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Sanitary landfill leachate treatment using combined solar photo-Fenton and biological oxidation processes at pre-industrial scale

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HIGHLIGHTS

- Complete leachate treatment train combining photocatalytic and biological processes.
- The recalcitrant character of the leachate is mainly due humic substances.
- Humic acids removal can be achieved by precipitation in the acidification step.
- The formation of ferricarboxylate complexes enhances the photo-Fenton reaction.
- Low temperatures affects greatly the nitrification and denitrification reactions.

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ABSTRACT

This work proposes a new strategy for the treatment of leachates from sanitary landfills after lagooning pretreatment, using a solar photo-Fenton oxidation process to eliminate the most recalcitrant organic compounds, leading to a biodegradability enhancement of the leachate and promoting its subsequent oxidation in an activated sludge biological reactor. The integrated leachate treatment process was conducted in a pre-industrial plant, incorporating a photocatalytic system with 39.52 m^2 of compound parabolic collectors (CPCs) and an activated sludge biological reactor, with 3.5 m^3 capacity, operated under aerated and anoxic conditions. An extensive physico-chemical characterization of the leachate after lagooning was performed during one year, from June 2010 to May 2011, showing its high recalcitrant character mainly associated with the presence of humic substances.

The efficiency of the combined treatment was evaluated concerning the leachate characteristics' variability after lagooning, availability of solar radiation during the year, and different operational process variables, such as the amount of hydrogen peroxide necessary to reach the required COD target value, biodegradability enhancement during the photo-oxidation process, iron reutilization in consecutive oxidation processes, removal of acidic sludge resulting from the acidification process and leachate temperature/average solar power. The elimination of the remaining organic carbon fraction and nitrogen compounds after the pre-oxidation step was also assessed in an activated sludge biological reactor, under aerobic and anoxic conditions, considering the composition variability of photo-treated leachate. Nitrification and denitrification rates were also evaluated.

1. Introduction

Sanitary landfill leachates treatment constitutes nowadays one of the major challenges for the scientific community, mainly due to the variability of leachates composition and quantity [1,2], reinforced by the presence of a complex mixture of recalcitrant organic contaminants. These may include humic and fulvic acids [3], phthalic esters [4,5] pesticides [6], and many other emerging organic pollutants, in concentration as low as nanograms (ng) or micrograms (μg) per liter (perfluorinated compounds-PFCs, pharmaceuticals and personal care products, polyaromatic hydrocarbons-PAHs) [7], inorganic compounds (chloride, sulfate, bicarbonate and carbonate, sulfide species, alkali and alkaline earth

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metals, iron and manganese) [8], nitrogen compounds in high concentration [9–11] and heavy metals [8,12].

Renou et al. [11] and Abbas et al. [13] presented reviews on different approaches used for landfill leachates treatment, divided in five different groups: (i) leachate channeling (combined treatment with domestic sewage; recycling back through the landfill); (ii) biodegradation (aerobic and anaerobic biological processes); (iii) chemical and physical methods (flotation, coagulation/flocculation, chemical precipitation, adsorption, ammonium stripping, chemical oxidation and ion exchange); (iv) membrane filtration (microfiltration, ultrafiltration, nanofiltration and reverse osmosis); (v) combination of the different processes reported above.

The UK Environment Agency presented in 2007 a guidance for the treatment of landfill leachates [14], which indicated that the *Best Available Technologies* for leachates treatment relied on the adoption of a multistage treatment process, possibly involving the use of primary, secondary, and tertiary processes, adjusted to the type of leachate, including the different technologies aforementioned.

During the late 90s, in Germany, the Netherlands, Belgium, France, Portugal and Spain, a lot of reverse osmosis (RO) leachate treatment systems were designed with an aerated lagoon in front of a 2-stages RO plant [14]. This configuration presented as advantage the aerated lagoon, which significantly reduced NH_4-N load, BOD_5 and COD due to its biologic activity. Although the production of a high quality effluent (permeate) was a significant advantage of the RO process, considering the removal of non-biodegradable components of the leachate, such as residual COD, chloride, and heavy metals, all these contaminants were present in the concentrate, which could be 10–25% of the leachate's volume [14]. In addition, all chemicals required for the effective operation of an RO plant, such as membrane cleaner and anti-scaling detergents (up to 0.3% per cubic meter of treated leachate) were also present in the concentrate [14]. Disposal of concentrate is a key factor to be addressed, and normally the concentrate is returned to the landfill or disposed of off-site. The return of concentrate to the landfill coincides with an increase of COD and NH_4^+-N concentration in the leachate as well as an increase in electrical conductivity [14].

Advanced oxidation processes (AOPs) constitute nowadays a promising technique for the removal of recalcitrant pollutants from landfill leachates, turning them into simpler and easily biodegradable compounds through the generation of powerful reactive chemical species, such as hydroxyl radicals ($^{\cdot}OH$) [15–20]. Hence, a subsequent biological oxidation step could allow getting in compliance with the discharge limits. Considering the high costs associated with energy and chemicals consumption, research has focused on the development of systems using renewable solar energy as UV photon source to promote the oxidation process [21–24].

Although solar AOPs constitute a promising technology for the treatment of recalcitrant wastewaters, few demonstration or industrial applications are available: (i) in 1993 a solar TiO_2 photocatalytic plant, with 158 m^2 of parabolic-trough concentrators collectors (PTCs) was installed at Lawrence Livermore National Laboratory for the treatment of groundwater contaminated with trichloroethylene (TCE) [25]; (ii) in 1998, 12 double-skin sheet photoreactors (DSSRs) with a total irradiated area of 27.6 m^2 and total volume of 1 m^3 were installed at Volkswagen AG factory (Wolfsburg, Germany) for the treatment of biologically pre-treated wastewaters [26–28]; (iii) in 2004 two Thin Film Fixed Bed Reactors (TFFBR), with a width of 2.5 m and a length of 10 m, corresponding to a total illuminated area of 50 m^2, oriented to the South and tilted 20°, were installed at a Tunisian textile industry (Menzel Temime) for the treatment of a biologically pre-treated textile wastewater and further combined with two bioreactors (SBR – Sequential Batch Reactors) with 15 m^3 capacity each one, used for the pre-treatment of the textile effluent [29]; (iv) in 2004 a 150 m^2 plant of compound parabolic collectors (CPCs) and total operation volume of 2.5 m^3 was installed at Albaida (Almeria, Spain) for the treatment of wastewaters contaminated with pesticides, and in 2010 the combination with a biological system based on two 1.23 m^3 immobilized biomass reactors was optimized [30]; (v) in 2007 a 100 m^2 unit of CPCs for the pre-oxidation of a saline industrial wastewater containing 600 mg/L of a recalcitrant pharmaceutical compound, α-methylphenylglycine, was installed at a pharmaceutical company, DSM DIRETIL, which was able to remove 50% of the initial dissolved organic carbon (DOC), being the remaining 45% removed in an aerobic biological treatment system [31].

Considering the application of AOPs to leachates treatment, few full-scale treatment plants have been reported in the literature, mainly using ozonation combined with biological processes. Between 1991 and 2002, 35 different plants combining biological processes and ozonation [32] were operated for the treatment of leachates, at a flow rate varying from 10,000 to 150,000 m^3/year, and COD levels between 2000 and 4000 mg/L. The Singhofen landfill leachate treatment plant (Germany) treated 29,200 m^3/year, combining a biological treatment step, consisting on a denitrification reactor followed by 3 nitrification reactors, a sedimentation tank and a sand filter, with an ozonation/UV stage and a final biological treatment step [32], producing a final effluent with 200 mg COD/L and 50 mg NH_4^+-N/L. The facility in Asbach (Germany) used the BIOQUINT® system since 1998 and treated up to 26,000 m^3/year, using a raw leachate basin (1000 m^3) followed by a biological treatment stage, with a nitrification fixed-bed biofilter (45 m^3), and two denitrification fixed-bed biofilters (2×10 m^3) and an ozonation system (4 kg O_3/h), achieving a final effluent with 200 mg COD/L, $<$ 50 mg NH_4^+-N/L, $<$ 2 NO_2^--N/L and <70 mg N_{total}/L. The landfill leachate treatment plant in Friedrichshafen (Germany) was based on an improved version of the BIOQUINT® system, where the biological treatment stage consisted on nitrification and denitrification activated sludge reactors with 100 and 25 m^3 capacity, respectively, followed by an ozonation (1.5 kg O_3/h)/biological recycle step, leading to 82% and 98% removal of COD and nitrogen, respectively [33]. Leachates from a sanitary landfill in Bord-Matin, near Saint-Etienne (France), containing 1750 mg COD/L and 850 mg NH_4^+-N/L, have been treated since 1972 by a combination of biological nitrification and denitrification processes, followed by chemical precipitation with lime in a lamellar settling tank and a final ozonation step [33].

The present work aims at developing a new strategy for the treatment of landfill leachates, after lagooning, using a solar photo-Fenton oxidation process to degrade the most recalcitrant organic compounds, leading to a biodegradability enhancement of the leachate, which may then be further oxidized in an activated sludge biological reactor. The elimination of the remaining nitrogen compounds fraction was also evaluated in the activated sludge biological reactor, under aerated and anoxic conditions, first promoting the aerobic nitrification of ammonia to nitrite/nitrate and then the anoxic denitrification of nitrate/nitrite to nitrogen gas, using methanol as external carbon source. The efficiency of the treatment strategy was evaluated in a pre-industrial plant, combining a photocatalytic reactor with 39.52 m^2 of compound parabolic collectors (CPCs) with an activated sludge reactor with 3.5 m^3 capacity, during 1-year. The efficiency of the treatment strategy was evaluated to understand the influence of the leachate composition, weather conditions and operational variables of the process (hydrogen peroxide dose necessary to reach the required COD target value, biodegradability enhancement during the photo-oxidation process, re-utilization of iron sludge in the photo-Fenton reaction, elimination of sludge resulting from the acidification process and influence of temperature/average solar