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Black slag fixed bed for toluene, ethylbenzene and *p*-xylene (TEX) biodegradation and meiofauna development

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ABSTRACT

In the past, black slag from an Electric Arc Furnace was dumped or stockpiled. Nevertheless, after much controversy, slag can no longer be considered a “waste”, and bearing in mind its positive properties, reuse alternatives are being sought. In this study, a black slag was used as an alternative packing material for toluene, ethylbenzene and *p*-xylene biofiltration, with these pollutants being fed both individually and jointly. Ethylbenzene recorded the highest elimination capacity when the ternary mixture was fed. The electrical conductivity of the leaching solution showed that the slag did not contribute to ion release or dissolution. The acid neutralizing capacity of the slag played a major role in preventing bed acidification. All the biofilters were invaded by mites, and other meiofauna including nematodes and rotifers also developed in the bed. Under these conditions, CO_2 production was attributed not only to contaminant degradation but also to the metabolic processes of the meiofauna originating from the inoculum. Despite the favourable evolution of the operating parameters and the suitable performance of the slag bed, its high bulk density restricts the size of the bed. Slag is nonetheless recommended for use as a co-packing material.

1. Introduction

Growing emphasis on sustainability over the past twenty years has boosted the application of biological processes for waste gas treatment, turning them into a robust and feasible alternative for treating gas emissions with relatively low pollutant concentrations (from 1 to 1000 mg L^{-1}) at high flow rates (Lebrero et al., 2012).

Among the different biotechnologies, biofiltration is the oldest and simplest bioreactor configuration, being the most popular biological technology for purifying gas emissions derived from wastewater and solid waste treatment processes (Estrada et al., 2011). It is a two-step process involving the compounds' transition from gas phase to liquid phase, with the subsequent oxidation of the contaminants by the active microbial cultures present in the filter bed.

The biofilm is developed on a support material, which can be organic (compost, peat, etc.) or inorganic. The latter can also be divided into natural inorganic materials or entirely synthetic materials. The support media's main functions are to provide the attachment surface for the microorganisms, distribute the gas flow evenly within the bed's cross-sectional area with minimal gas-phase pressure drop, distribute any liquid nutrients sprayed onto the bed surface, and facilitate easy elimination of excessive biomass. Amongst the innovative support materials for biofilters, the use of an Electric Arc Furnace (EAF) black slag may be a sustainable alternative, as it has generally been considered “inert” due to the thermal treatment that generates it.

In the past, slag was regarded as a waste material and, accordingly, it was dumped or stockpiled. Nevertheless, after much controversy, slag can no longer be considered a “waste”, but rather an “intentionally generated by-product” that helps to conserve natural resources and minimize emissions (Gurtubay et al., 2014). Despite its classification, around 20 million tonnes of this by-product are

Abbreviations: BTEX, benzene, toluene, ethylbenzene and xylene isomers; BSF, Blast furnace slag; CO_2, carbon dioxide; E, ethylbenzene; EAF, electric arc furnace; EBRT, empty bed residence time; EC, elimination capacity; IC, inlet concentration; IL, inlet load; PCO_2, carbon dioxide production rate; SBI, sludge biotic index; SEM, scanning electron microscope; T, toluene; TEX, toluene, ethylbenzene and *p*-xylene; WHC, water holding capacity; X, *p*-xylene.

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expected to be generated per year in Europe, and its efficient reuse becomes a major logistical, financial and environmental issue (Pellegrino et al., 2013). In fact, to date this material can be acquired at a very low price or even free of charge.

Thus, steel slag has been used as a secondary material in concrete production, soil amendment and civil construction. Blast furnace slag (BFS) has been used as filter media in low-rate and intermediate-rate trickling filters for secondary wastewater treatment unit processes. Other several value-added reuse alternatives have been proposed over the past few years, including CO_2 sequestration by slag carbonation or bioleaching as neutralizing agent (Gahan et al., 2009; Gurtubay et al., 2014). Additionally, EAF black slag has been proposed as an alternative packing material for biofilters (Rojo et al., 2015). Chou and Wu (1999) have used a biotrickling filter packed with blast-furnace slag to treat toluene in an air stream, recording a removal efficiency of 90% for an empty bed residence time (EBRT) of 18 s and an inlet load (IL) of around 30 g m^{-3} h^{-1}. Brandt et al. (2016) have considered the use of novel low-cost packing media based on a mixture of organic residues and sieved BFS slag from a local steel industry.

Toluene, ethylbenzene and *p*-xylene were selected to study the behaviour of the slag as packing material in a biofilter and to investigate their interactions on biodegradation performance in the slag biofilter. These petroleum derivatives are monoaromatic compounds with toxic characteristics and high mobility in the environment (either in gaseous, liquid or solid phase). Additionally, when they are mixed with benzene, the widely known BTEX compounds could represent as high as 80% of the total VOC emitted in a petrochemical plant (Fatehifar et al., 2008).

Although traditional biofilters use bacteria as biocatalyst, a number of recent studies indicate that fungi may favour the treatment of hydrophobic organic compounds (Cheng et al., 2016). Cheng et al. (2016) have compared fungal and/or bacterial biofilters in treating toluene, and have found that the combination of bacteria and fungi was the best option, leading to more stable removal and performance. Nevertheless, when activated sludge is used as an inoculum, a variety of additional predator species grow and develop on the packing surface, regardless of the support nature. Ideally, predation should balance bacterial/fungal production in order to obtain a stable biofilter performance (Yang et al., 2010). Furthermore, those predators (meiofauna) facilitate the mineralization of organic matter, enhance nutrient regeneration, and serve as food for a variety of higher trophic levels (Louati et al., 2013). Although many factors influence the proliferation of meiofauna, they are favoured by high organic matter content, room temperature, and high moisture content, which are precisely the optimal operating parameters in organic biofilters.

This paper focuses on the assessment of an EAF black slag as an alternative packing material in biofilters biodegrading simple aromatic compounds. The contaminants were fed both individually and jointly in order to establish possible interactions among them. An unintentional invasion of meiofauna occurred during operation, and so a second objective was to identify the species involved.

2. Material and methods

2.1. Packing material description

The inorganic packing material used in this study was an EAF black slag. Samples were taken from the storage piles at the Nervacero steelworks in Portugalete (Bizkaia, Spain). The freshly produced EAF black slag was stockpiled in the factory according to particle size (from smaller than 5 mm to bigger than 110 mm). Two-month-old slag with a particle size ranging from 5 to 6 mm was selected for this study. The elemental composition (expressed as major oxides in wt %) of the EAF slag is as follows: FeO 33.16; CaO 22.83; SiO_2 12.56; Al_2O_3 7.66; MgO 7.32; MnO 6.07; Cr_2O_3 2.00; TiO_2 0.55; P_2O_5 0.24; S 0.09 (Gurtubay et al., 2014).

The main properties of the EAF slag are shown in Table 1. The slag's water holding capacity (WHC) and retentivity were determined, as water availability is a key parameter for biomass growth (to keep the optimal activity of the immobilized microorganisms). The water slag was dried at 105 °C for 24 h and then immersed in water for 6 h. Finally, the slag was dried at 25 °C for 24 h to determine the water holding capacity (Kwon and Yeom, 2009). Water retentivity expresses how easily water is retained in the packing material regardless of the amount of water retained, and it involves measuring the rate at which the materials dry as air (with a relative humidity lower than 10%) passes through the slag at an EBRT of 60 s (Dorado et al., 2010). The BET surface area and external surface area were measured by means of the nitrogen adsorption technique with an ASAP 2010 V5.02H analyzer (Micromeritics, Georgia, USA).

Prior to packing and inoculating, the EAF black slag was sterilized in an ORTO-ALRESA 22L autoclave at 120 °C for 30 min (two cycles).

2.2. Biofilter and experimental conditions

Four laboratory-scale biofilters with an effective volume of 3.0 L were set up to treat an air flow contaminated with toluene (T), ethylbenzene (E), *p*-xylene (X) and mixed TEX, respectively. The biofiltration system was assembled with two consecutive PVC modules with an internal diameter of 0.10 m and an overall packing height of 0.4 m. Down-flow mode was selected.

The inlet flow was generated by mixing a contaminant-saturated air stream (non-humidified stream) and a water-saturated air stream. The non-humidified fraction of air used for contaminant saturation was a minor fraction of the whole influent air flow, and did not significantly alter the moisture content of the contaminated air stream entering the biofilter. Thus, the relative humidity of the contaminated air at the biofilter inlet remained above 99%. Asepsis conditions were ensured in each bioreactor's inlet flow, as air was filtered through a 0.22 μm nitrocellulose membrane-filter (GSWP Millipore - Bedford, Massachusetts, USA) mounted in a 47 mm in-line polypropylene filter holder.

The biofilter was equipped with several gas sampling valves to monitor inlet and outlet contaminant concentrations. It was additionally fitted with several ports located along the two PVC modules for measuring the relative humidity of the inlet air stream. These ports were also used for sampling the packing material in order to measure the moisture content in the bed throughout experimentation. During operation, room temperature varied between 18 and 26 °C. This temperature range has not significant influence on overall process performance (Clark et al., 2004; Lebrero et al., 2010).

Table 1
Physicochemical characteristics of the EAF slag.

Property	Value
Equivalent diameter (mm)	7.49
Bulk density (g mL^{-1})	2.97
Water holding capacity (g kg^{-1})	1.10
Water retentivity (% h^{-1})	−1.20
Acid neutralizing capacity (mmol H^+ g^{-1})[a]	3.30
BET surface area (m^2 g^{-1})	1.38
Langmuir surface area (m^2 g^{-1})	1.70
Micropore area (m^2 g^{-1})	0.157
Micropore volume (cm^3 g^{-1})	6.90 10^{-5}

[a] Gurtubay et al. (2014).

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