Characterization and photodegradation pathway of the leachate of Matuail sanitary landfill site, Dhaka South City Corporation, Bangladesh

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A B S T R A C T
This study was carried out to characterize the biogeochemical and physicochemical properties of landfill leachate from Matuail Sanitary landfill site, Dhaka, Bangladesh. In addition, the study also aimed to identify the photodegradation of landfill leachate under natural sunlight. The leachate pH was slightly alkaline (7.87–8.07) with a minimum level of dissolved oxygen, and low BOD5/COD ratio that are indicators of the matured methanogenic phase. Ca, Fe, Br, Rb, Cu was present in a considerable amount. A trace amount of Sr, Co, As, Pb, Cr was found in the leachate sample. Fourier Transform - infrared (FTIR) spectra of all three samples had five major peak regions notably at 3440–3450 cm⁻¹ (O–H groups of water), 1638 cm⁻¹ (C=O Amide I, carboxylates C=O, aromatic ring modes, or alkenes), 1385–1390 cm⁻¹ (deformation of the C-H bond in CH₂ and CH₃, or the asymmetric stretching of COO), 1115 cm⁻¹ (stretching of the C-O bond in phenol ethers and phenols) and 605 cm⁻¹ (S-O bonds of sulfates). In addition to the appearance of new peak, peak shifting on the 2nd-day and 5th-day phototreatment are in compliance with the 34% TOC reduction. From analyzing three-dimensional excitation/emission (3D-EEM) spectra of the raw sample pyrene-like or humic-like peak A (Ex 255/Em 465), soil fulvic-like peak Mp (Ex 315/Em 455), and humic-like peak C (Ex 370/Em 455) was found indicating more humified characteristics of the mature landfill site. From 1-hour to 6-hours phototreatment, all three substances slightly lost fluorescence intensity. From the 2nd day to the 5th day of photo-treatment, two unknown photo-product was identified within Ex 210/Em 457 and Ex 205/Em 408 at peak A region. Fluorescence intensity lost was 65% for peak A and 44% for peak C. Soil fulvic-like peak Mp was absent on the 5th day of photo-treatment.

1. Introduction

Landfilling is commonly practiced method for municipal solid waste management around the world. However, leachate is a significant drawback of landfilling, requiring treatment and the practice is expensive and insufficient (Morris et al., 2018). Dhaka is a megacity with the daily production of solid waste of more than 4000 Metric Tons, of which 200 Metric Tons of hospital and clinical waste contain toxic chemicals, radioactive elements, and pathological substances. In Bangladesh, due to lack of motivation, awareness, commitment, expertise, and budget, only 40–50% of wastes are collected and disposed of at Matuail and Amin Bazar sanitary landfill sites by the two city authorities—the Dhaka North City Corporation (DNCC) and the Dhaka South City Corporation (DSCC). The municipal solid wastes are usually sent to landfills without any physical separation of hazardous materials (Hai and Ali, 2005; Haque and Mondal, 2014). The unscientific managing and adhoc attitudes in landfill waste disposal led to unmanaged leachate production in the urban conglomerates (Naveen et al., 2017). The issue of solid waste is not only because of the increasing quantities but also because of inadequate management (Yasmin et al., 2017).

Leachate is the fluid percolating through the landfills. It is generated from liquids present in the waste and outside water, including rainwater, seeping through the trash, and taking up organic and inorganic products from both physical extraction and hydrolytic and fermentation processes (Jayawardhana et al., 2016). Rainfall, microbial action, and organic matter in solid waste generated loads of leachate. The physicochemical and biogeochemical attributes of the leachates can produce significant ecological shocks to the aquatic system if left untreated (Carvajal-Flórez...
Leachate from municipal solid waste is a complicated matrix of contaminants (Moody and Townsend 2017). Landfill leachate contains various chemicals involving large amounts of refractory organics with low molecular weight organic compounds and heavy metals inorganic salts, organic trace pollutants with variable concentrations (Chu et al., 2020). Leachate may also include suspended or colloidal particles, dissolved fractions, organic complexes, inorganic complexes, and free metal ions.

It can be assumed that dissolved organic carbon (DOC), besides the polymers, macromolecules, and low-molecular ions, consists of 20–200 nm large colloidal particles or aggregates (Ehrig and Robinson, 2011). Dissolve organic matter plays an essential role in heavy metal movement from municipal solid waste to water bodies via leachates (Wu et al., 2011). The high strength of ammonium and complex organic substances, including biodegradable volatile fatty acids, refractory aquatic humic substances, and micro-scale xenobiotic organic chemicals, are also found in leachates (Zhang et al., 2016).

Fluorescence three dimensional excitation–emission matrix (3D-EEM) can determine different fragments of FDOM, and it can also distinguish the age of the landfill leachate. Previously, DOM isolated from the leachates with varying ages of the landfill was fractionated into hydrophobic acid, hydrophobic neutral, hydrophobic base fractions, and hydrophilic matter based on hydrophobicity (He et al., 2016). EEM spectra of Protein-like fluorescence peaks dominate young landfill leachate, while fulvic-like and humic-like peaks dominate medium and old-aged landfill leachate (Huo et al., 2008). In addition, understanding the specific segments of DOM is crucial to identify DOM-metal speciation and migration (Wu et al., 2012). Wu et al. (2012) further informed the prospective risk of humified leachate as a heavy metal transporter. Additionally, photochemical degradation of DOM has a significant effect on its metal complexing capacity as the light can determine the future of DOM-metal complex shifted from soils to surface waters (Porcal et al., 2009). The leachate DOM can have a similar effect on metal speciation.

Matuail landfill site has become a severe problem for Dhaka city. Extend Over 100 acres, Matuail landfill site is almost 26 years old and reached its capacity. GHGSat satellite recently identifies the Matuail landfill site releasing approximately 4,000 kg of methane/hour (Clark 2021). It is clear that the physicochemical description cannot provide sufficient information about leachate composition, making the leachate treatment process ineffective (Baettker et al., 2020). It is, therefore, essential to quantify FDOM, ensure quality assessment, following treatment, and leachate management. As the nature of waste generation changes overtimes, the nature of municipal solid waste and associated leachate material also changes. It is significant to identify and characterize landfill leachate frequently for better management. This article aims to identify the physicochemical and biogeochemical properties of Matuail landfill leachate and identify the changes in dissolved organic matter under the natural sunlight condition.

2. Materials and methods

2.1. Sample collection and preparation

Two leachate samples in triplicates were collected from the north side of the Matuail Sanitary landfill site in May of 2019. Sample one was collected from the internal roadside drain located at 23’43’11.2”N and 90’26’58.8”E through which fresh raw leachate accumulated from the dumping site and flows to the leachate pond for biological treatment, and the other one was collected from the untreated pond located at 23’43’10.8”N and 90’26’56.9”E (Figure 1) in 2.5 L Premium amber glass bottles. The bottles were washed with detergent and tap water, followed by placing in an acid bath of 3:1 hydrochloric acid/nitric acid solution for 30 min, rinsed with DI water, and oven-dried. Before collecting the sample, bottles were rinsed with leachate two times to get a representative sample, and samples were collected from beneath the top surface following the standard method (AWWA, APHA, WPCF, 2005). The collected samples were transported to the laboratory quickly and preserved at 4°C refrigerators to determine the physicochemical properties.

2.2. Physicochemical analysis of landfill leachate

Physicochemical properties of leachate sample such pH, total dissolved solids (TDS), dissolved oxygen (DO) were measured by portable meters pocket type: HI9146 (HANNA), HI98301 (HANNA) and HI9146 (HANNA), respectively. To determine the COD values of the leachate samples Colorimeter (HACH, DR/890), COD Reactor (HACH, DRB 200) and COD Digestion Reagent High Range Vial (HACH) were used. The dry weight (DW) content of leachate samples was determined by taking a portion of the sample into the preweighed porcelain crucibles cleaned and dried in an oven previously and oven-dried at 105°C for 24 h. Then the oven-dried sample was heated in the muffle furnace at 550°C for 2 hour. The volatile dry weight (VDW) content was measured by calculating the differences between the two weights. The VDW corresponds to the organic fraction of samples (Simon et al., 2009). TOC of liquid samples were determined by Total Organic Carbon (TOC) Analyzer using combustion technique in the presence of oxidative catalyst working at 680°C with non-dispersive infrared detection NDIR system (TOC 5000A, Shimadzu).

2.3. Elemental analysis using Energy Dispersive X-Ray fluorescence (EDXRF)

Energy Dispersive X-ray Fluorescence (EDXRF) analysis is considered as it’s a non-destructive, multielement nuclear analytical instrumental method for qualitative and quantitative analysis of chemical elements based on the measurement of characteristic fluorescent radiation, which results from the de-excitation of inner shell vacancies produced in the sample elements using a suitable source of radiation. The data acquisition

Figure 1. Location of sampling point at Matuail sanitary landfill, Dhaka South City Corporation.
system and experimental setup consist of a Cd-109 radioisotope annular source, a Si(Li) detector (Canberra, Model SL 80175), a fast spectroscopy amplifier (Canberra, Model, 2024), a high voltage power supply (Tennelec, Model TC 950A), and a multi-channel analyzer (Canberra, Series 35, Model 3201). Sample pellets prepared from a homogeneously grounded powdered mass of each leachate sample using a pellet maker (Specac, UK) were irradiated by EDXRF for elemental analysis. The entire process and validation of the analytical system were described elsewhere (Hossain et al., 2020; Jolly et al., 2013, Khan et al., 2019; Akter et al., 2019).

2.4. Photodegradation of leachate

The leachate sample was first filtered with 0.45µm membrane filter paper, followed by dilution of filtered sample two times and taken in a Pyrex test tube. Test tubes were placed in a water bath prepared so that continuous water flow remains in the bath at a 45° angle. The samples were under natural sunlight exposure for five days. The experiment started at 12:00 pm on 17 May 2019 and ended at 6:00 pm on 21 May 2019. Sample tubes were collected at an interval of 0 hour, 1st hour (1:00 pm), 3rd hour (3:00 pm), 6 hour (6:00 pm), end of 2nd day (6:00 pm), and end of 5th day (6:00 pm). The average daytime maximum temperature during the experimental time was 37.1 ºC. The temperature data of Dhaka was collected from worldweatheronline.com (Supplementary Table 1), and hourly solar irradiation data (W/m²) was collected from solcast.com.au (Supplementary Figure 1). The average solar radiation varied from 12.4 W/m² at 5:00 am, 795.4 W/m² at 12:00 pm, 312 W/m² at 3:00 pm, and 5.8 W/m² at 6:00 pm, respectively.

2.5. 3D-EEM spectra analysis

The three-dimensional fluorescence (excitation–emission matrix, 3D-EEM) spectra of the leachate sample were recorded with a fluorescence spectrophotometer (F−4600, HITACHI, Japan) in scan mode with a 700–voltage xenon lamp at room temperature. The EEM spectra were collected at 5 nm increments over an excitation range of 200–400 nm, with an emission range of 250–500 nm by every 1nm. The excitation and emission slits were set to 5 nm of band–pass, respectively. The scan speed was 1200 nm min⁻¹. All the cuvettes before analysis were rinsed Milli-Q water. The Milli–Q water blank was subtracted from the sample's EEM spectra. Fluorescence peak data were recorded, and the peaks were identified using FL solution software and 3D-EEM spectra prepared by Sigmaplot 10.0.

2.6. Fourier Transform infrared spectroscopy (FTIR) analysis

Leachate samples were oven-dried at 60 ºC, and the dried samples were mixed with solid KBr in the ratio of 1:100. The KBr–leachate pellets of 13 mm diameter of the mixture were prepared at 8.103 kg cm⁻² pressure. Fourier Transform - infrared spectrometer (FTIR) was used to observe the functional group, both in the raw leachate and photo-treated leachate, using IR Affinity-1, Model No. SHIMADZU-A213748. The spectral resolution was 2 cm⁻¹ taken in the 400–4000 cm⁻¹ wavelength.

2.7. QA/QC

Quality control and quality assurance (QA/QC) was maintained throughout the study. Standard methods and procedures were applied for all the measurements. Necessary blank measurements and standards were performed. All other samples were measured/performed in three replications.

2.8. Statistical analysis

Standard deviation was calculated for each treatment, and figures were prepared using MS Excel, Origin pro 8.0 and Sigmaplot 10.0.

3. Results and discussions

3.1. General physicochemical properties of landfill leachate collected from Matuail

In this study, six physicochemical parameters, pH, DO, BOD₅, COD, TDS, and TOC, were measured for the samples collected from the Matuali landfill leachates (Table 1). The pH of the leachate samples was slightly basic or alkaline and varied from 8.07-7.87, which complies with the previous studies of Jahan et al. (2016) and others. DO range between 0.87-1.33 mg/L and also adhered to the earlier studies. BOD₅ ranged

| Parameter | Present study (2019) | Concentration as reported in previous studies | References | Bangladesh standards for discharging treated leachate into Inland surface water (DoE/GoB, 1997) |
|-----------|----------------------|---------------------------------------------|------------|-----------------------------------------------------------------------------------|
| pH        | 8.07–7.87            | 8.23 ± 0.12 (Jahan et al., 2016)             | 6–9        |
|           | 6.93                 | 8.34 (Azim et al., 2011)                     |            |
|           | 7.87 ± 0.14          | 8.34 (Mamhurd et al., 2012)                  |            |
| DO (mg/L) | 0.87–1.33            | 1.34 ± 0.5 (Jahan et al., 2016)              | 4.58       |
|           | 0.49                 | 0.49 (Azim et al., 2011)                     |            |
| BOD₅ (mg/L) | 157–182             | 1400–4000 (Mahmud et al., 2012)              | 50         |
| COD (mg/L) | 1397–1511           | 1343 ± 42 (Jahan et al., 2016)               | 200 (400)² |
|           | 1630 ± 944          | 1630 ± 944 (Azim et al., 2011)               |            |
|           | 6600–11,520         | 6600–11,520 (Mahmud et al., 2012)            |            |
| TDS (mg/L) | 662–4650            | 7120 ± 165 (Jahan et al., 2016)              | 2100       |
|           | 734                 | 734 (Azim et al., 2011)                      |            |
|           | 12,754              | 12,754 (Mamhurud et al., 2012)               |            |
|           | 7178 ± 171          | 7178 ± 171 (Haque et al., 2013)              |            |
| TOC (mg/L) | 682.93              | -                                            | -          |
| Biodegradability | BOD₅/COD        | <0.11–0.12                                  | -          |
| VDW (mg/g) | 29.1 ± 0.02         | -                                            | -          |

² Bangladesh standards for discharging treated leachate into Sewage system having secondary treatment option.
between 157-182 mg/L, which was much smaller than the previous study of Mahmud et al. (2012). The value of COD varied between 1397-1511, which is also lower than the value obtained in Mahmud et al. (2012) study. TDS (662-4650) concentration is also lower compared to the previous studies of Jahan et al. (2016), Azim et al. (2011), and Mahmud et al. (2012). TOC of the raw leachate was approximately 683 mg/L.

Biodegradability is expressed as BOD₅/COD ratio and COD/TOC ratio. BOD₅/COD ratio gives valuable information regarding the relative difficulty of degrading the organic substances, the supply of carbon source in denitrification, or the maturity phase dominating the landfill (Renou et al., 2008; Wiszniowski et al., 2004). In our study, BOD₅/COD is < 0.11–0.12, indicating low biodegradability. It demonstrates that leachates with these qualities need care with biological treatment and physicochemical treatments (Baettker et al., 2020).

3.2. Elemental concentration

We have measured the elemental concentration of the Matuail landfill leachate sample by EDXRF in the present study (Table 2). The elemental concentration of K (543.93 ± 3.25 mg/L) followed by Ca (181.75 ± 3.1) was highest in this study which complies with the previous studies of Jahan et al. (2016) and Azim et al. (2011). The concentration of Fe (14.43 ± 0.01 mg/L) and Cu (0.95 ± 0.02 mg/L) is significantly alarming as both the values crossed the limits of Bangladesh standards for discharging treated leachate into Inland surface water (DoE, 2004). The concentration of Rb (1.44 ± 0.001 mg/L), Sr (0.257 ± 0.001 mg/L), Zn (0.399 ± 0.01 mg/L), Cr (0.056 ± 0.02 mg/L), Br (3.25 ± 0.01 mg/L), Co (0.01 ± 0.001 mg/L), Ni (0.14 ± 0.001 mg/L) was also found in leachates with these qualities need care with biological treatment and physicochemical treatments (Baettker et al., 2020).

Table 2. The different metal concentration of landfill leachate reported in this study by EDXRF and previous studies from Bangladesh.

| Metals | Concentration (mg/L) Present study (2019) | Concentration (mg/L) Previous studies | References | Bangladesh standards for discharging treated leachate into Inland surface water (DoE/GoB, 1997) |
|--------|------------------------------------------|--------------------------------------|------------|--------------------------------------------------------------------------------|
| Fe     | 14.43 ± 0.001                            | 25.3 ± 1.75                          | (Jahan et al., 2016) | 2 |
|        |                                          | 17.2 ± 2.1 (summer), 25.3 ± 1.75 (monsoon), 3.41 ± 0.05 | (Hoque et al., 2014) | |
| Cu     | 0.95 ± 0.02                              | 1.5 ± 0.05                           | (Jahan et al., 2016) | 0.5 |
|        |                                          | 1.02 ± 0.08 (summer), 1.5 ± 0.05 (monsoon) | (Azim et al., 2011) | |
|        |                                          | 0.147                                | (Hoque et al., 2014) | |
|        |                                          | 0.09 ± .001                          | (Azim et al., 2011) | |
| Cr     | 0.056 ± 0.02                             | 0.36 ± 0.02                          | (Jahan et al., 2016) | 0.5 |
|        |                                          | 0.23 ± 0.02 (summer), 0.36 ± 0.02 (monsoon) | (Hoque et al., 2014) | |
|        |                                          | 0.744                                | (Azim et al., 2011) | |
| Zn     | 0.399 ± 0.01                             | 0.378                                | (Azim et al., 2011) | 5 |
|        |                                          | 2.3 ± 0.02                           | (Jahan et al., 2016) | |
| Ni     | 0.01 ± 0                                 | 4.46 ± 0.23                          | (Jahan et al., 2016) | 1 |
|        |                                          | 3.18 ± 0.28 (summer), 4.46 ± 0.23 (monsoon) | (Hoque et al., 2014) | |
|        |                                          | 1.048                                | (Azim et al., 2011) | |
|        |                                          | 0.17 ± 0.01                          | (Jahan et al., 2016) | |
|        |                                          | 1.01 ± 0.41                          | (Rikta et al., 2018) | |
| Br     | 3.25 ± 0.001                             | -                                    | -          | - |
| Rb     | 1.44 ± 0.001                             | -                                    | -          | - |
| Sr     | 0.257 ± 0.001                            | -                                    | -          | - |
| K      | 543.93 ± 15                              | 1125                                 | (Jahan et al., 2016) | - |
|        |                                          | 973 ± 13                             | (Azim et al., 2011) | |
| Ca     | 181.75 ± 3.1                             | 14                                   | (Azim et al., 2011) | - |
| Co     | 0.01 ± 0.001                             | -                                    | -          | - |
| Pb     | 0.01 ± 0.001                             | BDL                                  | (Jahan et al., 2016) | 0.1 |
|        |                                          | 0.02 ± 0.001                         | (Azim et al., 2011) | |
|        |                                          | 0.45 ± 0.35                          | (Jahan et al., 2016) | |
| As     | 0.01 ± 0.001                             | -                                    | -          | - |

It is evident that under alkaline pH, except Fe, most trace metals were in low concentration due to insolubility (Baettker et al., 2020). The concentration of Fe was seven times higher than the normal values. The heavy metals identified in the leachates were due to the over-dumping of household, industrial, and e-wastes that might be the causes of metal leaching due to precipitation and dissolution. Previously e-waste dismantling and recycling sites reported different heavy metals such as Ba, Cu, Pb, Zn, Sb, Cd, Co as significant soil and subsoil pollutants from China (Jiang et al., 2019; Han et al., 2018), India (Singh et al., 2018). The heavy metals found in this study, such as Pb, Zn, Cu, Cd, Cr, and Ni are not biodegradable and have severe toxic effects on living organisms when they exceed a particular concentration (Vaverková et al., 2018). In addition, the heavy metal speciation and metal–DOM complexes play a crucial part in the toxicity and bioavailability of heavy metals, which can not be overlooked here (Rikta et al., 2018).

3.3. Photo-treatment of leachate

The collected raw leachate sample was basic, with a pH value of 8.07. On the first day, no change was observed in the pH value, but on the 2nd day of photo treatment, the pH value was reduced to 7.0 and on the 5th day of photo treatment, pH values increased again (Figure 2a).
previous study of photodegradation of extracellular polymeric substances, similar phenomena of decreasing pH were observed until 2nd day of exposure (Shammi et al., 2017). Total dissolved solids (TDS) first increased in the 1st hour of photodegradation but decreased in the 3rd hour and increased on the 6th hour of photodegradation. TDS value decreased gradually from 6thhrs to 2nd day to 5th day of photo-treatment. This changing trend is shown in Figure 2b.

Total organic carbon (TOC) is a direct measurement of the carbon in the organics, organic matter in water or wastewater. In this study, TOC of the leachate sample was decreased gradually from 0 h to the 5th day of photodegradation. TOC concentration in the raw leachate sample was approximately 683 mg/L which dropped to 450 mg/L (Figure 2c), and about 34% TOC was observed to decrease at the end of the 5th day photo-treatment. The raw leachate was highly concentrated. Previously Zhang et al. (2013) also mentioned highly concentrated leachate DOC from membrane treatments up to 552.5 mg/L and leachate DOC 358.1 mg/L.

### 3.4. Changes in FTIR spectra

FTIR spectra represent qualitative chemical groups and bands in landfill leachate DOM and provide information on the photo-treatment of DOM evolution (Figure 3 and Supplementary Table 2). Raw leachate from Matuail landfill and photo-treated leachate collected at the end of the 2nd day and 5th day showed a significant change that complies with TOC changes. All three samples had five major peak regions, notably at 3440–3450 cm⁻¹, 1638 cm⁻¹, 1385 cm⁻¹, 1115 cm⁻¹, and 605 cm⁻¹. The broad stretching band at 3440–3450 cm⁻¹ belongs to the bonded and non-bonded O–H groups of water (Huo et al., 2008, 2009; Zhang et al., 2020). In the raw leachate sample, the band peak was not prominent, while 2nd-day and 5th-day photo-treated samples showed a distinct broad peak of O–H stretching.

The weak band at 2937 cm⁻¹ might be related to the C–H stretching vibration of aliphatic structures (He et al., 2015), which appeared on the 5th day, unlike the raw sample and 2nd-day photo-treated sample. The small but sharp peaks at 1638 cm⁻¹ related to the C=O Amide I, carboxylates C–C, aromatic ring modes, or alkenes. The band Wavenumbers 1385-90 cm⁻¹ might belong to the deformation of the C–H bond in CH₂ and CH₃, or the asymmetric stretching of COO(Huo et al., 2009; Zhang et al., 2020). The broad peak at 1115 cm⁻¹ might be related to stretching the C=O bond in phenol ethers and phenols. A weak band at 595 cm⁻¹ in the raw sample and a distinct broad peak on the 2nd day and 5th-day photo-treated sample might belong to the S–O bonds of sulfates (Huo et al., 2009; Zhang et al., 2020). The spectrum identified by FTIR indicates the presence of complex molecular structure of the DOMs present in the landfill leachates that changed structures upon photo-treatment with sunlight.
3.5. Characteristics of 3D-EEM spectra

FDOM spectra were analyzed by using sigma plot 10. The raw leachate samples represented two peak regions: Peak A and Peak C. Ex 255/Em 465 had a strong peak resembling Pyrene-like or humic-like peak A. Pyrene-like substances are polycyclic aromatic hydrocarbons (PAH). Peak C had a combined peak of soil fulvic-like Peak Mp (Ex 315 nm/Em 450 nm) humic-like Peak C (Ex 370 nm/Em 455 nm) substances (Figure 4 and Table 3). Wu et al. (2011) identified three humic-like components and one protein-like component in the municipal solid waste leachate. In addition, Wu et al. (2012) studies indicated more humic-like substances in aged leachate. It is clear that Matuail landfill is close to 26 years old, and the leachate is more humified by nature.

Within the first day of photo treatment (0–6 hour), there was no change in the peaks except increased fluorescence intensity and changed band shift of peaks. Pyrene-like or humic-like peak A shifted at Ex 255 nm/Em 458 nm (1st hour) Ex 255 nm/Em 457 nm (3rd hour), Ex 255 nm/Em 463 nm (6th hour), while soil fulvic-like Peak Mp moved at Ex 315 nm/Em 450 nm (1st hour) Ex 315 nm/Em 453 nm (3rd hour), Ex 315 nm/Em 453 nm (6th hour). Humic-like peak C also shifted towards Ex 365 nm/Em 449 nm (1st hour), Ex 370 nm/Em 453 nm (3rd hour), and Ex 370 nm/Em 453 nm (6th hour) (Figure 4 and Table 3).

An unknown photo-product peak at Ex 210 nm/Em 457 nm was found after the 2nd day of photo-treatment belonging to peak region A. Furthermore, the end of the 2nd-day photo-treatment resulted in band shift of soil fulvic-like Peak Mp, Ex 340 nm/Em 420 nm at Peak C region. Humic-like peak C also band shifted at Ex 370 nm/Em 455 nm compared to the 1st day of photo-treatment. Another unknown photo-product peak was developed at Ex 205 nm/Em 408 nm was found after the 5th day of photodegradation. Soil-fulvic-like peak Mp might have degraded entirely and converted into the new photo product. Porcal et al. (2009), in their study, showed that photo-irradiation caused a significant decline in the Fulvic acid-bound metal concentrations. Both the pyrene-like or humic-like peak A and humic-like peak C shifted their bands at Ex 255 nm/Em 466 nm and Ex 370 nm/Em 457 nm (Figure 4 and Table 3).

Peak A is the intense peak observed in all raw and photo-treated samples. Zhang et al. (2013) previously identified peaks in a similar region (Ex 240–260 nm/Em 440–470 nm) which indicated humic-like substances. Lu et al. (2009) identified 6 fluorophores in their leachate study: Ex 240, 310, 360 nm/Em 460 nm; Ex 220, 280/Em 340 nm; Ex 220, 270 nm/Em 300 nm; Ex 220, 280 nm/Em 360 nm; Ex 230, 320 nm/Em 420 nm; and Ex 220, 310 nm/Em 400 nm (Lu et al., 2009). Ex 260/Em 450 nm and Ex 330/Em 410 nm are closely associated with humic-like acid (Zhang et al., 2020). Furthermore, multiple Ex 240–243, 262–272, 306–343 nm/Em 373–398 nm might belong to the pyrene and its alkyl derivates (He et al., 2016). The photo-product belongs to the peak A region and might be the degradation product of humic-like and soil-fulvic-like substances.

Fluorescence peak intensity for humic-like or pyrene-like substances was 624.5 RU in the raw sample and 214 RU on the 5th day of the photo-treated sample. The overall fluorescence intensity of Peak A humic-like or pyrene-like substance was reduced by approximately 65%. The humic-like peak C substance of the raw sample had the fluorescence intensity of 1586 RU, and the sample after the 5th day had 879 RU. Approximately 44% fluorescence intensity was lost for peak C. Peak Mp, a soil fulvic-like substance in the peak C region, decreased its intensity within the first 6 h but gained significantly on the end of the 2nd day. On the 5th-day phototreated sample, the peak was not found (Table 3).

On the contrary, an unknown photoproduct was developed at the end of the 2nd day with a peak intensity of 111.7. Moreover, at the end of the 5th day of photo-treatment, another unknown photo-product was identified with a peak intensity of 637.2 (Table 3). The development of photo-products might be from the degradation or rearrangement of the pyrene-like or humic-like substances and soil fulvic-like substances.
3.6. A conceptual model on old-landfill leachate photodegradation

Different metal-containing wastes are thrown in the Matuail landfill sites, including household waste, hospital wastes, e-waste, and industrial waste. Considering the results of 3D-EEM spectra containing soil fulvic-like substance and humic-like substance, it is evident that Matuail is an old-aged landfill site with leachates requiring special attention. During precipitation, many metals dissolve and leak to the leachate pool. The leached metals might complexed with the Humic-like Substances (HLS), Fulvic-like substances (FLS), and unknown DOM photo-products (eq 2).

The leached metals might complex with the HLS, FLS, and unknown DOM photo-products (eq 2). Bringing the metal to the leachate-DOM. A fulvic-acid-like portion of old landfills Metal-metal-DOM binding affinity. Yuan et al. (2018) further informed that Ni and Pb were bound to fulvic-like, humic-like, and protein-like components in the leachate-DOM. A fulvic-acid-like portion of old landfill leachate DOM plays a vital role in heavy metal speciation (Wu et al., 2011). The elements mentioned above might be in complexation with the leachate DOM. The following reaction might occur in the leachate media to release the metal (eq 1):

landfilled Metal + precipitation → Metal (M^{2+}) (leaching in the dissolution) (1)

During the summer, photo exposure at 798.6 W/m² - 795.4 W/m² can cause leachate DOM to break down into Humic-like Substances (HLS), Fulvic-like substances (FLS), and unknown DOM photo-products (eq 2). The leached metals might complex with the HLS, FLS, and unknown DOM photo-products due to their labile nature (eq 3).
leachate DOM + hυ → Humic-like Substances (HLS) + Fulvic-like substances (FLS) + unknown DOM photo-products (UD) (2)

HLS + FLS + UD + M^{n+} + hυ → PLS-M + HLS-M + UD-M (3)

The leaching of metals in the landfill leachate sites mainly follows in the initial leaching phase. The leaching actions are regulated by the diffusion of surface metals in the leachate matrix (Li et al., 2021). Cui et al. (2017) showed the leaching of Cu and Zn from e-waste recycling sites due to rainfall and irrigation water in the surface soil contributed by Cu(OH)_{2}, CuCO_{3}, Zn_{5}(CO_{3})_{2}(OH)_{6}, and amorphous Fe/Mn oxides. In addition, Fe contamination in the groundwater and aquifer at various landfill sites indicates reductive dissolution of iron (hydr-)oxides (Oppong-Anane et al., 2018).

Uncontrolled household wastes, e-waste, and other industrial wastes dumping in the Matuail landfill site might be the source of heavy metals in our study. The local precipitation-dissolution balance might interfere in the leaching of metal and forming DOM-M^{n+} complexes which migrate easily and compete with each other for DOM-binding sites such as humic acids and fulvic acids, and other unknown photo-products. The conceptual model of the leachate-DOM photodegradation pathway is shown in Figure 5. Humic-like substances and soil fulvic-like substances make complexes with the metal (M^{n+}) therein in the aqueous leachate. During photodegradation, the M^{n+} can be released from the leachate, precipitate, or flocculate and return to the leachate-DOM complexes.

4. Conclusion

We have analyzed the status of Matuail sanitary landfill site leachate. It is found that the leachate characteristics are of advanced matured age, suggesting landfills in the methanogenic phase and explains the relation with the heavy methane emission from these particular landfill sites, which requires exceptional management. The leachate is low biodegradable and alkaline. The concentration of metals, particularly the concentration of Fe and Cu, was beyond Bangladesh standards. Trace amounts Rb, Sr, Ni, Co, Pb were also present in the study.

Consequently, there might be an increased risk of surface and groundwater contamination from heavy metal and other contaminants such as more humified DOM and metal-binding processes. From the photodegradation of leachate samples for five days, it has been found that humic-like substances of DOM are degraded to some extent, and consequently, some unknown photo-products developed. The photochemical reaction DOM-M^{n+} decomposes, and the metals recycle back to make complexes with the leachate DOMs. DOM-M^{n+} complex decomposition can be more labile to reach and pollute the groundwater aquifer and other aquatic systems. Increasing the efficiency of leachate treatment in the sanitary landfill site is highly recommended with proper environmental assessment. In addition, waste segregation, including the concept of 3R-reduce, reuse, and recycle should be strictly followed for metal-containing wastes.

Declarations

Author contribution statement

Sumaiya Akter: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Mashura Shammi: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Yeasmin Nahar Jolly, Shafl M Tareq: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Abid Azad Sakib: Performed the experiments; Wrote the paper.
Md. Mostafizur Rahman: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data included in article supplementary material/referenced in article.

Declaration of interest statement

The authors declare no conflict of interest.

Additional information

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