



# Basic Oxygen Furnace steel slag aggregates for phosphorus treatment. Evaluation of its potential use as a substrate in constructed wetlands



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## ARTICLE INFO

### Article history:

Received 29 July 2015

Received in revised form

4 November 2015

Accepted 27 November 2015

Available online 2 December 2015

### Keywords:

Phosphorus

Steel slag

Batch experiment

Column experiment

Constructed wetland

## ABSTRACT

Basic Oxygen Furnace (BOF) steel slag aggregates from NW Spain were tested in batch and column experiments to evaluate its potential use as a substrate in constructed wetlands (CWs). The objectives of this study were to identify the main P removal mechanisms of BOF steel slag and determine its P removal capacity. Also, the results were used to discuss the suitability of this material as a substrate to be used in CWs.

Batch experiments with BOF slag aggregates and increasing initial phosphate concentrations showed phosphate removal efficiencies between 84 and 99% and phosphate removal capacities from 0.12 to 8.78 mg P/g slag. A continuous flow column experiment filled with BOF slag aggregates receiving an influent synthetic solution of 15 mg P/L during 213 days showed a removal efficiency greater than 99% and a phosphate removal capacity of 3.1 mg P/g slag. In both experiments the main P removal mechanism was found to be calcium phosphate precipitation which depends on  $\text{Ca}^{2+}$  and  $\text{OH}^-$  release from the BOF steel slag after dissolution of  $\text{Ca}(\text{OH})_2$  in water.

P saturation of slag was reached within the upper sections of the column which showed phosphate removal capacities between 1.7 and 2.5 mg P/g slag. Once  $\text{Ca}(\text{OH})_2$  was completely dissolved in these column sections, removal efficiencies declined gradually from 99% until reaching stable outlet concentrations with P removal efficiencies around 7% which depended on influent  $\text{Ca}^{2+}$  for limited continuous calcium phosphate precipitation.

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## 1. Introduction

Phosphorus (P) removal in constructed wetlands (CW) occurs through a combination of several processes: peat/soil accretion, plant uptake, microbial growth, substrate adsorption and chemical precipitation (Vymazal, 2007). Among these, adsorption and chemical precipitation play the largest role, particularly in saturated subsurface flow CWs where the contact between wastewater and substrate is enhanced (Babatunde et al., 2009; Vymazal, 2005). Sand, gravel and soils have been traditionally used as filter materials in CWs with limited results in terms of P removal (Vohla et al.,

2011).

For more than two decades research has been directed to selection of alternative materials (Drizo et al., 1999; Yamada et al., 1986). Long-term P removal depends on the physico-chemical characteristics of the material such as Al, Fe and Ca content; specific surface area; porosity; particle size distribution; and hydraulic conductivity because they all affect the P retention capacity (Barca et al., 2012; Drizo et al., 2002; Reddy et al., 1980); whereas its suitability as a substrate is site specific, and depends on its recycling potential, cost and local availability (Drizo et al., 1999). A large number of studies have been conducted on a wide variety of materials for potential use as substrates in CWs or in other small-scale filter systems, including natural materials (minerals, rocks, soils and marine sediments), industrial by-products (from the steel, mining and power plant industry), and man-made products (light-weight aggregates) (Johansson, 2006).

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Among them, slag materials from the steel industry demonstrate promising properties with regard to P sorption capacity (Barca, 2013; Bowden et al., 2009; Drizo et al., 2002; Johansson, 1999; Shilton et al., 2006). In Europe there are three main types of steel industry slag, each named after the process involved in their production: Blast Furnace (BF) iron slag, Basic Oxygen Furnace (BOF) steel slag and Electric Arc Furnace (EAF) steel slag. BF slags are the by-products of iron production, while BOF and EAF slags are by-products of steel production (Proctor et al., 2000). Many studies have been conducted to investigate the potential of slag materials to remove P from wastewater (Bowden et al., 2009; Claveau-Mallet et al., 2013; Drizo et al., 2002, 2006; Xue et al., 2009). Variation of results may be attributed to differences in experimental conditions, physical and chemical compositions of materials, which may vary depending on the ore resource, the process temperature, the factory or even the batch test conditions (Drizo et al., 2002; Xie et al., 2012). However, when comparing steel production slags under the same experimental procedures, BOF slags show greater phosphate removal capacities than EAF slags (Barca et al., 2012).

Batch experiments are commonly used to compare P sorption efficiency of different materials due to their simplicity and short time requirements. However, batch experimental parameters are arbitrarily set, and the results are often non-comparable and misleading (Cucarella and Renman, 2009). Moreover, the use of isotherm equations can lead to biased and unrealistic estimates of the adsorption parameters if the experimental data obtained from the batch experiments is intended to be used for the estimation of P retention capacities in field scale applications. As a result, while batch experiments can be useful to compare the P retention capacities of different materials, such tests should be coupled with longer-term column experiments, with similar hydraulic conditions to those present in CWs, for the estimation of longevity, P removal efficiencies and retention capacities of steel slag filters to be used in CWs (Drizo et al., 2002).

In this study a locally available BOF slag in NW Spain was submitted to batch and column experiments in order to: (i) determine its P removal capacity, (ii) identify the main P removal mechanisms, and (iii) evaluate its suitability to be used in constructed wetlands.

## 2. Materials and methods

### 2.1. BOF slag characterization

The BOF slag tested in this study was collected from the ArcelorMittal steel factory LD-II located in Veriña de Abajo, Gijón, NW Spain. Particle-size distributions were determined using dry-sieving techniques (European Norm EN, 933-1:1997) to calculate  $d_{10}$ ,  $d_{60}$  (mesh diameter allowing, respectively, 10 or 60% of the material mass to pass through) and uniformity coefficient ( $UC = d_{60}/d_{10}$ ). Porosity was determined from the amount of water needed to saturate a known volume of component, and density was measured by the volume of water displaced by a known mass of medium. The specific area of particles was evaluated from the size distribution, assuming grains to be spherical.

A representative BOF slag sample (Spanish norm UNE-EN 932-2:1999) was crushed for its chemical and mineralogical characterization. Inductively Coupled Plasma Atomic Emission Spectroscopy was used to determine the content of major elements (Ca, Fe, Mg, Al and P) using an Optima 8300 Perkin–Elmer spectrometer. The following sample digestion procedure was selected after confirming a complete digestion of the sample: 0.5 g of sample were acid digested with a mixture of 10 mL of HNO<sub>3</sub> 65% and 3 mL of HCl 35%, with a reflux system under atmospheric pressure. The following digestion steps were used: temperature increase to 45 °C in 30 min, stable temperature at 45 °C for 1 min, temperature increase to 65 °C

in 25 min, stable temperature at 65 °C for 5 min, temperature increase to 100 °C in 15 min, and stable temperature at 100 °C for 120 min.

X-ray diffraction (XRD) was used to study the mineralogical composition of the representative BOF slag sample. XRD data were recorded at ambient temperature on a Bruker D8 Advance powder diffractometer, in the angular range 5–70° (2θ), collected with a step of 0.02° and a step time of 8 s.

Before and after column experiments larger BOF slag particles were gold coated (Balzers SCD 004) prior to observation using a JSM-6480 LV JEOL scanning electron microscope (SEM). The surface composition of the BOF slag particles before and after column experiments was assessed on carbon coated BOF slag particles with an EDX microanalysis instrument (Energy Dispersive X-ray System) coupled to the SEM.

### 2.2. Kinetic batch experiments

Initial PO<sub>4</sub>-P concentration of 30 mg/L similar to concentrations present in dairy parlors were prepared in 500 mL Erlenmeyer flasks using KH<sub>2</sub>PO<sub>4</sub> in distilled water, and adjusted to pH 7 using NaOH before each test. Then, 20 g of slag were added to each flask, leading to a slag to solution mass ratio of 1:25 (adapted from Nair et al. (1984)). Flasks were covered and kinetic batch experiments were carried out with three replicates on an orbital shaker at 120 rpm under controlled temperature conditions (25 °C). A slag granular size of <10 mm was used to perform the batch experiments since it has been suggested that sieving of unsorted fines would not be necessary to increase reactivity and efficacy in full-scale treatment systems (Bowden et al., 2009). Solutions were measured for pH, P and Ca<sup>2+</sup> concentrations at 0.5, 1, 2, 3.5, 5, 10, 24 and 48 h.

Potential Ca<sup>2+</sup> release capacity was calculated as:

$$Q_t = \frac{Ca^t V^t}{M} \quad (1)$$

where  $Q_t$  is the potential Ca<sup>2+</sup> release capacity at time  $t$  (mg/g),  $V^t$  is the volume of the solution at time  $t$  (L),  $M$  is the mass of slag (g), and  $Ca^t$  is the Ca<sup>2+</sup> concentration of the solution at time  $t$  (mg/L).

Then, the potential Ca<sup>2+</sup> release capacity was plotted according to the pseudo-first order kinetic equation of Lagergren (1898):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (2)$$

where  $Q_e$  is the potential Ca<sup>2+</sup> release capacity at equilibrium (mg/g),  $Q_t$  is the potential Ca<sup>2+</sup> release capacity at time  $t$  (mg/g),  $t$  is the time (h) and  $k_1$  is the rate constant of pseudo-first order release (1/h).

If pseudo-first order kinetics are applicable, this suggests that one of the reactants is present in great excess over the other reactants in the reaction mixture.  $Q_e$  must be known to exploit equation (2) with experimental data.  $Q_e$  was considered an adjustable parameter whose value was estimated by trial and error. The experimental potential Ca<sup>2+</sup> release capacities observed after 48 h were used as initial  $Q_e$ -trial in order to calculate  $Q_e$  from the intercept of the plot of  $\ln(Q_e\text{-trial} - Q_t)$  against  $t$ . Then the  $Q_e$ -trial was adjusted until the difference between  $Q_e$ -trial and  $Q_e$  was less than 0.1% of the value of  $Q_e$ -trial.

The relationship between Ca<sup>2+</sup> and OH<sup>-</sup> was evaluated through linear regression analysis.

### 2.3. Isotherm batch experiments

Isotherm batch experiments tested a broad range of initial PO<sub>4</sub>-P concentrations (5, 10, 25, 50, 100, 200, 300 and 400 mg/L). Initial P

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