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Comparison of different types of landfill leachate treatments by employment of nontarget screening to identify residual refractory organics and principal component analysis

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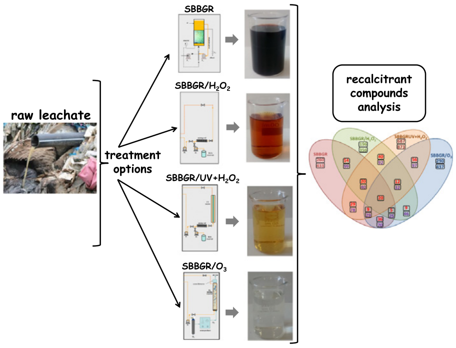
HIGHLIGHTS

- A comparative investigation among four oxidation treatments of leachate is reported.
- UPLC-HRMS profiles were analyzed with PCA.
- Exact masses of recalcitrant compounds after non-target screening were determined.
- Classification of compounds was determined according to the four oxidation treatments.
- The chemical nature of recalcitrant fractions was widely revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

Three different chemical oxidation processes were investigated in terms of their capability to degrade organic chemical components of real mature landfill-leachate in combination with biological treatment run in a Sequencing Batch Biofilter Granular Reactor (SBBGR). H_2O_2, H_2O_2 + UV and O_3 were integrated with SBBGR and respective effluents were analyzed and compared with the effluent obtained from biological SBBGR treatment alone. In agreement with their respective oxidative power, conventional bulk parameters (residual COD, TOC, N_{tot}, TSS) determined from the resulting effluents evidenced the following efficacy ranking for degradation: SBBGR/O_3 > SBBGR/UV + H_2O_2 > SBBGR/H_2O_2 > SBBGR. A more detailed characterization of the organic compounds was subsequently carried out for the four treated streams. For this, effluents were first subjected to a sample preparation step, allowing for a classification in terms of acidic, basic, strongly acidic and strongly basic compounds, and finally to analysis by liquid chromatography/high resolution mass spectrometry (LC/HR-MS). This classification, combined with further data post-processing (non-target screening, Venn Diagram, tridimensional plot and Principal Component Analysis), evidenced that the SBBGR/H_2O_2 process is comparable to the pure biological oxidation. In contrast, SBBGR/O_3 and SBBGR/UV + H_2O_2 not only resulted in a very different residual composition as compared to SBBGR and SBBGR/H_2O_2, but also differ significantly from each other. In fact, and despite of the SBBGR/O_3 being the most efficient process, this treatment remained chemically more similar to SBBGR/H_2O_2 than to SBBGR/UV + H_2O_2. This finding may be attributable to different mechanism of degradation involved with the use of UV radiation. Apart from these treatment differences, a series of recalcitrant compounds was determined in all of the four treatments and partly identified as hetero-poly-aromatic species (humic acids-like species).

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1. Introduction

It is well known that leachate is formed as a consequence of waste degradation in landfills and the washing out action of rain water during percolation through wastes. The resulting black/brownish leachate contains organic and inorganic chemicals, heavy metals as well as pathogens. It can pollute the groundwater and therefore represents a health risk. Its chemical composition can change both from time to time and from site to site being influenced by a number of factors including seasonal precipitation changes, waste composition, and, mainly, the age of the landfill (Foo and Hameed, 2009). Leachate of sanitary landfills is generally characterized by high concentrations of total dissolved solids (TDS), heavy metals, chemical oxygen demand (COD), ammonia as well as high colour (El-Fadel et al., 1997; Renou et al., 2008; Robinson, 2005; Tchobanoglous and Kreith, 2002). The age of the landfill site is one of the main variables that affects the leachate characteristics (Bashir et al., 2009; Foo and Hameed, 2009; Renou et al., 2008). Specifically, young landfill leachates are characterized by a large fraction of biodegradable organic matter (i.e., volatile fatty acids) which, in turn, is smaller in older landfills due to anaerobic decomposition of the waste. The decrease of the volatile fatty acids fraction of the organic matter leads to refractory compounds to become more concentrated. The latter are mainly related to humic and fulvic acid-like compounds with a concomitant reduction of the biochemical oxygen demand (BOD_5)/COD ratio (Harmsen, 1983).

Therefore, and according to widely employed regulations, leachate has to be properly treated in order to safely dispose of the resulting effluent in receiving water bodies. It is worth noting that other methods were also tested including landfill reinjection of concentrated leachate produced by membrane treatment (Calabrò et al., 2010) as well as reusing treated leachate for fertirrigating (a technique by which fertilizer are applied with the water of the irrigation system) the walls of the same landfill (Del Moro et al., 2016a). Indeed, aged landfill leachates are known to be more difficult to treat than young ones. This is due to several reasons, among them (i) high levels of ammonia that induce a potential toxic effect to conventional nitrification-denitrification biological process, (ii) high salinity, (iii) the increasing presence of non-biodegradable organics that hinders reaching the target COD discharge limit of the resulting effluent. Conventional biological treatments followed by a tertiary step based on physico-chemical methods have been considered for years as the best available technologies for treating leachates (Chemlal et al., 2013; Chemlal et al., 2014; Renou et al., 2008). Indeed, physico-chemical processes are also used as pre-treatment methods before biological process to reduce toxicity as well as to improve biodegradability of refractory wastewater (Chemlal et al., 2014). When dealing with medium age leachate, however, more effective biological systems based on a sequencing batch biofilter granular reactor (SBBGR) were demonstrated to be very effective (Di Iaconi et al., 2009; Di Iaconi et al., 2006; Di Iaconi et al., 2011). The SBBGR system was successfully employed in combination with electrochemical oxidation treatment on both raw and biologically treated leachate (Del Moro et al., 2012; Del Moro et al., 2016b) as well as integrated or combined with several advanced oxidation processes (AOPs) (Cassano et al., 2011; Del Moro et al., 2013).

The employment of the aforementioned combination of treatment techniques allows reaching the target discharge limits, which are often solely based on sum parameters such as COD and/or BOD_5 and total nitrogen (TN) when accounting for organic composition, e.g., by properly optimizing the treatment conditions in terms of residence time, oxidant dose and other relevant operating conditions. It is worth noting, however, that the various tested AOPs combinations reach the target discharge COD limit suggesting that they behave roughly in a similar manner in terms of organics degradation (Cassano et al., 2011; Di Iaconi, 2012). In addition, by applying more powerful oxidative conditions (e.g. by increasing the oxidant dose with the various AOP combination) the COD can be further lowered, until reaching a plateau value suggesting the presence of a final effluent composition that is quite recalcitrant to further degradation (Cassano et al., 2011; Di Iaconi, 2012). It follows that in order to get insights about the effectiveness of the AOPs employed as well as the organic composition responsible for the final recalcitrant effluent composition it would be necessary to characterize the effluents in terms of their organic composition. It is worth noting that when different biological-AOP processes are used for leachate treatment, the comparison of obtained effluents in terms of residual organics is quite challenging because the effluents still potentially contain several hundreds of compounds, namely both the residual parent compounds and their transformation products (TPs) (Jiménez et al., 2002; Naveen et al., 2017). As most of them are likely to be polar as a consequence of the biological-AOP processes to which the landfill leachate was subjected, liquid chromatography interfaced to high resolution mass spectrometry (LC/HR-MS) is the method of choice to fulfill such a task. It has been reported, in fact, that the evolution of LC/HR-MS in recent years allowed new opportunity for the detection of polar organic contaminants in complex samples (Krauss et al., 2010; Schymanski et al., 2015). The comprehensive screening for characterizing a complex effluent for its composition in organic trace substances and TPs has to be carried out in terms of target analysis, suspect screening and non-target screening (Chiaia-Hernandez et al., 2014; Schymanski et al., 2014b). In addition, the comparison of environmental samples in terms of organics composition requires proper post-processing tools, such as principal component analysis (PCA), in order to reflect the variety of compounds that are usually detected in such complex effluent samples (Müller et al., 2011).

In this work, the treatment of the leachate of a medium age landfill was investigated by employing SBBGR alone and enhanced by ozonation and UV/H_2O_2. In addition, another experimental phase (SBBGR/H_2O_2 set-up) was carried out aimed at evaluating the contribution of hydrogen peroxide as a reactive agent. The comparison of the treatment set-ups focuses on the residual organics contained in the final effluents and was performed by applying a non-target screening using LC/HR-MS and post-processing by PCA. The main objective of the investigation was to compare the composition of the remaining fractions after the different treatments in order to elucidate common classes or specific compounds in the different recalcitrant effluents. In addition, another objective was the classification of the employed integrated treatment methods based on the effluents composition in terms of organics detected.

2. Materials and methods

2.1. Leachate characterization

The raw leachate used throughout the investigation was sampled from a medium-aged municipal landfill located in Apulia, Southern Italy. The landfill contains non-hazardous waste including municipal solid waste. In the present study, leachate was characterized according to Standard Methods (Rice et al., 2012). The obtained chemical and physical properties are listed in Table 1.

2.2. Biological system (SBBGR)

The lab-scale biological plant system consisted of a sequencing batch biofilter granular reactor (SBBGR) whose details are reported elsewhere (Di Iaconi et al., 2009; Di Iaconi et al., 2006). Briefly, the SBBGR consists of a cylindrical reactor, partially filled with a biomass-supporting plastic material (KMT-k1 elements from Kaldness, Norway; main characteristics: high 7 mm, diameter 8 mm, specific area 650 m^2/m^3, relative density 0.95, bed porosity 0.74) packed between two sieves, with a bed volume of 16 L. The reactor was equipped with two peristaltic pumps for filling (M-range model with variable flow rate adjustment from Sydex pump srl, Italy) and internal recirculation (M-range model with a flow rate of 90 L/h from Sydex pump) operations, an aerator for air