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Steel slag filters to upgrade phosphorus removal in small wastewater treatment plants: Removal mechanisms and performance

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ABSTRACT

Electric arc furnace steel slag (EAF-slag) and basic oxygen furnace steel slag (BOF-slag) were used as filter substrate in horizontal subsurface flow laboratory-scale filters designed to remove phosphorus (P) from a synthetic solution (~10 mg P/L). The main objective of this study was to evaluate the influence of various parameters, including slag type, slag size, and slag composition, on P removal performance. Also, a series of chemical and mineralogical analyses was performed to determine the mechanisms of P removal achieved by steel slag in the filters. Over a period of 52 weeks of filter operation, small-size EAF-slag (5–16 mm) and small-size BOF-slag (6–12 mm) removed 98% and >99% of the inlet total phosphorus (TP), whereas big-size EAF-slag (20–40 mm) and big-size BOF-slag (20–50 mm) removed 88% and 95% of the influent TP, respectively. The main mechanism of P removal was related to CaO dissolution from slag followed by Ca phosphate precipitation and accumulation of the precipitates into the filters. P removal performance improved with increasing the CaO-slag content and with decreasing slag size, most probably because the specific surface available for CaO dissolution was increased. Also, the experimental results suggested that small-size slag was more efficient than big-size slag for the self-filtration of P precipitates. Chemical and mineralogical analyses indicated that, after precipitation, Ca phosphates may crystallise into the most stable form of hydroxyapatite.

1. Introduction

Although phosphorus (P) represents an essential nutrient for biomass growth in several ecosystems, an excessive intake of P in water bodies such as rivers, lakes or lagoons, causes an abnormal growth of algae and aquatic plants resulting in the degradation of the water quality. Consequently, legislation on P rejects for municipal wastewater treatment plants (WWTPs) is becoming stricter in Europe (European Union Directives 91/271/EEC and 2000/60/EC), and research on low cost techniques to upgrade P removal in WWTPs has gained a growing attention. Several international studies have demonstrated that the addition of separate filter units containing reactive materials with high affinities for P binding is a suitable technique to upgrade P removal in small WWTPs such as stabilisation ponds and constructed wetlands (Vohla et al., 2011). In the last two decades a wide variety of potential filter substrates, including natural materials, man-made products and industrial co-products, have been tested in laboratory-scale experiments which aimed to determine their P removal performance and retention capacities (Johansson-Westholm, 2006). In fact, the P retention capacity is an important parameter to compare and select potential materials to be used in filter systems (Drizo et al., 2002).

Among the materials tested, steel slag has shown a high affinity for P binding. This suggested an interesting potential market for its use as filter substrate to treat wastewater (Chazarenc et al., 2008). The steel industry produces mostly two types of slag: (i) basic oxygen furnace slag (BOF-slag), which originates from the

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further refining of iron in a basic oxygen furnace; and (ii) electric arc furnace slag (EAF-slag), which is derived from melting recycled scrap in an electric arc furnace. Steel slag is primarily made of iron (Fe) and calcium (Ca) minerals: Fe derives from the raw minerals used to produce steel, whereas Ca derives from the use of fluxing agents (mainly lime) during the steelmaking process (Motz and Geiseler, 2001).

Many laboratory-scale studies have demonstrated that steel slag is a suitable reactive material for efficient P removal from wastewater (e.g. Drizo et al., 2002; 2006; Chazarenc et al., 2007; Bowden et al., 2009; Claveau-Mallet et al., 2012). The main mechanisms of P removal on steel slag were related to CaO dissolution from slag followed by Ca phosphate precipitation, and to phosphate adsorption onto metal hydroxides (Chazarenc et al., 2008). However, the large differences in experimental conditions, such as slag size, inlet P concentration, filter volume, hydraulic retention time, and loading mode, lead to difficulties in comparing the results of the different studies (Johansson-Westholm, 2006), and further experiments are needed to define the effect of various operating parameters, including slag type, slag size and slag composition, on P removal performance.

Within the framework of the European research project "SLASORB" (Slag as sorbent for P removal from wastewater, Research Fund for Coal and Steel (RFCS)), our study aimed to evaluate the P removal performances of EAF-slag and BOF-slag produced in Europe and to determine their P removal mechanisms. A set of six laboratory-scale filters (42 or 84 L of volume each) were filled with EAF-slag and BOF-slag in different grain-sizes.

The originality and importance of this paper are highlighted by the following two points:

(i) A comparative study on P removal performance. All the filters were operated according to the same experimental condition: room temperature, influent synthetic P solution of about 10 mg P/L, continuous horizontal subsurface flow, and void hydraulic retention time of 24 h. This enabled the results of the different filters to be compared to evaluate the influence of slag type, slag size, and slag composition on P removal performance;
(ii) An in-depth critical investigation of the P removal mechanisms. Various chemical and mineralogical analyses, including X-ray fluorescence (XRF), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD), and wet chemical extractions were employed to investigate the mechanisms of P removal achieved by steel slag in the filters. Indeed, the knowledge and understanding of the reactions leading to P removal on steel slag is of great importance in order to determine the environmental impact and improve the filter system design.

2. Materials and methods

2.1. Slag selection and preparation

Two types of steel slag were tested in this study: (i) EAF-slag from the production site of Esch Belval (Luxemburg) and (ii) BOF-slag from the production site of Fos-sur-Mer (France). These slag samples were selected by comparative batch experiments which were performed to determine the P retention capacities of several samples of slag produced in Europe (Barca et al., 2012). The samples of steel slag used in this study were fresh of production (produced less than 6 months before their use in the filters). Two different sizes of slag were tested: (i) small-size slag (5–16 mm for EAF-slag, 6–12 mm for BOF-slag), and (ii) big-size slag (20–40 mm for EAF-slag, 20–50 mm for BOF-slag). These granular sizes were considered large enough to prevent filter clogging, as found in a previous study (Chazarenc et al., 2007). The bulk density of EAF-slag was about 1.8 g/cm^3 whereas the bulk density of BOF-slag was about 1.6 g/cm^3.

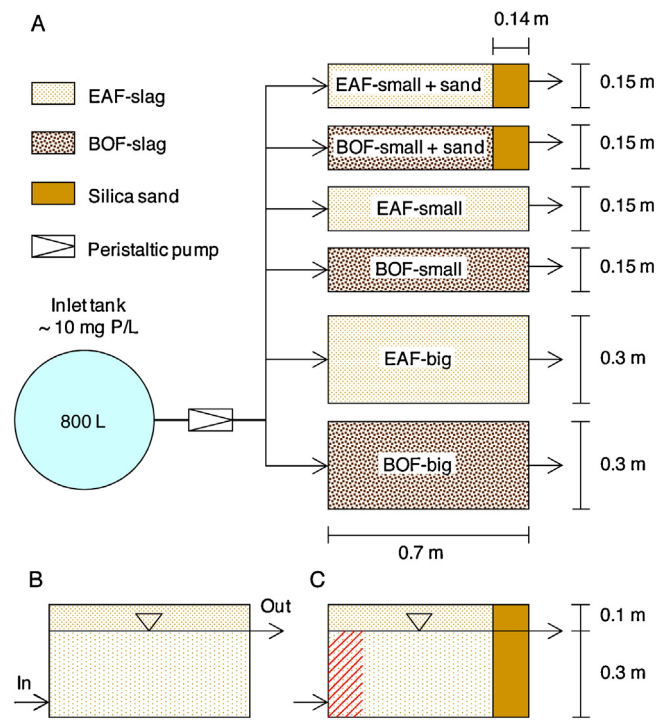

Fig. 1. Experimental setup: (A) top view of the filters; (B) cross section view of the filters filled only with slag; (C) cross section view of the filters EAF-small + sand and BOF-small + sand: the dashed area shows the slag used for chemical and mineralogical investigations.

2.2. Experimental setup

Six filters were designed in two different sizes: (i) four small-size filters (about 42 L of total volume each), and (ii) two big-size filters (about 84 L of total volume each). Fig. 1 shows the geometric dimensions of the filters.

The design of the filters was adapted from a previous study that investigated the effect of different sizes of slag on the hydraulic performances (Anjab, 2009). The ratio of width to length was <0.5 for all the filters, in order to favour dissipation of initial turbulence as shown by Alcocer et al. (2012).

Also, the ratio of width of the filter to size of slag was always >10, in order to improve hydraulic performances and limit wall effects (Zeiser et al., 2001). The big-size filters were filled one with EAF-slag size 20–40 mm (filter EAF-big), and one with BOF-slag size 20–50 mm (filter BOF-big). Two small-size filters were filled one with EAF-slag size 5–16 mm (filter EAF-small), and one with BOF-slag size 6–12 mm (filter BOF-small). The remaining two small-size filters were filled one with EAF-slag size 5–16 mm, and one with BOF-slag size 6–12 mm as above, but with the addition of a vertical layer of silica sand (size 1–2.5 mm) replacing 20% of slag volume before the outlet (filters EAF-small + sand and BOF-small + sand, respectively) (Fig. 1). This was done to evaluate the effect of the sand layer on the filtration of P particulates.

During the full period of operation, the filters were continuously fed with a synthetic P solution of about 10 mg P/L (tap water + KH_2PO_4), which is into the range of the typical P concentrations of municipal wastewaters (4–16 mg P/L, according to Tchobanoglous et al., 2003). The average pH value, Ca concentration