Science of the Total Environment 648 (2019) 636–668

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Landfill leachate treatment by sorption in magnetic particles: preliminary study

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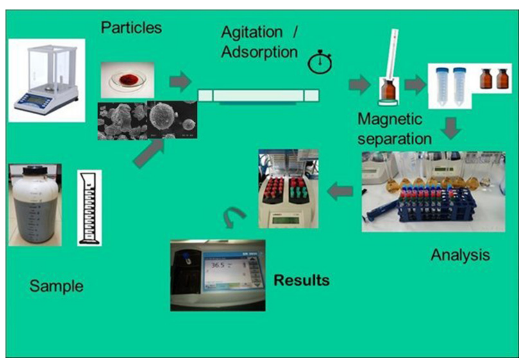
HIGHLIGHTS

- First-time Adsorption, Regeneration and Re-use of magnetic particles treating real leachates
- -9550, 3355, 6580, 1305 mg/L for COD, N_{total}, Cl, PO_4 and 43.1, 89.7, 86.6, 54.5% for NO_2, NO_3, NH_4, PO_4, have been removed
- Removal by adsorption gets worse when a pre-dilution or pre-filtration steps are applied
- The effect of the concentration on the removal efficiency depends on the contaminant.
- Applying a non-aggressive regeneration method enables the particles to be reused again

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 May 2018
Received in revised form 1 August 2018
Accepted 4 August 2018
Available online 08 August 2018

Keywords:
Sorption
Magnetic particles
Leachate
Real samples
Magnetic separation
Miex particles
Pre-filtration
Dilution
Contaminants removal

ABSTRACT

Leachates are still an open issue in environmental protection. Many of the applied methods for their treatment present low efficiency and thus need to be used collectively. In practice reverse osmosis is mostly used, as it is the most effective option, regardless of its cost. Magnetic methods to treat effluents have been used for water and wastewater treatment by the use of magnetic particles together with magnetic separation for the removal of contaminants. However, large-scale applications are few or even non-existent when we deal with complex contaminated media such as landfill leachates, for which not even research studies at laboratorial scale with real samples have been done yet. In this work, we apply for the first time magnetic sorption for the treatment of leachates, and close the full cycle by studying the regeneration and re-use of the magnetic particles; we also study the influence of the concentration of magnetic particles, the use of several pre-treatment methodologies and the type of particle used in the process, in real landfill samples from the waste treatment plant of Salamanca (Spain), for the removal of COD, NO_3^-, NO_2^-, NH_4^+, Total-N, PO_4^{3-}, SO_4^{2-} and Cl^-. Regeneration of the magnetic particles after being used in the sorption stage is also studied, as well as their efficiency regarding their re-use. It is also determined the optimum number of batches for complete desorption and for regeneration of the particles, the effect of successive regeneration and re-use cycles, the use of two different regeneration methods, the efficiency of the desorption, the effect of the quantity of solvent and the influence of the time of sorption. Due to its innovative character and the complexity of the media, this work represents a first preliminary approach and, although some promising results have been obtained, further studies are required to completely understand and evaluate the proposed treatment process.

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https://doi.org/10.1016/j.scitotenv.2018.08.056
0048-9697/

Table 1
Environmental parameters, applicable methods and used kits.

Parameter	Method	Kit type
COD	Dichromates (ISO15705)	LCK 514 100–2000 mg/L O_2
Nitrates	2,6 Dimetilphenol (EN 38405 D-2)	LCK339 0.23–13.5 mg/L NO_3^-—N
Nitrites	Diazotization (EN ISO 26777)	LCK341 0.015–0.6 mg/L NO_2^-—N
Ammonium	Indophenol Blue (ISO 7150-1, DIN 38406 E5-1, UNI 11669:2017)	LCK303 2–47 mg/L NH_4^+-N
Total nitrogen	Koroleff digestion (peroxodisulfate) and photometric detection with 2,6 dimetilphenol	LCK238 5–40 mg/L NT
Fosfates	Fosfomolibden Blue (EN ISO 6878) with digestion for total P	LCK349 ortofosfate/total fosfate 0.05–1.5 mg/L PO_4^{3-}—P
Chlorides	Iron (III)-thiocyanate with 2 measure ranges using the same kit	LCK311 1–70 mg/L Cl^- and 70–1000 mg/L Cl^-
Sulfates	Barium sulfate	LCK153 de 40–150 mg/L de SO_4^{2-}

Fig. 1. Some of the environmental analysis kits used.

1. Introduction

Modern environmental protection defends that the most important actions must be done at the beginning of the waste production cycle, by trying to reduce waste production. However, some waste always results and although there are different ways to treat it, is usually required, at some stage, the introduction of concentrated wastes in landfill cells. As is well known, water percolates through this landfill cells and generates a fluid highly concentrated in contaminants and other substances that is denominated *leachate*. During the decomposition of the waste a series of biochemical reactions take place, and can be classified in four stages (Torretta et al., 2016a, b): 1) Aerobic phase; 2) Anaerobic or acidogenic phase; 3) Methanogenic phase (unstable); 4) Stable

Table 2
Leachate sampling characteristics (examples).

Parameter	Unities	Sample 1	Sample 2	Sample 3
Total solids (TS)	mg/L	33,768	33,924	32,963
Total volatile solids (TVS)	mg/L	11,256	12,636	12,328
Suspended solids (SS)	mg/L	3067	3811	3242
pH		7.8	8.0	7.4
Conductivity	μS/cm	45.0	39.7	40.1
COD	mg O_2/L	21,400	21,500	23,300
Ammonia	mg/L	2950	2640	2920
Nitrates	mg/L	122	127	131
Nitrites	mg/L	5.3	3.3	4.9
Total nitrogen	mg/L	3250	3550	3650
Phosphates	mg/L	22.7	62.8	34.1
Sulphates	mg/L	2325	2390	2495
Chloride	mg/L	7420	7080	7240

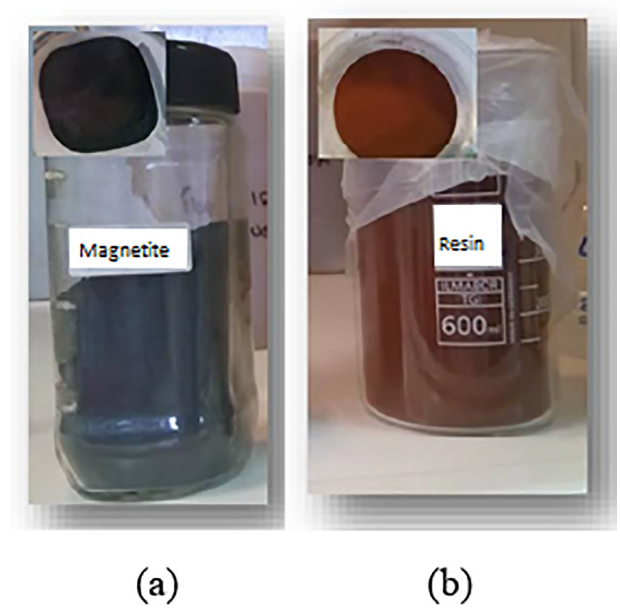

Fig. 2. Particles used: a) magnetite; b) resin covered magnetite.

methanogenic phase. Some other authors refer also a fifth phase of oxidation that puts an end to the degradation reactions of the biodegradable components of the landfill, where again micro aerobic organisms decompose remnants of CH_4 and H_2S into CO_2, water vapor and sulfur compounds (Turovskiy and Mathai, 2006). In general, leachates are composed of a high proportion of biodegradable organic matter but also other types of pollutants called refractory or persistent pollutants such as humic acid, ammonia nitrogen, organic chlorides, salts and heavy metals, which are not easily biodegradable (Kang et al., 2002; Fan et al., 2006; Wang et al., 2002). The problem lies in the diversity of pollutants and substances that leachate possesses, some of them considered dangerous, which makes it a contamination risk for water bodies if not properly controlled and managed (EU Directive 1999/31/CE). The composition of the leachate varies enormously depending on the age of the landfill. Young dumps contain a large amount of biodegradable organic matter; thus a rapid anaerobic fermentation occurs producing volatile fatty acids. For organic wastes with high moisture content, acid hydrolysis (acetogenesis) will occur, leading to the formation of compounds such as propyanates and butyrates (Wang et al., 2003). As the age of the landfill increases, the content of N-NH_3 (Renou et al., 2008) and the decomposition process of organic matter enters a phase called methanogenic, in which microorganisms convert fatty acids into methane gas (CH_4) and carbon dioxide (CO_2). A remnant of organic fraction, called refractory, is not biodegradable and is composed mainly of humic substances, straight chain hydrocarbons and other persistent substances (Renou et al., 2008). Another important characteristic of leachates is that their composition is never the same, as the leachate media continues to degrade. Therefore, slight changes of, for example, pH are sufficient to produce important modifications in leachate composition.

In general, leachate treatment techniques (Pastore et al., 2018) can be divided into three groups: 1) biological treatments (aerobic or anaerobic), 2) chemical and physical processes and 3) processes resulting from the combination of the previous treatments (Wiszniowski et al., 2006; Torretta et al., 2016a, b). As *aerobic biological treatments* we may point-out: Recycling (Diamadopoulos, 1994; Gao et al., 2015), Lagooning (Mehmood et al., 2009; Bove et al., 2015), Wetlands and phytoremediation (Kivaisi, 2001), Treatment of active sludge (Gao et al., 2015; Renou et al., 2008; Bove et al., 2015; Aluko and Sridhar, 2013; Cui et al., 2016), Rotating biological discs (Cortez et al., 2008),