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Mature landfill leachate treatment by coagulation/flocculation combined with Fenton and solar photo-Fenton processes

Carlos Amor [a], Estefanía De Torres-Socías [b], José A. Peres [a], Manuel I. Maldonado [b], Isabel Oller [b], Sixto Malato [b], Marco S. Lucas [a,*]

[a] Centro de Química de Vila Real, Universidade de Trás-os-Montes e Alto Douro, UTAD, Quinta de Prados, 5000-801 Vila Real, Portugal
[b] Plataforma Solar de Almería (CIEMAT), Carretera de Senés, Km 4, 04200, Tabernas, Almería, Spain

HIGHLIGHTS

- Treatment of a mature landfill leachate with a BOD_5/COD ratio = 0.1.
- Combination of coagulation/flocculation and solar photo-Fenton processes.
- Coagulation/flocculation with $FeCl_3{\cdot}6H_2O$ allow remove 63% COD, 80% turbidity and 74% total polyphenols.
- Solar photo-Fenton demonstrates excellent ability to treat the remaining pollutant load of the landfill leachate.

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ABSTRACT

This work reports the treatment of a mature landfill leachate through the application of chemical-based treatment processes in order to achieve the discharge legal limits into natural water courses. Firstly, the effect of coagulation/flocculation with different chemicals was studied, evaluating the role of different initial pH and chemicals concentration. Afterwards, the efficiency of two different advanced oxidation processes for leachate remediation was assessed. Fenton and solar photo-Fenton processes were applied alone and in combination with a coagulation/flocculation pre-treatment. This physicochemical conditioning step, with 2 g L^{-1} of $FeCl_3{\cdot}6H_2O$ at pH 5, allowed removing 63% of COD, 80% of turbidity and 74% of total polyphenols. Combining the coagulation/flocculation pre-treatment with Fenton reagent, it was possible to reach 89% of COD removal in 96 h. Moreover, coagulation/flocculation combined with solar photo-Fenton revealed higher DOC (75%) reductions than single solar photo-Fenton (54%). In the combined treatment (coagulation/flocculation and solar photo-Fenton), it was reached a DOC reduction of 50% after the chemical oxidation, with 110 kJ L^{-1} of accumulated UV energy and a H_2O_2 consumption of 116 mM. Toxicity and biodegradability assays were performed to evaluate possible variations along the oxidation processes. After the combined treatment, the leachate under study presented non-toxicity but biodegradability increased.

1. Introduction

Human activities have always contributed to waste generation. This fact has not been considered as a major issue while human population has been relatively small, but became a serious problem with industrialisation and growth of urban areas [1].

Landfill waste disposal represents a key management strategy in most developed countries, mainly due to its economic advantages [2,3]. The landfill leachate generated by the decomposition of organic wastes and rainfall percolation through the waste material [4] is nowadays one of the most pressing issues surrounding the operation of sanitary landfills. The composition of leachate, a complex and high-strength wastewater, is featured by the presence of large amounts of organic matter, ammonia, heavy metals and toxic materials [5]. Several factors influence leachate's characteristics: waste age, climatic conditions, waste composition, landfill design and operational practice. The specific composition of leachates determines their relative treatability, which is evaluated as a function of landfill's age and/or by its BOD_5/COD ratio [6].

As landfill becomes older, it goes through the successive degradation stages of organic waste, ranging from an initial aerobic to a longer anaerobic decomposition period in which properties, such

* Corresponding author. Tel.: +351259350202.
E-mail address: mlucas@utad.pt (M.S. Lucas).

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as COD, BOD_5/COD ratio, ammonium nitrogen (NH_3–N) and pH, widely vary [5].

Young landfill leachate (<5 years) is usually characterized by high concentrations of biochemical oxygen demand (BOD) (4000–15,000 mg $O_2\,L^{-1}$) and COD (25,000–60,000 mg $O_2\,L^{-1}$), moderately high strength of ammonium nitrogen (500–2000 mg L^{-1}), high BOD_5/COD ratio (0.15–0.25) and pH around 4 [7]. An intermediate leachate (from 5 to 10 years) is characterized by the presence of substantial loads of recalcitrant COD, volatile fatty acids and pH > 7 [8,9]. A mature or stabilized leachate (>10 years) is featured by high molecular weight contaminants (compounds which are not easily biodegradable), high strength of ammonium nitrogen (3000–5000 mg L^{-1}), moderately high strength of COD (5000–20,000 mg L^{-1}) and a BOD_5/COD ratio lower than 0.1 [8].

When leachates from young landfills exhibit BOD/COD ratios around 0.25, they can be subjected to standard biological treatment processes [10]. However, landfills ageing make waste decomposition difficult to be biologically treated, due to the presence of toxic and/or biorecalcitrant substances. Therefore, the application of physicochemical treatment processes in older landfills is compulsory [6]. The most common physicochemical processes used for leachate remediation are coagulation/flocculation [11–13], reverse osmosis [14] activated carbon adsorption [6] and advanced oxidation processes (AOPs) [15,16].

Coagulation/flocculation is a relatively simple technique that can be successfully employed in the remediation of old landfill leachates. Selection of appropriate coagulant, determination of best experimental conditions, assessment of pH effect and investigation of optimal reagents dosage are required for performance optimization [12,17].

AOPs are considered feasible technologies for the treatment of effluents containing refractory compounds similar to leachate [3]. Fenton's oxidation and solar photo-Fenton are examples of AOPs which can degrade organic recalcitrant pollutants by the action of hydroxyl radicals ($HO^\bullet$) [18]. Hydroxyl radicals effectively mineralize refractory organic matter (OM) into more biodegradable compounds and so it could be subsequently treated by using more economic biological-based methods [19]. Fenton process uses H_2O_2 as an oxidizing agent and the reduced form of iron (Fe^{2+}) as a catalyst to generate $HO^\bullet$ in acidic conditions [20,21]. Solar photo-Fenton is based on Fenton process and the use of UV–vis radiation to improve reaction through regeneration of Fe^{2+} from Fe^{3+} produced in Fenton, as well as the generation of photoactive complexes and more hydroxyl radicals [22–24]. This process is considered as one of the most promising AOPs for recalcitrant organic compounds removal from wastewater though they involve high investment and operating costs. Using sunlight as a source of irradiation in AOPs can reduce processing costs and makes it more affordable for commercial use as a complex water treatment technology [25].

The aim of this study is to treat a mature landfill leachate trying to reach the legal limits of release in natural waters (especially COD < 150 mg $O_2\,L^{-1}$). In a first stage the leachate was submitted to a coagulation/flocculation process and subsequently the efficiency of Fenton and solar photo-Fenton techniques were evaluated, taking into account toxicity and biodegradability evolution during the oxidation processes.

2. Material and methods

2.1. Landfill leachate

Leachate under study was collected in a municipal landfill located in the north of Portugal, Vila Real. This landfill is in operation since 2000, receiving approximately 75,000 ton of household wastes per year. The landfill has a leachate recirculation system which operates mainly in the summer period (May–September). The leachate was taken directly from a collection box at the exit of the landfill cell, just before the wastewater treatment facilities (stabilization pond and coagulation/flocculation process). Due to the landfill characteristics the generated leachate can be classified as stabilized. The landfill leachate's main physicochemical characteristics are shown in Table 1.

Table 1
Characterization of landfill leachate.

Parameters	Values
pH	7.8
Turbidity (NTU)	140
COD (mg $O_2\,L^{-1}$)	5700
BOD_5 (mg $O_2\,L^{-1}$)	400
BOD_5/COD	0.07
DOC (mg C L^{-1})	2400
Total polyphenols (mg gallic acid L^{-1})	750
Total Suspended Solids (mg L^{-1})	130
Total iron (mg Fe L^{-1})	4.1
Zinc (mg $Zn^{2+}\,L^{-1}$)	0.7
Arsenic (μg $As^{2+}\,L^{-1}$)	37.0
Lead (μg $Pb^{2+}\,L^{-1}$)	28.5
Cadmium (μg $Cd^{2+}\,L^{-1}$)	1.1
Copper (μg $Cu^{2+}\,L^{-1}$)	46.9
Total chromium (mg Cr L^{-1})	2.2
Nickel (μg $Ni^{2+}\,L^{-1}$)	3.0

2.2. Chemicals

In coagulation/flocculation trials, calcium hydroxide, $Ca(OH)_2$; aluminium sulphate, $Al_2(SO_4)_3{\cdot}18H_2O$; ferrous sulphate, $FeSO_4{\cdot}7H_2O$ and ferric chloride, $FeCl_3{\cdot}6H_2O$, all purchased from Panreac, were used. Hydrogen peroxide (30% w/w), sulphuric acid and sodium hydroxide were supplied by Sigma–Aldrich. Ultra-pure distilled–deionised water was collected from a Milli-Q (Millipore Co.) system.

2.3. Analytical determinations

COD analysis was performed using Merck Spectroquant® cuvette tests (HACH Co.). Samples were pre-filtered through 0.20-μm syringe nylon filters (25 mm, Millex® GN, Millipore). Turbidity was determined in a HACH 2100N turbidimeter. Organic matter concentration and mineralisation were monitored by DOC, through direct injection of filtered samples into a Shimadzu TOC-V CSN analyser, equipped with an ASI-V autosampler and calibrated with standard solutions of potassium phthalate. BOD_5 was determined according to standard methods using an OXITOP® system. Total iron and hydrogen peroxide concentrations were monitored using a PerkinElmer UV–vis spectrophotometer lambda 25 and UNICAM 2 spectrophotometer. Colorimetric determination of total iron concentration was performed with 1,10-phenantroline (510 nm) according to ISO 6332. Hydrogen peroxide concentration was followed using titanium (IV) oxysulfate (DIN 38 402H15 method) at 410 nm. Total polyphenol content was measured by spectrophotometry at 765 nm using the Folin–Ciocalteau reagent (Merck) [26]. The total polyphenol content is expressed as mg gallic acid L^{-1}. Total and volatile suspended solids were determined according to standard methods [27].

2.4. Experimental setup

Solar photo-Fenton experiments were carried out in a CPC solar pilot plant located in Plataforma Solar de Almería (PSA), Spain (latitude 37°N, longitude 2.4°W). The pilot plant consists of a pho-