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Determination of leachate compounds relevant for landfill aftercare using FT-IR spectroscopy

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ABSTRACT

Controlling and monitoring of emissions from municipal solid waste (MSW) landfills is important to reduce environmental damage and health risks. Therefore, simple and meaningful monitoring tools are required. This paper presents how Fourier Transform Infrared (FT-IR) Spectroscopy can be used to monitor leachate from various landfill sites. The composition of percolated leachate provides information about reactivity or stability of organic matter in landfills. Chemical compounds of investigated leachate are depicted by distinct spectral pattern. Partial least squares regression (PLS-R) models, a multivariate analysis tool, were developed based on infrared spectra to determine simultaneously conventional parameters such as ammonium, nitrate, sulfate, and dissolved organic carbon. The developed models are appropriate for application in waste management practice with respect to their excellent coefficients of determination, namely $R^2 = 0.99$, 0.99, 0.98, and 0.98, their low errors of cross-validation and their high ratios of performance to deviation (RPD = 9.3, 12.5, 6.5, 7.3). Thus, FT-IR spectroscopy turned out to be a reliable, time-saving tool to determine four parameters relevant for landfill aftercare monitoring by one single easy adaptable measurement.

1. Introduction

Controlling and monitoring of emissions from municipal solid waste (MSW) landfills currently represents important issues in European Environmental Policy (CEC, 1999, 2008). Due to the predominantly anaerobic decomposition of waste organic matter both gaseous compounds (mainly CH_4 and CO_2) and degradation products in the leachate (ammonium, dissolved organic carbon) are generated over a long-time period (Bogner et al., 1998; Krümpelbeck, 2000; Scharff and Jacobs, 2006). Since the collection and treatment of landfill gas and leachate is very costly, different remediation methods are more and more applied to stabilize organic waste matter (e.g. in-situ aeration) and to shorten the time for landfill aftercare. Simple and meaningful monitoring tools are required in order to identify and evaluate the success of diverse stabilization techniques.

Moreover, the knowledge of leachate composition is crucial to gain insight into the ongoing processes in the waste body for both, projections on the long-term environmental impacts of landfills and selection of suitable treatment measures. In general, landfill leachates contain very high concentrations of dissolved organic matter and inorganic components, heavy metals and xenobiotic compounds (Kjeldsen et al., 2002). The chemical composition of leachates varies in a wide range dependent on the decomposition stage and the environmental conditions (e.g. water supply, redox potential). The development of organic compounds and ammonia concentrations in the leachate reveal the age of a landfill (Krümpelbeck, 2000; Kulikowska and Klimiuk, 2008). It is influenced by waste stabilization techniques (Prantl et al., 2006; Ritzkowski et al., 2006).

Particularly ammonium is of high importance in terms of post closure care and environmental compatibility as it decreases only slowly or remains in the same range for decades (Kjeldsen et al., 2002; Krümpelbeck, 2000). Dissolved organic carbon (DOC) is a sum parameter covering a variety of organic degradation products that determine the length of the aftercare phase. The European Standard EN 1484 defines the DOC as the sum of organically bound carbon present in water originating from compounds which will pass a membrane filter of pore size of 0.45 μm. Cyanate and thiocyanate are also measured. The DOC is also a very common and significant parameter in other scientific fields as soil and water science. Zimmermann et al. (2007) used infrared spectroscopy combined with partial least squares regression to predict different organic carbon in different soil fractions including the DOC. The use of spectroscopic methods to predict the DOC in natural water was carried out by Marhaba et al. (2003) with the objective to find more effective and rapid methods to determine the DOC. Nitrate

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and sulfate are oxidation products which reflect aerobic conditions in landfills and are therefore of particular interest for monitoring stabilization processes like in-situ aeration.

Due to the fact that the determination of these leachate parameters is very time consuming the development of a new quick and cost-effective method is a target to be reached. Besides these conventional physico-chemical analyses only a few methods characterizing landfill leachate are currently available. Wimmer et al. (2013) found that monitoring of stable isotopic signatures of landfill leachates over a longer time period (e.g. during in situ aeration) is a powerful tool for characterizing the biodegradability and stability of organic matter in landfilled municipal solid waste and can be used for monitoring the progress of in situ aeration. Fluorescence spectroscopy coupled with chemometric analysis was recently employed to investigate dynamics of dissolved organic matter in leachate polluted groundwater (He et al., 2014). In a study of Xiaoli et al. (2013) elemental analysis, FT-IR spectroscopy and ^{13}C Cross-Polarization Magic Angle-Spinning Nuclear Magnetic Resonance (^{13}C CP/MAS NMR) were carried out to characterize the chemical and structural properties of humic acids (HA) extracted from the leachate of both semi-aerobic and anaerobic full-scale landfill.

In the past, FT-IR measurements have been proven to be less error-prone and to be an appropriate method to assess the stage of organic matter decomposition in solid waste materials very quickly (Smidt and Meissl, 2007). However representative sampling of solid waste is very time consuming and challenging (e.g. perforation of the coverage, excavation, laboratory sample preparation) due to the heterogeneity of the landfilled solid waste mass. Compared to solid waste sampling the collection and control of leachate emissions is less complicated and time consuming and already state-of-the-art, and e.g., obligatory in Austria (Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, 2008; ÖWAV, 2008). The application of FT-IR spectroscopy on landfill leachate has already been used in a preliminary study to characterize freeze-dried leachate from landfill simulation reactors (Gamperling et al., 2009; Smidt and Meissl, 2007). Leachate characteristics are reflected by a specific infrared spectroscopic pattern. Based on the relationship between results of reference analyses and FT-IR spectra partial least squares regression (PLS-R) models for the prediction of NH_4-N, NO_3-N, SO_4-S and DOC were calculated (Gamperling et al., 2009).

In the present study a large number of leachate samples from six different landfill sites, one lysimeter and two long-term investigations in laboratory simulation reactors were investigated by classical wet chemical analyses and by FT-IR spectroscopy. FT-IR spectra of leachates were recorded from the liquid samples. FT-IR spectra and results from reference analyses were correlated to develop models for the prediction of ammonium-nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), sulfate-sulfur (SO_4-S) and dissolved organic carbon (DOC). The application of the developed prediction models on a single FT-IR spectrum of an unknown leachate sample provides the required parameters reliably and quickly.

2. Material & methods

2.1. Materials, sampling and sample preparation

Leachate gathered from abandoned Austrian municipal solid waste (MSW) landfills, a field-trial lysimeter and lab-scale landfill simulation reactors (LSR) was analyzed using both Fourier Transform-Infrared (FT-IR) spectroscopy and classical wet chemical analyses. Six different abandoned Austrian MSW landfills comprising different sections were sampled quarterly over a period of 15 months. One of these landfills and the lysimeter have been remediated by in-situ aeration. The lysimeter comprised 4 chambers filled with the same MSW but covered with different substrates (chamber A: sewage sludge – compost cover, chamber B: sand – compost cover, chamber C: silt – loess cover, chamber D: loess cover) Details of the landfills are listed in Table 1. The sample set comprises 295 leachate samples.

For lab scale experiments MSW from two different Austrian landfills with different waste composition and reactivity has been excavated. Material I was 10–15 years old household waste, material II was a mixture of household and bulky waste with the same age. Gas-leak proof landfill simulation reactors (LSR, Ø = 20 cm, h = 65 cm) made of acrylic glass were filled with about 6 kg (material I) and 9 kg (material II) dry matter of MSW (sieved < 20 mm). The experiment was set up in a climate chamber at 24 °C. During the investigation of material I 3 columns were kept anaerobic as a reference, 6 columns have been aerated right from the start. All columns filled with material II have been kept anaerobic right from the start. After 6 weeks of weekly irrigation 7 columns were aerated and 3 columns have been kept anaerobic. Aeration was conducted continuously, depending on the reactivity of the waste material, from the bottom, irrigation with 375 ml H_2O each was performed weekly at the top of the column. The amount of

Table 1
Metadata of the sampled landfills.

Landfill	Deposited waste material	Section	Period of landfilling	In-situ aeration performed
Landfill 1	Household waste, bulky waste, construction waste, household-type commercial waste	Section 1/2 Section 3/4/5	1975–1990 1988–1997	No No
Landfill 2	Household waste, bulky waste		1982–2003	No
Landfill 3	Household waste, bulky waste, construction waste, household-type commercial waste		1970–1985	No
Landfill 4	Household waste, bulky waste, construction waste, household-type commercial waste		1977–1985	No
Landfill 5	Household waste, construction waste, bulky waste hospital waste, lime	Section 1/2/3 Section 4/5 Section 2/1 Collection basin	Since 1985 Younger than 1985 Till 2000	No No No
Landfill 6	Household waste, bulky waste, household-type commercial waste, residues of waste composting, construction waste		1976–1996	Yes
Lysimeter	Residual waste	Chamber A Chamber B Chamber C Chamber D	2008 2008 2008 2008	Yes Yes Yes Yes