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Research Article

REMOVAL OF 254 NANOMETER IRRADIATION QUELLING POLLUTATNS FROM PRETREATED LANDFILL LECHATES BY FENTON PROCESS AS A POST-TREATMENT SYSTEM

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ABSTRACT
Landfill leachates usually comprise of contaminants which cannot be treated with conventional treatment methods. Most of these contaminants can interfere with installed treatment facilities as 254 nm irradiation quelling pollutants. Fenton's reagent treatment for biologically treated landfill leachates is examined in this study as a post-treatment step to make landfill leachates acceptable to conventional installed treatment facilities. The optimum conditions for the Fenton's reagent treatment are explored. The molecular weight and hydrophobic–hydrophilic nature based fractions of the Fenton's treated leachate samples are analyzed to provide insight into the leachate fractions targeted by the Fenton's reagent. The results indicate that Fenton's reagent can act as a good compliment to biological treatment as it can remove leachate fractions which are widely considered to be bio-refractory. Results showed a great yield in this system. The treatment mainly targeted the high weighted molecules which have high absorbance rate of 245 nm irradiation. This treatment showed excellent yield and could easily be utilized for landfill leachate treatment.

Keywords: *Fenton Process, Landfill Leachates Treatment, 254 nm Irradiation Quelling Pollutants, Hydrogen Peroxide, Post-Treatment Systems*

INTRODUCTION
The discharge of landfill leachates (biologically pretreated or without any type of pretreatment) to municipal wastewater plants is frequently done to reduce the cost for its disposal. Humic substances (humic acids and fulvic acids) contained in the leachate, which are normally considered non-biodegradable (Poblete *et al.,* 2011), can create problems at municipal treatment plants that use UV disinfection. Specifically, it is reported that landfill leachates from a variety of sources absorb UV light in the wastewater treatment plants and interfere with the UV disinfection process (Zhao *et al.,* 2012). Bio-refractory organic compounds such as humic substances (mainly >1 kDa), were found to be responsible for the UV quenching phenomenon (Zhao *et al.,* 2013b). Physicochemical treatment technologies are needed to compliment biologicaltreatment and eliminate the interference of landfill leachates with the UV disinfection facilities (Gupta*et al.,* 2014).
Advanced oxidation processes generate and utilize OH radicals which can break down organic compounds that cannot be destroyed by biological processes and other conventional oxidation methods. It has many advantages over conventional physical and chemical leachate treatment techniques. The main advantage of Fenton's process is that oxidation and flocculation occur simultaneously which results in greater organic matter removal without producing any toxic byproducts. Also, the process uses relatively cheap and non-toxic reagents, does not require any form of energy as catalyst and is relatively simple to perform (Li *et al.,* 2010), The Fenton's reagent reaction depends on a number of parameters such as reaction time, pH, H_2O_2 to Fe(II) molar ratio, Fenton's reagent dosage, initial COD strength, feeding modes, type of flocculants, and temperature (Zhang *et al.,* 2005; Deng, 2007;Gupta *et al.,* 2014).
The application of Fenton's reagent is reported widely for the treatment of landfill leachates and it has been the subject of numerous publications and reviews (Wang *et al.,* 2003; Kurniawan *et al.,* 2006; Renou *et al.,* 2008; Abbas *et al.,* 2009). It has been found to improve the biodegradability of recalcitrant organic pollutants to values making biological treatment economical (Wang *et al.,* 2003; Morais and Zamora,

2005; Renou *et al.*, 2008). Reported COD removal efficiencies for landfill leachates ranged from 45 (Kim *et al.*, 2001) to 85% (Roddy and Choi, 1999; Gupta *et al.*, 2014).

Fenton's reagent was used in this study as a polishing step for biologically treated landfill leachate because of its operational simplicity and effectiveness (Lopez *et al.*, 2004). The treatment efficiency of Fenton's reagent for the bio-refractory organic matter, especially UV quenching materials which has not been well documented and has very limited literature available, was examined through an elaborate molecular weight (MW) and hydrophobic– hydrophilic nature based fractionation(Gupta *et al.*, 2014).

MATERIALS AND METHODS

Leachate Collection and Sampling

This study was conducted on two landfill leachates. The samples were collected form Karaj Halqe-Darre (HD-SBR) and Tehran Kahrizak (K-LFL). The HD-SBR sample was treated biologically using active sludge in Semi Batch Reactors and K-LFL sample was treated biologically using anaerobic microorganisms. The leachate samples were shipped in polyethylene containers directly from the landfills to our lab, and stored at 5 °C in the dark immediately after being received to reduce microbial activity. Before sampling for analysis, the previously stored containers were shaken well to re-suspend settled particles.

Fenton's Treatment

Fenton's reagent is basically a solution of hydrogen peroxide and an iron catalyst. The initial pH range of the leachate samples was 7.0–8.0. First, the pH was optimized for maximum chemical oxygen demand (COD) removal for a particular dosage of the Fenton's reagent (Figure 1). The pH was adjusted using 93% concentrated sulfuric acid solution. Fe^{2+} was supplied as laboratory grade $FeSO_4.7H_2O$ and the H_2O_2 was provided as a 31% solution. The Fenton's reaction was carried out in a 250 mL glass beaker with 100 mL of the sample. The beakers in the jar test apparatus (Phillips and Bird, Richmond, VA) were stirred at 100 rpm for 5 min and at 40 rpm for 25 min and then allowed to settle for 1 h. Details of the method can was reported earlier by other authors (Zhao *et al.*, 2013a;Gupta *et al.*, 2014).

The supernatant from the beakers was used for analyzing for overall removal. Most studies indicate the optimum molar ratio of H_2O_2 to Fe^{2+} for the treatment of landfill leachates to range from 1.5 to 3.0 (Zhang *et al.*, 2005; Batarseh, 2006; Deng, 2007; Hermosilla *et al.*, 2009). The dosage of the ferrous ion and hydrogen peroxide was optimized by varying the H_2O_2 to Fe^{2+} molar ratio within the range if 1.5–3.0 followed by analysis for maximum COD removal at the optimum pH of 4.0 (Figure 1). The optimum dosages of H_2O_2 and Fe^{2+} can be found in Table 1.

MW and Hydrophobic–hydrophilic Nature based Fractionation

Ultrafiltration of leachate samples was conducted using a dead end batch 200 mL stirred ultrafiltration apparatus (Model 8200, Amicon, Belford, MA), a nitrogen gas tank (pressure: 120 kPa) and membrane discs with the MW cut offs (MWCOs) of 0.5, 1, 3 and 100 kDa (YC05, YM1, PLBC, and PLHK, Millipore, Billerica, MA). Landfill leachate samples were fractionated into humic acids (HA), fulvic acids (FA) and hydrophilic (Hpi) fractions based on their chemical nature and solubility characteristics. Methods developed by other authors (Leenheer, 1981; Thurman and Malcolm, 1981; Christensen *et al.*, 1998) were used in this study since they have long been a standard method for the isolation and separation of humic substances from aquatic samples. Chemical precipitation is used to remove HA and then a non-ionic XAD resin is used to sorb FA. The remaining organic matter is considered to be the Hpi fraction (Gupta *et al.*, 2014).

Table 1: Optimum dosage of Fenton's reagent at pH = 4.0 for the treatment of biologically treated landfill leachates

Leachate Sample	$[Fe^{2+}]$ (M)	$[H_2O_2]$ (M)	$[H_2O_2]/[Fe^{2+}]$
K-LFL	0.061	0.093	1.52
HD-SBR	0.034	0.093	2.75

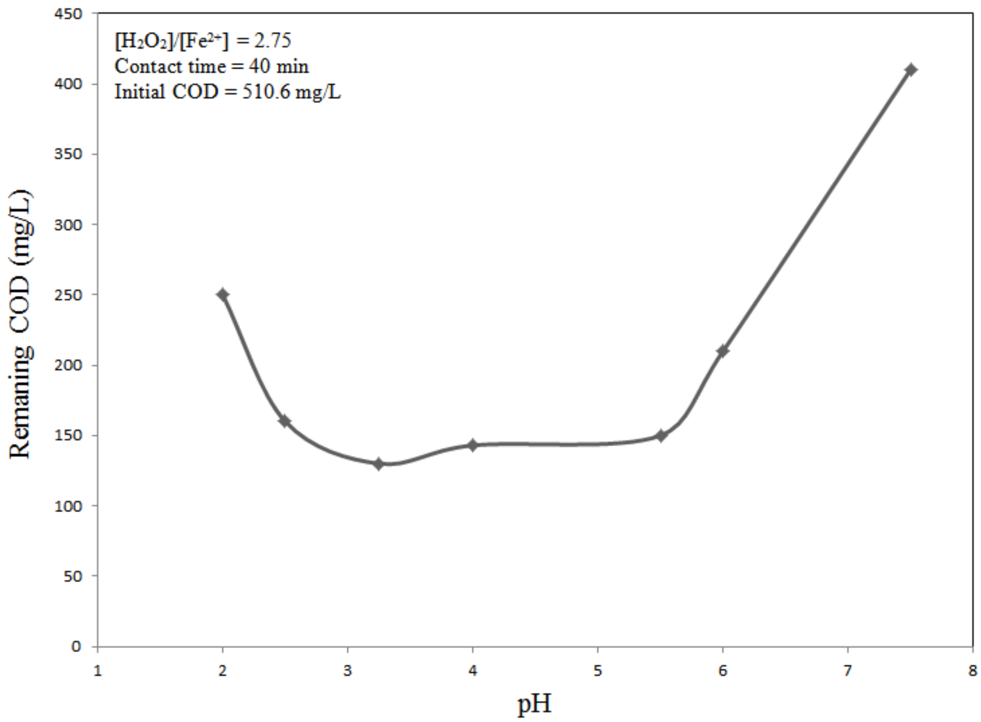

Figure 1: Effect of pH on the removal of chemical oxygen demand (COD) by Fenton's treatment for the biologically treated HD-SBR landfill leachate

Analysis

COD was analyzed using high temperature combustion with a COD analyzer (Stamolys CA71COD Ednress Hauser). Ultraviolet absorbance at 254 nm (UV_{254} absorbance) was measured with a spectrophotometer (Hach DR 5000). The leachate samples and filtrates were diluted in order to yield a reading within the detection range. UV_{254} readings were multiplied by the corresponding dilution factor to give the final UV_{254} absorbance values. The pH of each leachate sample was measured by a pH meter (HachsensION+ PH3).

RESULTS AND DISCUSSION

Optimum pH

Figure 1 shows the effect of the pH on the removal of COD by Fenton's treatment for the biologically treated HD-SBR landfill leachate. It can be observed that the COD removal initially increases and then decreases with an increase in pH. The minimum effluent COD and thus maximum COD removal (up to 82%) is observed between pH 3.0–5.0. The pH value is a critical factor that influences the Fenton's treatment efficiency. The drop in efficiency on the basic side can be attributed to the precipitation of ferrous and ferric ions making them escape the Fenton's system leading to decreased production of hydroxyl radicals (Deng and Englehardt; 2006,Gupta *et al.*, 2014).

Removal of COD and UV_{254} Absorbance

Fractionation based on MW: Figure 2a shows the distribution of COD among the MW based fractions in the raw and Fenton's reagent treated K-LFL and HD-SBR landfill leachates under optimized conditions of pH and reagent molar ratio. For the raw i.e. the mature K-LFL leachate sample it was observed that around 82% of the organic matter in terms of COD was smaller than 1 kDa MWCO. Whereas, for the SBR treated PA landfill leachate, 34% of the organic matter was <1 kDa. The difference in organic matter distribution post biological treatment in the leachates could affect the removal by the Fenton's reagent (Gupta *et al.*, 2014).

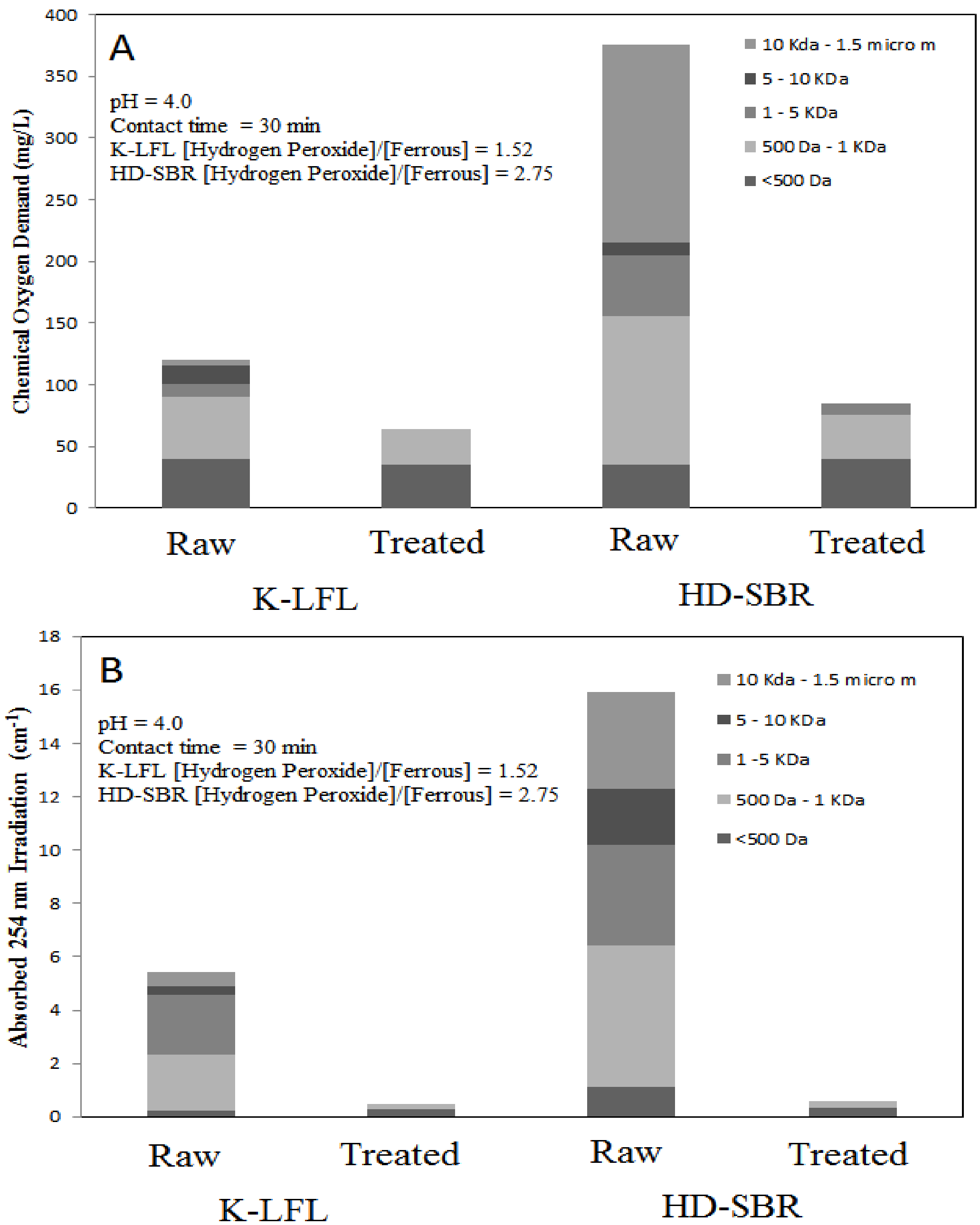

Figure 2: Molecular weight distribution of chemical oxygen demand (a) and UV_{254} absorbance (b) in the raw and Fenton's reagent treated K-LFL and HD-SBR landfill leachates under optimized conditions of pH and reagent molar ratio

From Figure 2a for the Fenton's reagent treated landfill leachate samples, it can be observed that the maximum degradation of organic matter took place for the fractions >1 kDa. In both K-LFL and HD-SBR, up to 90% of the organic matter >1 kDa was removed by the Fenton's reagent leaving most of the organic matter in the fractions <1 kDa. For the fractions <1 kDa, removal efficiencies of just 41% and 48% were observed for the K-LFL and HD-SBR landfill leachates, respectively. There is not much difference in the organic matter values for the 1 kDa and 1.5 µm fractions. The Fenton reagent's removal mechanism mainly targets the larger MW (>1 kDa) organic matter. The smaller MW (<1 kDa) organic matter is much less susceptible to the Fenton's reagent reaction. Looking at the overall removal of organic matter, removal efficiencies of 60 and 78% were observed for the K-LFL and HD-SBR landfill leachates, respectively. The higher removal for HD-SBR can be attributed to the greater amount of organic matter >1 kDa as compared to K-LFL which comprised mostly of the organic matter <1 kDa (Gupta *et al*., 2014).

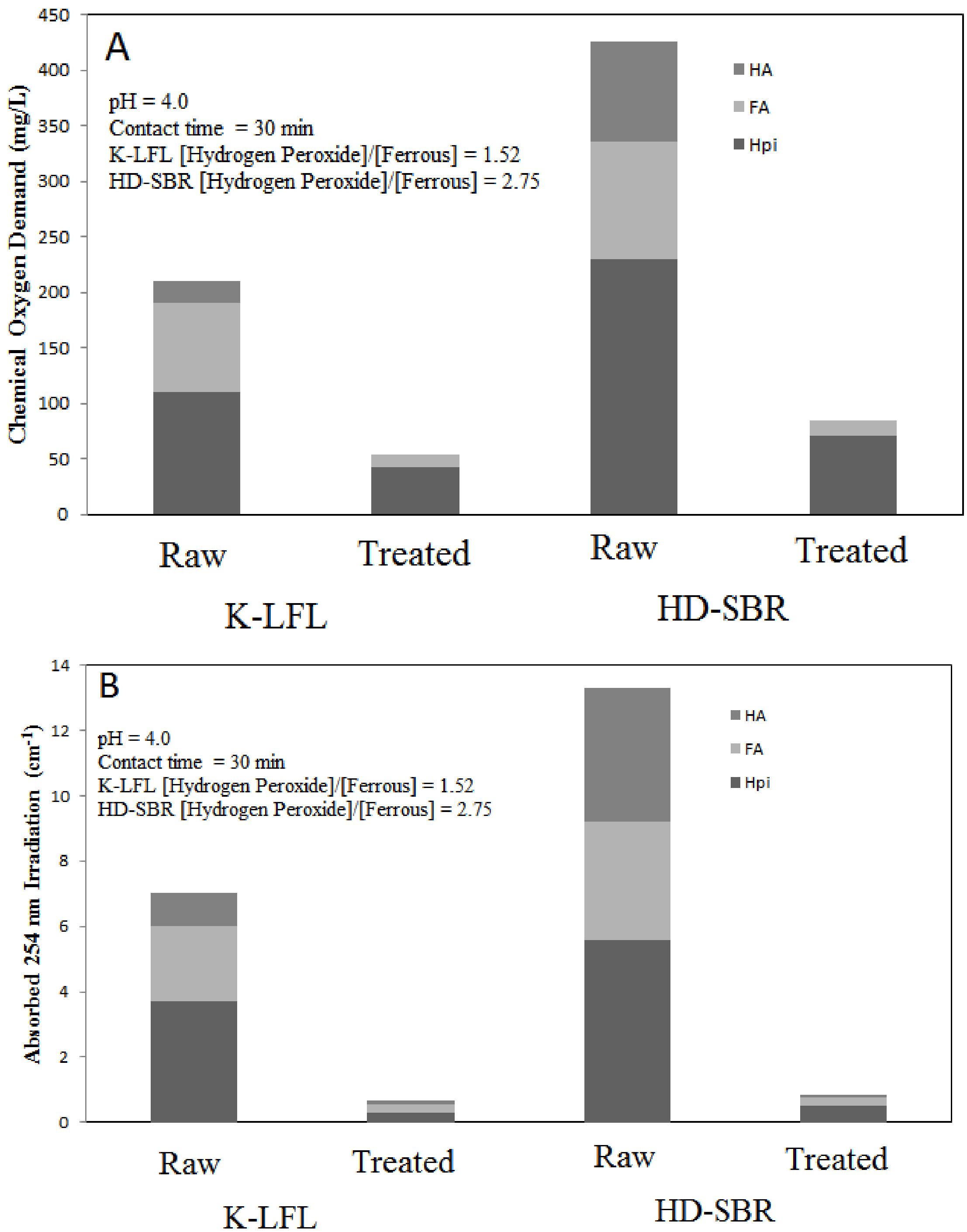

Figure 3: Distribution of chemical oxygen demand (a) and UV_{254} absorbance (b) among the hydrophobic–hydrophilic nature based fractions in the raw and Fenton's reagent treated K-LFL and HD-SBR landfill leachates under optimized conditions of pH and reagent molar ratio

From Table 1, it can also be observed that the dosage of the ferrous ion for the optimum treatment of the K-LFL leachate was much greater than the HD-SBR leachate for the same amount of hydrogen peroxide, even though HD-SBR contained almost three times more organic matter.

For effective coagulation–flocculation at higher concentrations of the natural organic matter (NOM), less coagulant is needed, whereas, at the lower concentration of the particles, a higher coagulant dose is required (Crittenden *et al.*, 2012), so the K-LFL required more ferrous ion when compared with HD-SBR for the coagulation–flocculation part of the Fenton's reaction.

Figure 2b shows the distribution of the UV_{254} absorbance among the MW based fractions in the raw and Fenton's reagent treated K-LFL and HD-SBR landfill leachates under optimized conditions of pH and reagent molar ratio. UV_{254} quenching substances are considered to be more biologically refractory than COD in leachates (Zhao *et al.*, 2013b). The distribution of the UV_{254} quenching substances in the biologically treated leachate samples was relative even between the <1 and >1 kDa fractions with around 53% of the UV_{254} absorbance due to particles with MW >1 kDa for both the leachate samples being evaluated in the study (Gupta *et al.*, 2014).

From the Fenton's treatment of the landfill leachate samples, it could be observed that around 92% of the UV_{254} quenching substances >1 kDa got removed for both the leachate samples. For the UV_{254} quenching substances <1kDa, removal efficiencies of 80% and 83% were observed for the K-LFL and HD-SBR leachate samples, respectively. This shows that though the Fenton's reagent mainly targets the larger MW (>1 kDa) fractions but also exhibits good removal for the UV_{254} quenching substances <1 kDa.

The overall UV_{254} quenching removals achieved by Fenton reagent's reaction were observed to be 89% and 93% for the K-LFL and HD-SBR leachates, respectively. This can be mainly attributed to the higher amount of >1 kDaUV_{254} quenching substances in the leachate samples due to ineffective biological degradation and due to the ability of the Fenton's reagent to effectively remove UV_{254} quenching substances irrespective of their MW. Also, it can be observed that the overall removal achieved for the UV_{254} substances is much greater than that for the organic matter. This is different from biological degradation which is more effective for biodegradable organic matter removal and less effective for the removal of UV_{254} quenching substances (Gupta *et al.*, 2014).

Fractionation based on hydrophobic–hydrophilic nature: Figure 3 shows the distribution of the COD and UV_{254} absorbance among the hydrophobic–hydrophilic nature based fractions in the raw and Fenton's reagent treated K-LFL and HD-SBR landfill leachates under optimized conditions of pH and reagent molar ratio. For the biologically treated samples, it can be observed that the Hpi is the major contributor of organic carbon (51% and 52% in K-LFL and HD-SBR, respectively) and the humic substances (HA and FA) are the major contributors of the UV_{254} quenching (40% and 55% in K-LFL and HD-SBR, respectively).

For the COD distribution (Figure 3a), it can be observed that there was 90% and 96% removal of the humic substances (HA and FA fractions) in K-LFL and HD-SBR leachate samples, respectively. However, there was around 49% and 70% removal of the Hpi fraction in the K-LFL and HD-SBR leachate samples, respectively. Similarly for the UV_{254} absorbance distribution (Figure 3b), it was observed that there was 81% and 93% removal efficiencies for the humic substances and 87% and 90% removal efficiencies for the hydrophilic fraction in the K-LFL and HD-SBR leachate samples, respectively. The removal of UV_{254} quenching substances which were hydrophilic in nature was greater than that for the hydrophilic organic matter. It can be observed that the humic acids and fulvic acids (humic substances) were significantly removed after the Fenton's treatment, leaving most of the organic matter in the Fenton's treated leachate to be hydrophilic in nature (Gupta *et al.*, 2014).

Conclusion

In this study, the impact of Fenton's reagent treatment on the bio-refractory organic matter and UV_{254} quenching substances in landfill leachates which have undergone different types of biological treatment was explored. The aim of the study was to find the optimum conditions under which the Fenton's treatment was most effective for biologically treated leachates in such a way that it can allow for the removal of the bio-refractory leachate fractions. The different MW and hydrophobic–hydrophilic nature based fractions before and after treatment were studied. The major conclusions of the study included the observation that the optimum pH for Fenton's treatment of biologically treated landfill leachates was 3.0–5.0.

Fenton's treatment was found to be more effective for the removal of organic matter >1 kDa in terms of MWand humic substances in terms of chemical nature of the landfill leachates. When compared with removal of organic matter, Fenton's treatment was observed to be more effective for the removal of bio-refractory UV_{254} quenching substances over all MWs. It was also observed that most of the treatment by Fenton's reagent targeted the bio-refractory humic substances which are mainly >1 kDa.

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