	2 ± 0.79*	840 ± 18	40 ± 9	800 ± 21
COD (mg/L)	18,000 ± 165	90,000 ± 393	17,870 ± 186	100,000 ± 387
TOC (mg/L)	4,000 ± 32	30,000 ± 149	3,380 ± 57	33,000 ± 201
UV Absorbance (cm^{-1})	41 ± 3	280 ± 15	120 ± 8	250 ± 12
Volatile Acids (as mg/L CH_3COOH)	785 ± 10.45	22,850 ± 10.34	1,628 ± 44.28	27,700 ± 588
SUVA (L/mg·m)	1.025	0.933	3.550	0.758

*: ± is standard deviation.

Leachate samples were collected in 5-gallon sealed opaque buckets, transported, and stored at 4 °C before further testing and analysis.

2.2 Coagulants

Ferric chloride (BeanTown Chemical, Hudson, NH, USA) and aluminum sulphate (VWR International, Radnor, PA, USA) were used as coagulants. Ferric Chloride and Aluminum Sulphate were chosen as coagulants as they are industrially accepted and widely applied in water and wastewater treatment in primary treatment. Stock solutions of the coagulants were prepared and stored at 4 °C for experimental use. The concentration of prepared stock solutions of ferric chloride and aluminum sulphate was 10 g/L. Application of stock solution is preferred compared to adding solid coagulant for testing, since the dissolved coagulants can mix rapidly compared to the solid coagulant. For every coagulation experiment, fresh stock solutions were prepared on weekly basis for quality control.

2.3 Experimental Setup

Jar test experiments were set up to replicate CEPT treatment. Experiments were carried out using a Velp flocculator jar testers with six paddles (Cole-Parmer, Vernon Hills, IL, USA) that comply with ASTM D2035 (Bridgewater et al., 2012). Samples were prepared by mixing 5% leachate and 95% sewage to mimic the blending of sewage and landfill leachate in POTWs. Then coagulation-flocculation tests were performed on these samples. Prior to running any jar test, samples were brought to room temperature and filtered through 0.45 µm filter paper. The 10 g/L of stock solutions for each coagulant was used to add the coagulants to each jar with different doses. For this study, no fixed coagulant range was predetermined as the normal leachate and concentrated leachate had significantly different organic matter concentration levels. Hence, in this study, the coagulant dose was added in increments of 200 mg/L using the 10 g/L stock solution, until a plateau trend was observed in the organic matter removal, indicating a maximum percentage removal achievable. As per the Standard Method ASTM D 2035 (Bridgewater et al., 2012), 1 minute of rapid mixing at 100 rpm and 30 minutes of slow mixing at 25 rpm was performed after the addition of coagulant stock solution to each jar at different doses. After the mixing, 30 minutes was considered for settlement of precipitates. The supernatants from the jar test were collected after filtering through 0.45 µm filter paper to remove precipitates completely. The filtered supernatants were collected and stored at 4 °C for further analysis.

The same coagulation-flocculation experiments were conducted for a mixture of 5% leachate and 95% de-Ionized water for (a) to compare the result with co-treatment of landfill leachate and sewage, and (b) to determine whether sewage has a different effect on the treatment than water.

De-ionized water was collected from a benchtop Milli-Q water purification system (MilliporeSigma, Burlington, MA, USA) for the experiments. The results for the experiments for 5% leachate and 95% de-ionized water have been shown in the supporting documents for reference.

2.4 Chemical Analysis

All the tests were carried out by following standard methods provided by American Public Health Association (APHA)(Bridgewater et al., 2012). All the glassware used in the analysis were cleaned, rinsed and dried before usage for quality control purpose.

The collected supernatants were analyzed for pH, Chemical Oxygen Demand (COD), volatile acids, Total Organic Carbon (TOC), residual iron and aluminum concentration, UV absorbance, and characterized with Fourier-Transformed Infrared analysis (FTIR). COD was tested using DR 6000 spectrophotometer (HACH, Loveland, CO, USA) with HACH ultra-high range TNT823 (250-15000 mg/L) and high range TNT822 (20-1500 mg/L). TNT872 test kit ((HACH, Loveland, CO, USA) was used for the volatile acid. TNTplus 858 (HACH, Loveland, CO, USA) was used for iron (Fe) with 1,10-phenanthroline method (ASTM E394, (Bridgewater et al., 2012)). TNTplus 848 (HACH, Loveland CO, USA) was used for aluminum (Al) with Chromazurol S method. pH value was tested with an Intellical PHC281 water quality laboratory refillable pH electrode (HACH, Loveland, CO, USA). TOC was tested using TOC analyzer (Teledyne Tekmar, Mason, OH, USA) with three trials for each sample to obtain accurate results and were averaged to measure the standard deviation for accuracy checks and quality control.

The UV absorbance of the supernatant was measured at 254 nm using HACH DR6000 spectrophotometer with a 1 cm wide quartz cuvette. One key factor for UV spectroscopy was filtering the supernatant by 0.45 μm filter paper to avoid any error in UV absorbance testing due to solids in the supernatant, as suspended and colloidal solids can scatter the light and cause the change in the value of UV absorbance.

Samples for FT-IR spectroscopy were prepared by freeze-drying the supernatants and preparing KCl pellet with a hydraulic press. 20 mL of each supernatant was freeze-dried using FreeZone Legacy freeze dryers (Labconco Corporation, Kansas City, MO, USA) as the moisture in the sample can interfere with FTIR spectra. Nicolet iS50 FTIR spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) was used for generating FT-IR spectra provided in the results.

3. RESULTS AND DISCUSSION

3.1 Organic Matter removal

Figure 1 shows the COD removal for normal and concentrated leachate samples from sites A and B by ferric chloride and aluminum sulphate, respectively. Figure 1(a) is for site A. As shown in Figure 1(a), the COD concentration of site A normal leachate was decreased from 990 mg/L to 459 mg/L and 365 mg/L by ferric chloride and aluminum sulphate, respectively. And the COD concentration of site A concentrated leachate decreased from 4,592 mg/L to 3,136 mg/L and 3,178 mg/L by ferric chloride and aluminum sulphate, respectively. Maximum COD removals of 63.35% and 31.71% were achieved by coagulation for site A normal and concentrated leachates, respectively.

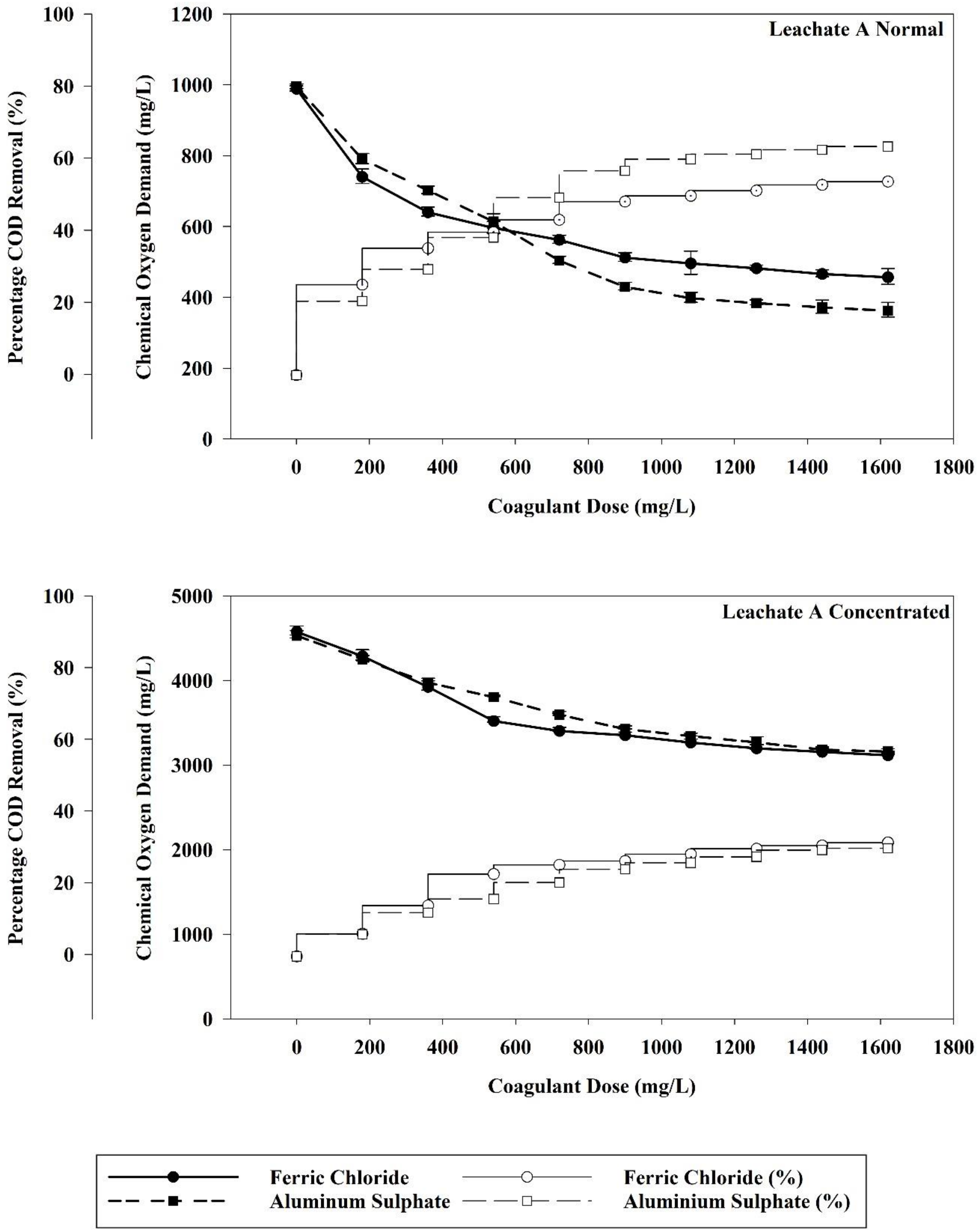


Figure 1(a): Chemical Oxygen Demand removal from Site A normal and concentrated leachate (error bar represents standard deviation)

Figures 1(b) is for site B. As shown in Figure 1(b), COD concentration of site B normal leachate decreased from 898 mg/L to 232 mg/L and 521 mg/L by ferric chloride and aluminum sulphate, respectively. And COD concentration of site B concentrated leachate, as shown in figure 1(b), decreased from 5320 mg/L to 3825 mg/L and 5020 mg/L to 3990 mg/L by ferric chloride and aluminum sulphate, respectively. Maximum COD removals of 74.16 % and 28.1% were achieved by ferric chloride for site B normal and concentrated leachates, respectively.

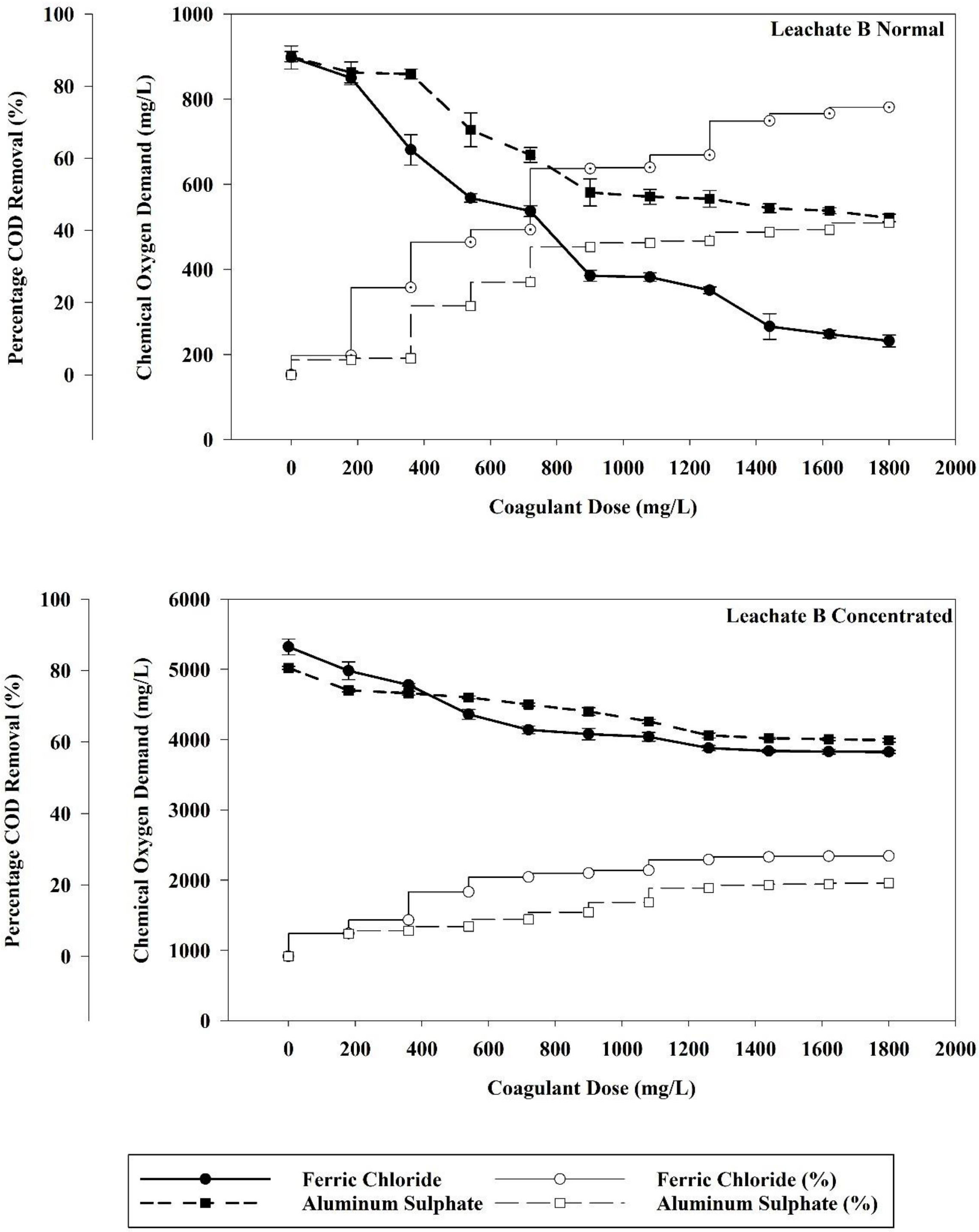
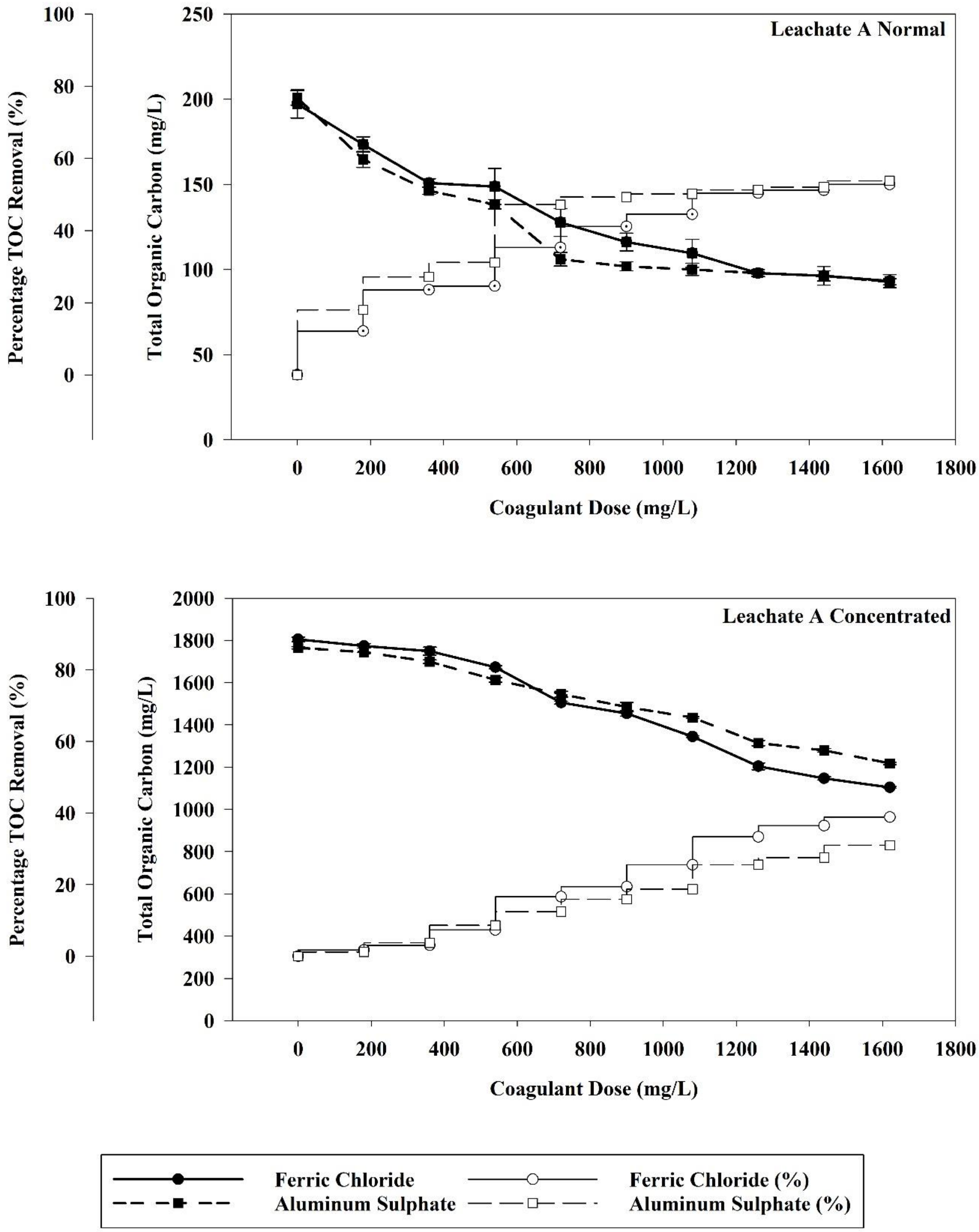


Figure 1(b): Chemical Oxygen Demand Removal from Site B normal and concentrated leachate

For a conventional primary sedimentation tank or clarifier, the expected percentage removal for organic matter is 25 – 40% (Tchobanoglous et al., 2003). Although for enhanced treatment such as CEPT, the expected percentage removal is 50 – 70% (Burton et al., 2013). Based on figure 1, treatment performance of both the coagulants for sites A and B normal leachate was in typical range of CEPT method. However, neither aluminum sulphate nor ferric chloride could perform effectively for sites A and B concentrated leachate.

Although not a monitored parameter for POTWs discharging limits, TOC is an important parameter to indicate the organic carbon concentration, as organic carbon or the compounds containing organic carbon are the major contributor to UV absorbance.

Figure 2 shows TOC removal for normal and concentrated leachate samples from sites A and B by ferric chloride and aluminum sulphate, respectively. Figure 2(a) is for site A. As shown, TOC concentration of normal leachate decreased from about 180 mg/L to 93.2 mg/L and 90.0 mg/L by ferric chloride and aluminum sulphate, respectively. For concentrated leachate, 1800 mg/L of TOC was decreased to 1,103.8 mg/L and 1,217.5 mg/L by ferric chloride and aluminum sulphate, respectively. A maximum of 53.8% and 38.8% of TOC was removed by coagulation from site A normal and concentrated leachates, respectively.



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196 *Figure 2(a): Total Organic Carbon removal from Site A normal and concentrated leachate*

Figures 2(b) is for site B. For normal leachate, the TOC concentration dropped from 133.4 mg/L to 59.0 mg/L and 97.9 mg/L by ferric chloride and aluminum sulphate, respectively. For concentrated leachate, TOC concentration decreased from 1,700.0 mg/L to 1,196.5 mg/L and 1,358.0 mg/L by ferric chloride and aluminum sulphate, respectively. A maximum of 63.9% and 31.6% of TOC concentration was removed by ferric chloride from site B normal and concentrated leachates, respectively.

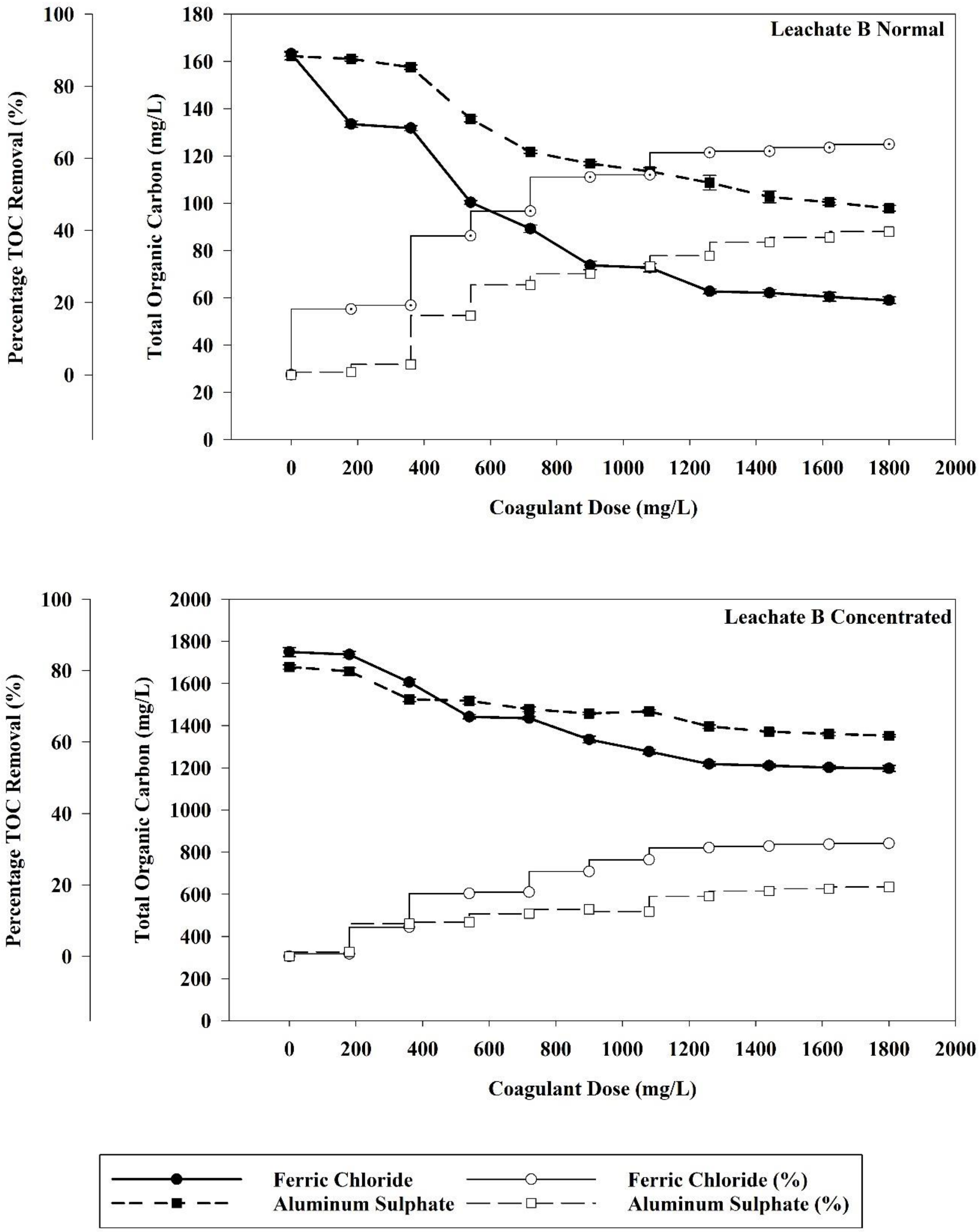

Figure 2(b): Total Organic Carbon removal from Site B normal and concentrated leachate

Figures 1 and 2 provide the evidence to the effectiveness of CEPT in the removal of organic matter from leachate-sewage co-treatment.

Based on several previous published works, it was found that the amount of coagulant dose required for coagulation-flocculation process is directly related to the initial concentration of organic matter in the leachate sample (Assou et al., 2016; Campos et al., 2013; Malathi et al., 2016; Mojiri et al., 2013; Rui and Daud, 2011). Compared to these previous studies, in this study coagulant dose was applied in increment of 200 mg/L until a flat curve was obtained for organic matter removal to evaluate the coagulant dose required for coagulation-flocculation for two leachate samples that have significantly different water quality characteristics (especially organic matter and pH).

Previous studies provide following points for leachate treatment with coagulation and flocculation:

i) High coagulant dose is required for both ferric and alum for high strength leachate. ii) COD removal is extremely difficult in case of high strength leachate than low strength leachate due to low biodegradability. iii) Ferric chloride tends to perform better in COD removal than aluminum sulphate.

Like the studies mentioned above, this study shows that high dosage is required to achieve higher organic matter removal from highly concentrated landfill leachates by CEPT. However, in terms of practical application, using such high coagulant dose may raise concern in term of cost, chemical handling, sludge production and dissolved solids of high coagulant dosage.

In addition, the difference of organics removal rates of normal leachates (up to 74% in terms of COD and 64 % in terms of TOC) and concentrated leachates (up to 32% in terms of COD and

39% in terms of TOC) is caused by their different organic compositions. In normal leachate samples (both sites A and B), a considerable portion of COD is contributed by recalcitrant humic substances which are higher molecular weight and prone to be removed with coagulation-flocculation (7). While, concentrated leachate samples (in both sites A and B) contain a significant amount of short chain organic acids (shown in table 1) that tend to stay soluble in a coagulation-flocculation process and limited removal could be achieved (Gawande, 2018). While the percentage removal is lower for the concentrated leachate samples, the mass removal on an unit volume basis is higher than that for normal leachate samples.

3.2 Change in pH

pH is a major factor that affects the effectiveness of the coagulation-flocculation and precipitation processes due to the different solubility of the metal ion at different pH and the availability of hydroxyl group for complexation. For that purpose, the change in pH was recorded to observe the effects of pH on treatment performance and solubility of ferric and aluminum ion in the supernatant after the treatment. Figure 3 shows the change in pH in all four samples by both ferric chloride and aluminum sulphate.

As mentioned above, for optimum removal of contaminants, pH for both ferric chloride and aluminum sulphate should be in an optimum range of 5.5 – 8.5 (“Water Treatability Database,” n.d.). If pH is below 5, the solubility of both metal ions will increase and impact the coagulation-flocculation performance.

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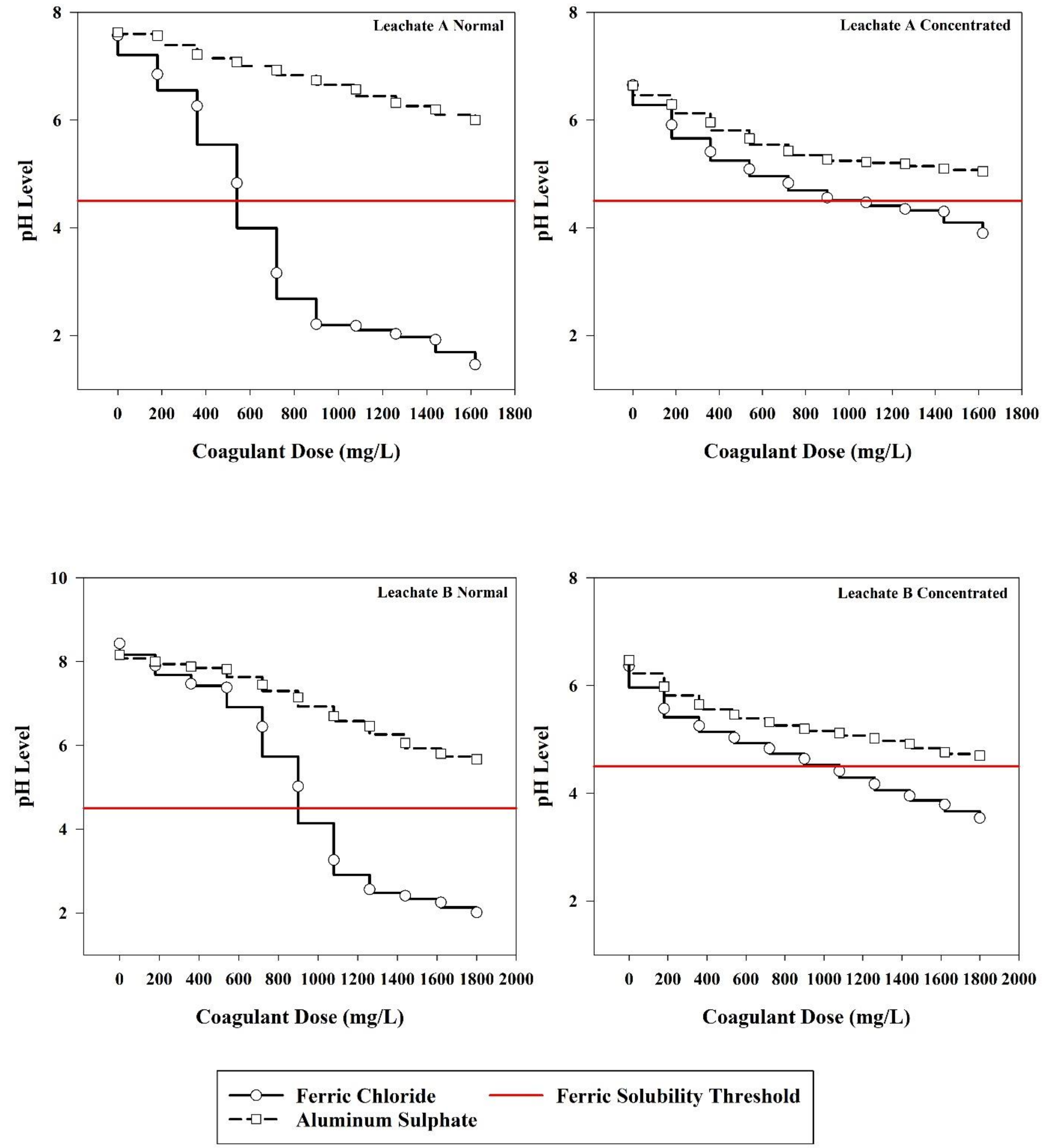


248 *Figure 3: Change in pH due to coagulation for Site A and B, normal and concentrated leachate*

As shown in Figure 3, a decrease in pH was observed due to the addition of both ferric chloride and aluminum sulphate. However, different trends were observed for aluminum sulphate and ferric chloride. Aluminum sulphate did not cause any dramatic change in pH for either normal or concentrated leachate from sites A and B. After aluminum sulphate was dosed, the pH decreased from 7.6 to 6 and from 6.6 to 5 for site A normal and concentrated leachate respectively, and for site B, aluminum sulphate lowered the pH from 8.16 to 5.16 and from 6.4 to 4.7 for normal and concentrated leachate, respectively. Different from aluminum-based coagulant, ferric chloride caused much greater pH change, especially for normal leachate samples. The change in pH caused by ferric chloride for normal leachate from sites A and B was found significant. Figure 3 shows that when more than 540 mg/L of ferric chloride was dosed, the pH dropped dramatically to 2 or lower for normal leachate from both sites A and B. Meanwhile, ferric chloride did not have such impact on pH level for concentrated leachate from sites A and B. For concentrated leachate from sites A and B, the pH reduced from 6.6 to 3.9 and from 6.4 to 3.54, respectively. Figure 3 shows that when ferric chloride is dosed in high amounts, it will reduce the pH below 5, which is a solubility threshold for ferric ions, below which hydrolyzed ferric complexes become soluble.

The different behaviors of pH change during ferric chloride coagulation between normal and concentrated leachates are believed due to the "buffer effect" of the high level of short chain organic acids in found in leachate samples. Short chain organic acids or Volatile Acids (VAs) are weak organic acids and their conjugate base stay in equilibrium in a solvent (in this case leachate). Volatile acids have lower dissociation constant (pKa) value which gives them the buffer capacity or resistance (in simple terms) towards the change in pH. Some commonly known volatile acids are acetic acid, butyric acid, propionic acid, etc. These acids are also considered as Volatile Fatty Acids (VFAs) that are typically produced during the acidogenesis phase during decomposition of organic waste in landfills. Volatile acids (VAs) test was conducted for raw leachate sample only to understand how the concentration levels of these acids play a role in change in pH during coagulation by providing a buffer capacity to the leachate. Volatile acids (VAs) test determined that Leachate A and B normal sample had a total VAs concentration of 785 mg/L and 1628 mg/L respectively, while concentrated leachate for A and B had 22,850 mg/L and 27,700 mg/L of VA concentration respectively, as shown in figure S8. Hence, concentrated leachate had significantly higher VAs concentration than normal leachate for both A and B sample. Carbon chain may vary in volatile acids; hence, total volatile acid concentration was measured in mg/L as CH_3COOH (Acetic Acid).

By connecting the results from the change in pH and the Volatile Acids test, it can be said that there is a possibility of observing residual soluble metal cations after coagulation, but the observation for normal and concentrated sample would be significantly different. Due to high buffer capacity from Volatile Acids, concentrated leachate samples can handle more ferric than normal before residual Fe increases that results in increase in the UV absorbance post-coagulation. Figures 4 and 5 provide the results obtained for residual ferric and aluminum concentration in the supernatants. It is shown that for all the leachate samples, the concentration of aluminum decreased and reached approximately zero, even for higher coagulant dose. However, a different trend was observed for ferric chloride. For normal leachate from sites A and B, it can be seen from Figure 4 that after a certain amount of ferric chloride dose (i.e. 540 mg/L), the residual ferric concentration increased and kept on increasing with the dose. Also, when compared to figure 3, after 540 mg/L of ferric chloride dose, the pH dropped below 5, and as aforementioned, soluble hydrolyzed ferric complexes increases, resulting in increase in residual ferric post-coagulation. While for concentrated leachate from sites A and B, it was found that for the lowest dose, the residual ferric concentration increased. After a higher dose was applied, it decreased, then increased again after 900 mg/L or more dose of ferric chloride was applied. The increase of iron concentration coincides with the pH drop as shown in figure 3. Similarly, when more than 900 mg/L of ferric chloride was added for concentrated leachate from site A and B, the pH dropped below 5 (as shown in figure 3), resulting in increased residual ferric post treatment in form of soluble hydrolyzed ferric complexes.

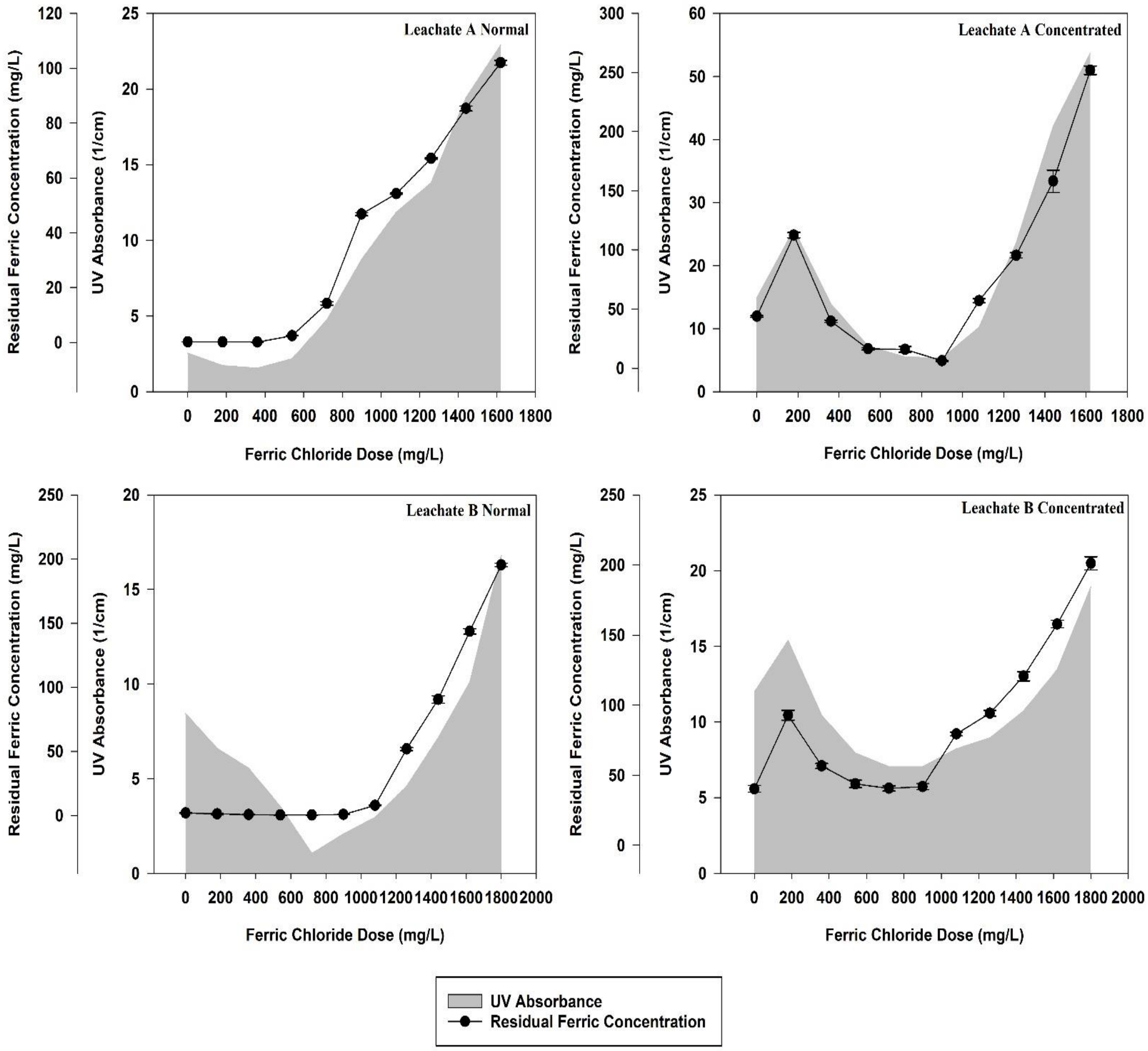


Figure 4: Change in UV absorbance and residual ferric concentration post-coagulation in Sites A and B, normal and concentrated leachates.

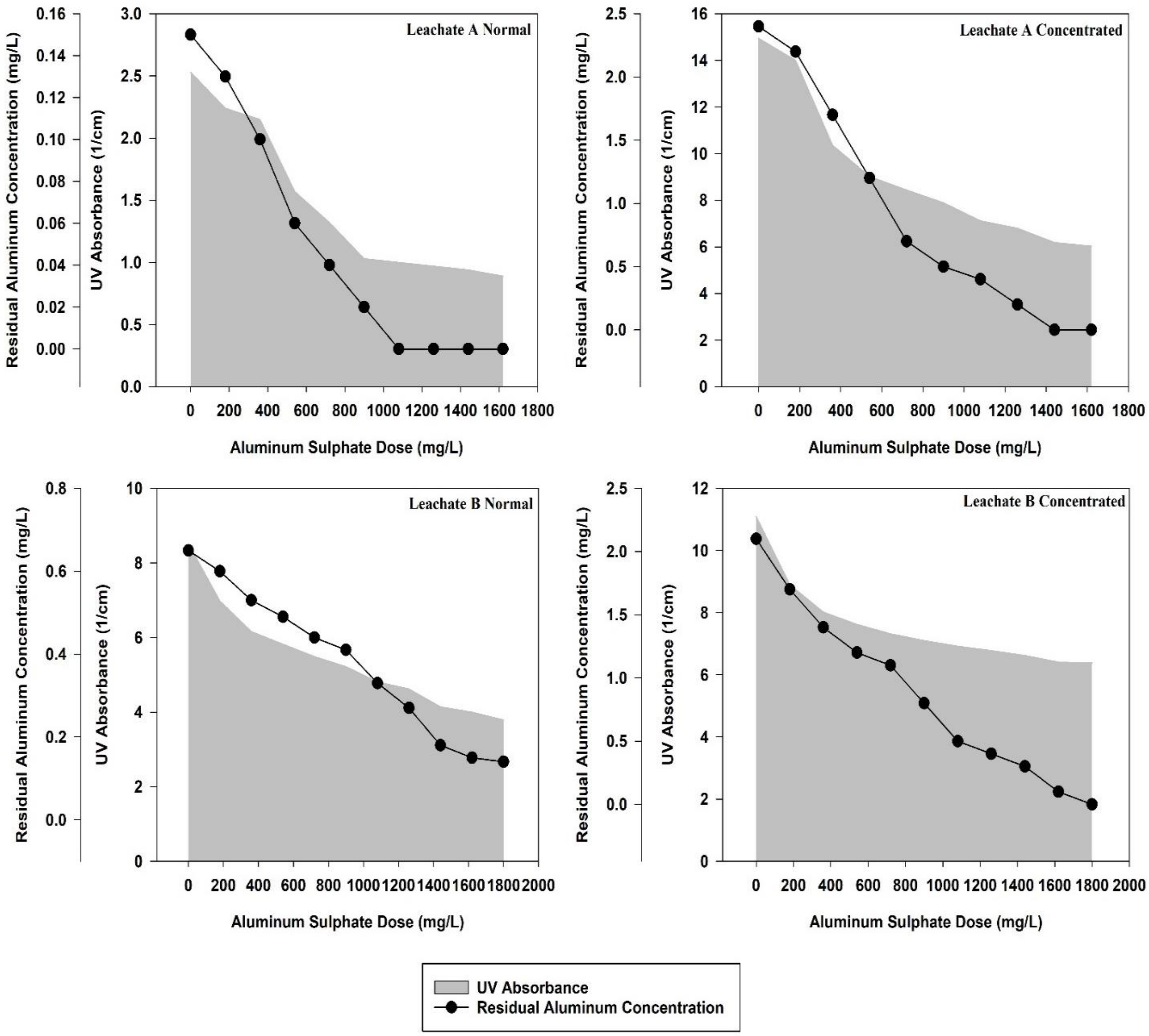


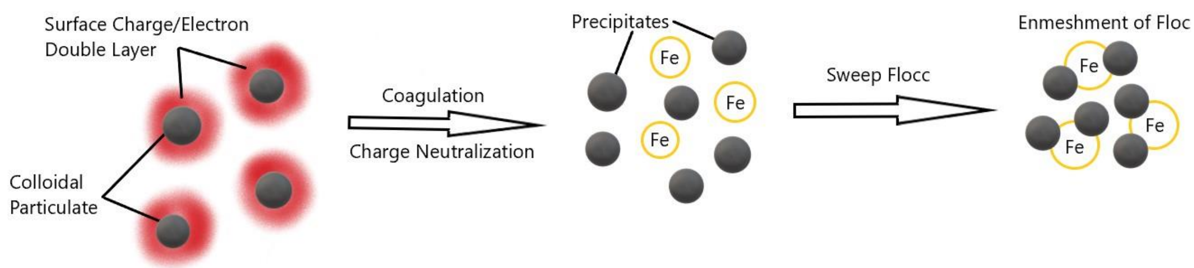
Figure 5: Change in UV absorbance and residual aluminum concentration post-coagulation for sites A and B, normal and concentrated leachates.

For domestic wastewater, optimum pH for the coagulation process is 6 – 8 for ferric chloride and 6 – 9 for aluminum sulphate (Burton et al., 2013) . While for landfill leachate, previous studies show that the optimum pH required is 7 – 10.5 for both ferric chloride and aluminum sulphate (Campos et al., 2013; Farrokhi et al., 2015; Malathi et al., 2016; Rui and Daud, 2011; Wang et al., 2009). In some practices, pH is adjusted before coagulation to improve the removal efficiency of primary treatment. However, POTWs do not always adjust the pH as introduction of extra chemicals may increase the cost of operation, elevate the effluent dissolved solids and may have aftereffects on the downstream processes. Hence, in this study pH adjustment was not carried out.

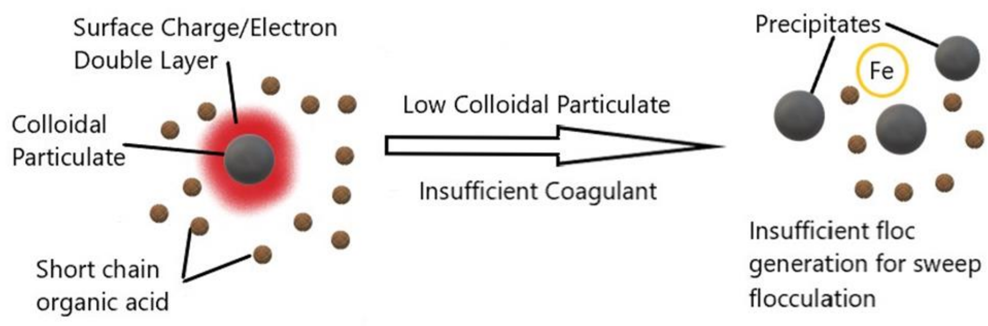
3.3 Co-precipitation behaviors of ferric chloride as function of pH

Figure 6 illustrates the hypothetical models that can explicate the co-precipitation behaviors of ferric chloride and leachate organic matter in this study under various pH scenarios.

(a) scenario 1-a. Complete destabilization and neutralization of anionic organic matter at optimum coagulant dose



(b) scenario 1-b. For leachate A and B concentrated (when 180 mg/L of ferric chloride is added)



(c) scenarios 2. Restabilization of hydrolysed species of ferric caused by excess coagulant dose and acidic pH

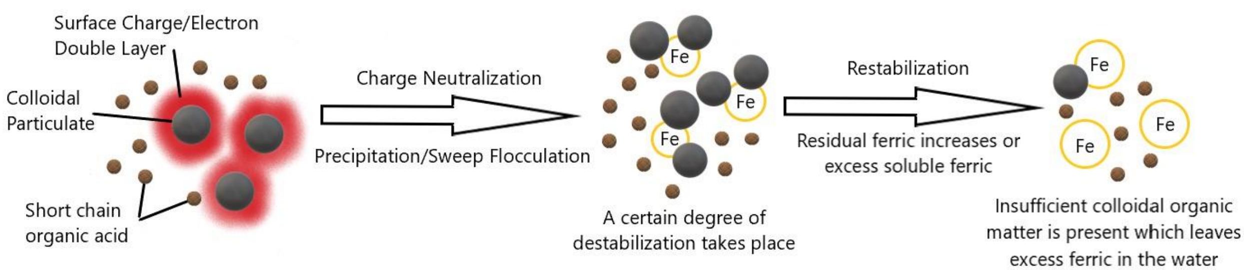


Figure 6: Hypothetical models of co-precipitation behaviors under various pH scenarios. (a) scenario 1-a, (b) scenario 1-b, (c) scenario 2.

Scenario 1: pH is in neutral range (above 6).

Scenario 1 (a). When the pH was in the neutral range (i.e. above 6), the coagulation mechanism followed precipitation and sweep flocculation for both leachate A and B, normal and concentrated.

As shown in figure 3 and figure 4, for leachate A and B normal from coagulant dose 180 mg/L to 540 mg/L, precipitation and sweep flocculation was observed and no residual ferric was detected. Similarly, for leachate A and B concentrated from coagulant dose 360 mg/L to 900 mg/L coagulation mechanism followed by precipitation and sweep flocculation, minimal residual ferric concentration was found. Figure 6 (a) shows the stepwise coagulation mechanism for precipitation and sweep flocculation. An effective coagulation occurs when Critical Coagulation Concentration (CCC) is used, where the Critical Coagulation Concentration (CCC) can be defined as the minimum concentration of cations required to neutralize and destabilize the anionic organic matter for coagulation of colloidal particles. Hence, effective coagulation such as this can be achieved when pH of the solution; colloidal concentration in the solution; and Critical Coagulant Concentration (CCC) are in relation with each other as shown in figure S9 taken from (Bratby, 2016; Stumm and O'Melia, 1968). for zone 2 and zone 4. Figure 6 (a). Shows the coagulation mechanism for scenario 1 (a), where precipitation and sweep flocculation take place.

Scenario 1 (b). However, as shown in Figure 4, for leachate A and B concentrated, when 180 mg/L of ferric chloride was dosed, the residual ferric concentration was found to increase even when the pH was close to 6. Such observation is explained by the concept of Critical Coagulant Concentration (CCC) and colloidal or particulate matter concentration (4). A study (4) discusses the relation between CCC and colloidal concentration and indicated that when the colloidal organic matter concentration is low, the required CCC is higher compared to the case of high colloidal organic matter concentration. Figure S9. shows the relationship between CCC and colloidal concentration (Bratby, 2016; Stumm and O'Melia, 1968).

In this study, the organic matter is classified as humic-like substances (high molecular weight compounds) and short chain organic acids. The colloidal organic matter refers to the humic-like substances which are more settleable and can be destabilized much easily than short chain organic acids. Studies have shown that normal leachate and concentrated leachate have different proportions of humic-like substances, and humic-like substance fraction is higher in normal leachate than concentrated leachate (Gawande, 2018; Gupta et al., 2014b; Iskander et al., 2018; Zhao et al., 2013a). In this study, it is shown that organic matter in normal leachate is humic-like substances dominated, while concentrated leachate short chain organic acids dominated. Due to insufficient amount of colloidal concentration and coagulant dosage, this condition is observed for concentrated leachate which has lower proportion of humic-like substance compared to normal leachate. This scenario corresponds to the point X shown in figure S9. The mechanism for this scenario is shown in Figure 6 (b).

Scenario 2: pH is acidic (below 6).

Based on previous theories, optimum pH for ferric chloride coagulation is 5 – 8, where residual metal concentration increased below pH 5 (3,4). Similarly, in this study it was observed that the residual ferric concentration increased when pH dropped below 5. For example, after dosing 540 mg/L of ferric chloride, the pH dropped below 5, and the residual metal concentration increased for leachate A and B normal, as shown in figure 3 and figure 4. And after dosing 900 mg/L of ferric chloride, the pH dropped below 5 for leachate A and B concentrated, which resulted in increase in residual ferric concentration, as shown in figure 3 and figure 4. The sudden drop in pH observed by ferric chloride dosing for leachate A and B normal, is due to excess amount of ferric chloride added, which cause the coagulation to go beyond the degree of destabilization, and the flocs get re-stabilized in the water becoming soluble and increasing the residual concentration of ferric chloride (Foster, 1969; Xie and Guan, 2015). After a certain degree of destabilization, the leftover concentration of colloidal organic matter will be insufficient for further coagulation and excess coagulant will stay in the water increasing the turbidity of the supernatant. As shown in figure S9, zone 3 (destabilization region) refers to such condition where the colloidal concentration is too low relative to coagulant dosage. Figure 6 (c) shows the mechanism of how the residual ferric concentration increases due to insufficient leftover colloidal concentration in the water.

Due to the varied outcomes in coagulation, theories behind coagulation mechanism can only provide a qualitative approximation of the entire mechanism. Selection of the type and dose of coagulant depends on the characteristics of the coagulant, the concentration and type of particulates, concentration and characteristics of NOM, water temperature, and water quality. Due to the interdependence of these five elements, prediction of the optimum coagulant, combination from characteristics of the particulates and the water quality is not yet possible ("10.2," 2013; Xie and Guan, 2015).

3.4 UV Absorbance

Figure 4 and 5 represents the result of the UV absorbance at different coagulant doses in normal and concentrated leachates for ferric and aluminum, respectively. As observed the two coagulants showed different patterns for UV absorbance.

For aluminum sulphate, the UV absorbance decreases with higher coagulant dose for all cases as shown in Figure 5, along with decrease in residual aluminum concentration.

On the contrary, ferric chloride caused significant increase of UV absorbance. In the case of normal leachate from sites A and B, the UV absorbance decreased at lower dosage, but after a certain threshold (when pH drops below 5, resulting in increased soluble hydrolysed ferric complexes), the UV absorbance started to increase proportionally with coagulant dose higher than the threshold point. However, beyond the threshold point, the colour of the supernatant begins to turn yellowish orange and gradually becomes bright red at higher dose of ferric chloride. On the other hand, in the case of concentrated leachate from both sites A and B, a different trend was observed. UV absorbance increased with coagulant dose when 180 mg/L ferric chloride was added, then decreased as more coagulant was dosed. As mentioned in scenario 1(b) in Figure 6, the CCC was lower than the required amount for the colloidal concentration in both concentrated leachate A and B. In turn, the level of destabilization required for floc generation for sweep flocculation was not met, and colloidal fraction stays in a suspended state in the solution without being settled. This colloidal fraction in the supernatant was observed to even pass through 0.45 µm syringe filter. When the supernatants from leachate A and B concentrated were tested for UV absorbance, the suspended colloidal fraction in the solution can cause increase in UV absorbance by means of absorbance or light scattering. However, when the leachate A and B concentrated were subjected to a higher coagulant dose, the required CCC was met and the level of destabilization required for sweep flocculation was achieved and no colloidal fraction was observed in suspended state in the supernatant. Hence, after adding more than 180 mg/L ferric chloride, the UV absorbance was observed to decrease. During experiments, it was observed that the supernatant turns hazy due to formation of micro colloids that do not settle and stay suspended, which can cause the UV absorbance to increase due to light scattering.

From Figure 4, the elevation of supernatant UV absorbance coincides with the increase in residual soluble ferric concentration, which indicates a possible relevance between ferric cation and UV absorbance. Similar phenomenon was observed and reported in previous studies that reported the influence of ferric ion in UV absorbance at 254 nm (Doane and Horwáth, 2010; Stefánsson, 2007; Turner and Miles, 2011). Few other studies showed that it was the hydrolysed species of iron (III) and their concentration responsible for UV absorbance (Grieve and Marsden, 2001; Korshin et al., 1997; Monique Meier et al., 1999; Moore, 1988; Weishaar et al., 2003; Wilson, 1959). However, it was found in some studies that the presence of iron (III) along with DOM (NOM in environmental conditions) and the iteration between iron (III) and DOM was the cause of increased UV absorbance (Ghassemi and Christman, 1968; Karathanasis et al., 1988; Maloney et al., 2005; M. Meier et al., 1999; Namjesnik-Dejanovic et al., 2000; Sholkovitz and Copland, 1981; Smal and Misztal, 1996; Tipping, 1981; Vestin et al., 2008). More specifically, the formation of organometal complex compound between ferric and recalcitrant organic matter (or DOM) that hypothetically has characteristic absorption in the UV range. Previous studies have shown metal complexation between organic matter and metal ions and ammonia exist in the natural environment, surface water and wastewater treatment processes, etc. (Buffle et al., 1988; Bundy et al., 2015; Lawrence, 2009; Suffet, 1989). Hence, in this study, supported by the previous studies, the phenomenon of metal complexation between ferric and organic matter and its impact on UV absorbance is further explained.

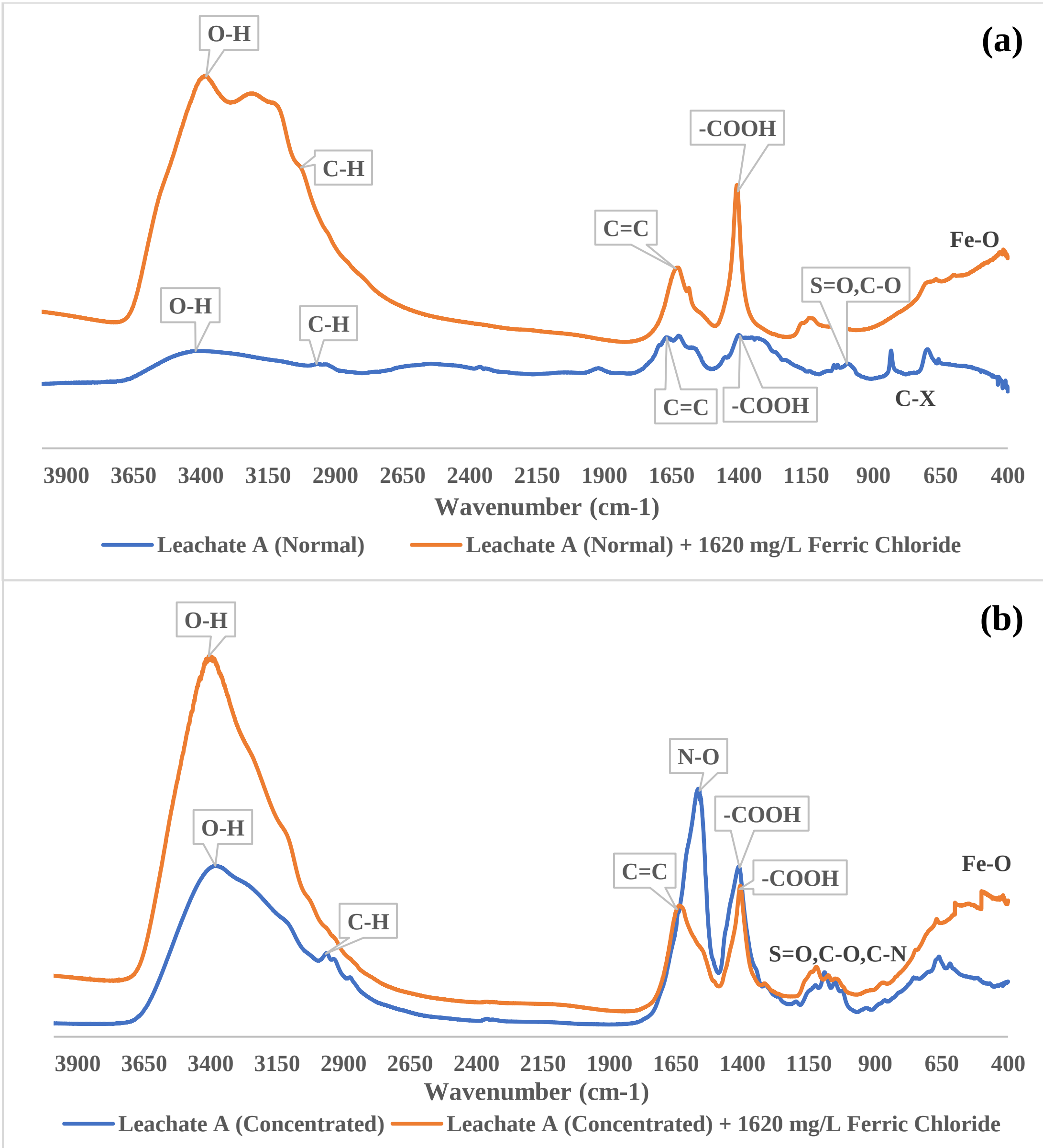
In this study, the metal ion refers to ferric (Fe^{+3}) and the ligand is the dissolved organic matter present in the leachate. Ferric cation (Fe^{+3}) has 6 empty orbitals and it can accept 6 electrons from a donor ligand, allowing it to form 6 coordinate covalent bonds with 6 anionic ligands (Lawrence, 2009). As the dissolved organic matter have different functional groups that can act as binding sites (electron donors) for metal complexes such as carboxylic (-COOH), phenolic (-OH), amine (NH_2), Nitro (-NO), etc. But the major functional group present is the carboxylic and phenolic group. Certain dissolved organic matter (DOM) model, such as humic acid, also show that metal is partially bonded to water molecule at the oxygen atom as a binding site and partially bound to oxygen present in hydroxyl part of the carboxylic and phenolic group (Buffle et al., 1988). Hence, in this study, the major functional groups, present in the DOM, i.e., carboxylic and phenolic group have been considered. Elemental analysis of landfill leachate show that oxygen is the second most abundant element in organic compounds (Gawande, 2018). Dissolved Organic Matter (humic substance) consists approximately 30 – 40 % oxygen depending upon the source, which is second to carbon (50 – 60 %) (Iskander et al., 2018). Due to availability and an extra pair of electrons to donate, oxygen presents itself as the most suitable binding site for metal complexes in DOM (humic substance) which is also supported by a recent study (Zhou et al., 2015). Ferric and oxygen from DOM form metal complex with ML_6 (M-Metal and L-Ligand) structure and octahedral geometry (Buffle et al., 1988; Lawrence, 2009). One such example of DOM-iron complexation is Kleinhempel's model of humic substance (Buffle et al., 1988).

The ML_6 orbital diagram of the Fe-O coordinate covalent bond is shown in figure S10 (Bauman, 1962; Foster, 1969; Graddon, 2017; Lawrence, 2009). When the metal complex is formed, the 3d orbital in ferric splits into e_g^* and t_{2g} orbital with different energy level than before, as explained by crystal field theory and ligand field theory (Gillam and Stern, 1955; Spectroscopy based Adsorption, 2013; Xie and Guan, 2015). The difference in energy is represented by Δ in the figure. Compared to the initial ferric orbital, the energy required by an electron to jump from t_{2g} to e_g increases when the 3d orbital splits into e_g^* and t_{2g} (Ashcroft and Mortimer, 1970; Bamford, 2014; Basolo and Johnson, 1986; Foster, 1969; Kettle, 1969; Kramer and Duinker, 1984). Due to this increase, electron absorb higher amount of energy in form of photons from light to jump from t_{2g} to e_g^*. In this study, it is hypothesized that the energy required to make the electron transition, matches that of UV light in electromagnetic spectrum. Hence, it suggests that when metal complexes are formed with Fe-O bond, the UV absorbance increases.

3.5 FT-IR Analysis

FT-IR spectroscopy serves as a tool to identify the organic functional groups present in the sample. Figures 7 (a), (b), (c) and (d) show the FTIR spectra for normal and concentrated leachates from sites A and B, before and after ferric chloride coagulation. It is shown that functional groups such as alcohol and carboxylic (-OH), alkane (C-H), alkene (C=C), sulfoxide (S=O), and halogen compound (C-X) were found in normal leachate from sites A and B. In addition to similar functional groups with normal leachates, ester (C-O) and nitro compound (N-O) were found in concentrated leachates for sites A and B ("IR Spectrum Table & Chart," n.d.).

Various studies on different materials have shown that Fe-O bond mostly exists in the region 600 - 400 cm^{-1} or below 400 cm^{-1} IR spectrum region and also the structure of the Fe-DOM (Fe-Humic) complex (Hossain et al., 2017; Kim and Park, 2002; Novoselova, 2016; Ou et al., 2009; Rahman et al., 2010; Stevenson and Fitch, 1986; Zhou et al., 2015). These studies have used different ferric solution and organic compounds to analyse the Fe-O bond. Similarly, in this study it was observed that the absorbance peak increased post-treatment in the region below 600 cm^{-1} for the leachate sample treated with ferric chloride. This increase in absorbance below 600 cm^{-1} wave number is hypothesized to be due to Fe-O bond stretch that occurs in the metal complex formed from covalent co-ordinate between ferric ion and oxygen in organic ligands (in this case humic acid/macromolecules). Not only the peak increased with increase in ferric dosage, but also it was noticed that the peak for O-H also increased and shifted towards lower wave number, indicating that the ferric cation maybe causing an increase in the stretch of O-H bond. It was also observed that for the raw sample, the peak in the region 600 - 400 cm^{-1} shows a decreasing trend for both normal and concentrated leachate from sites A and B. While the coagulation-flocculation supernatant from highest coagulant dose shows a clear peak in that region. The above evidence indicates and supports the theory of possible metal complexation between ferric cation and DOM.


(a)
O-H
C-H
-COOH
C=C
Fe-O
S=O,C-O
O-H
C-H
C=C
-COOH
C-X
3900 3650 3400 3150 2900 2650 2400 2150 1900 1650 1400 1150 900 650 400
Wavenumber (cm-1)
Leachate A (Normal)
Leachate A (Normal) + 1620 mg/L Ferric Chloride
(b)
O-H
N-O
O-H
-COOH
C=C
-COOH
Fe-O
C-H
S=O,C-O,C-N
3900 3650 3400 3150 2900 2650 2400 2150 1900 1650 1400 1150 900 650 400
Wavenumber (cm-1)
Leachate A (Concentrated)
Leachate A (Concentrated) + 1620 mg/L Ferric Chloride

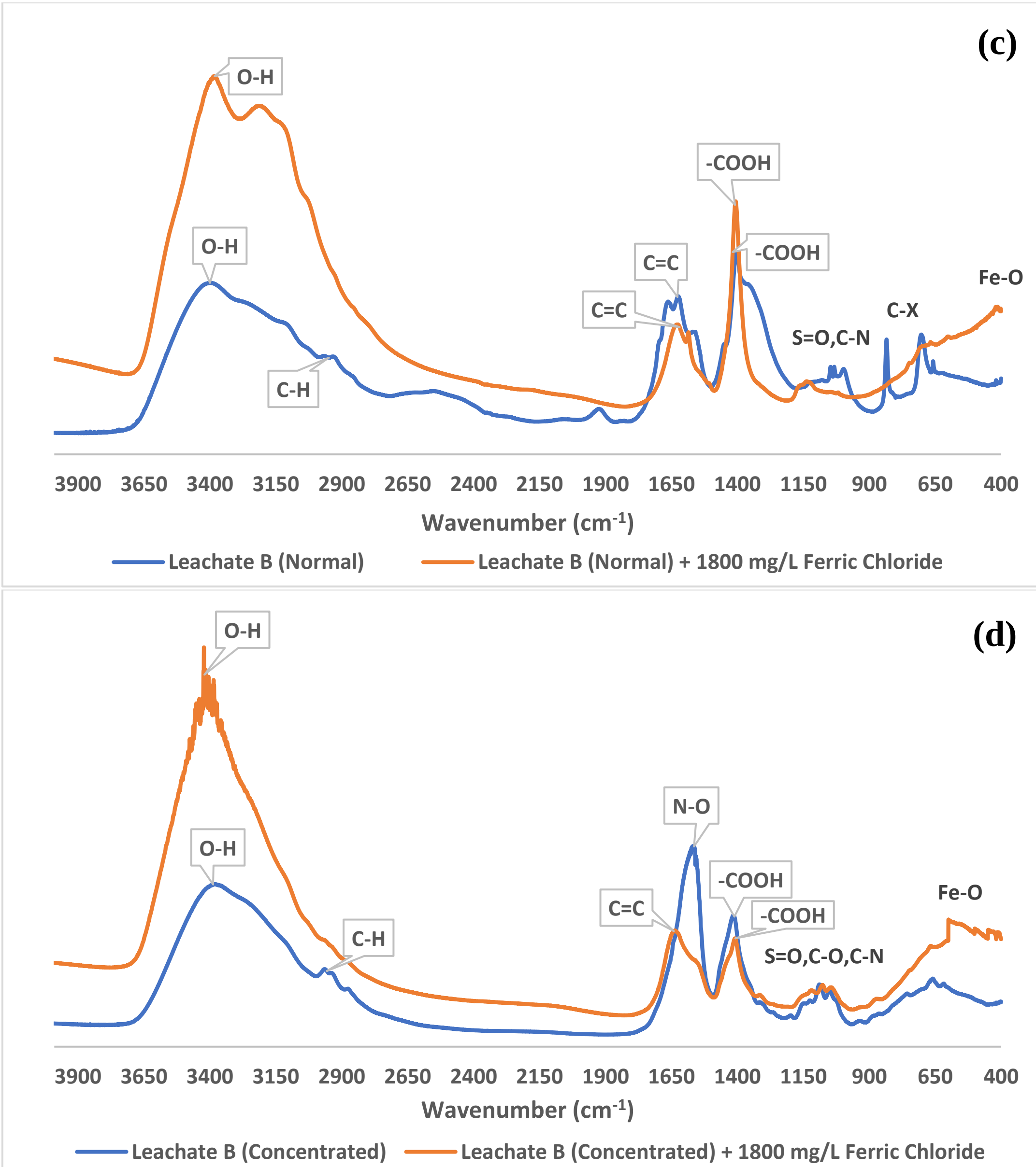


Figure 7: FT – IR spectra. (a) normal leachate from site A, (b) concentrated leachate from site A, (c) normal leachate from site B, (d) concentrated leachate from site B.

4. CONCLUSIONS

In this study, lab scale tests with coagulants were conducted for blended landfill leachate and sewage to mimic the co-treatment in POTWs. Main findings are as below:

1) Ferric coagulant can cause significant UV abs. increase while aluminium cannot. The high UV abs. coincide with high residual ferric concentration. It is hypothetically believed that the UV abs. increase is caused by the complexation of soluble ferric and leachate organic matter, which produce the Fe-O complex with the molecular structure that has characteristic absorption in the UV range. The Fe-O structure is proved by FT-IR spectra.
2) Both aluminium and ferric coagulants perform well for organic matter removal in landfill leachate. For both aluminium and ferric coagulants, organic matter removal efficacy for normal leachate is better than concentrated leachate. For normal leachate, 64% TOC and 74% of COD removal were achieved. For concentrated leachate, 39% TOC and 32% of COD removal were achieved. However, in terms of mass-based removal per unit volume of sample, concentrated leachate had higher organic matter removal than normal leachate samples.
3) Both aluminium and ferric coagulants lower the pH during the coagulation-flocculation process for landfill leachate. Ferric reduce pH more than aluminium in all cases. Particularly, pH value was dropped dramatically to less than 2 by ferric for normal leachate. No dramatic pH drop was observed for the concentrated leachates due to the buffer effects of high levels of organic acids (weak acids).
4) The relationship between colloidal destabilization and coagulant dose under various pH scenarios can be elucidated by theoretical models presented in this study, such as the critical coagulant concentration required to completely destabilize the anionic organic molecules while not exceeding the maximum allowable coagulant dose beyond which concentration of

residual metal cations can increase and interact with organic macromolecules to exacerbate UV absorbance.

Appendix A. Supporting Information.

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