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Phosphate removal from synthetic and real wastewater using steel slags produced in Europe

Cristian Barca [a,b,*], Claire Gérente [a], Daniel Meyer [a,b], Florent Chazarenc [a], Yves Andrès [a]

[a] L'UNAM Université, École des Mines de Nantes, CNRS, GEPEA, UMR 6144, 4 rue Alfred Kastler, B.P. 20722, F-44307 Nantes Cedex 3, France

[b] Epur Nature SAS, ZAC des Balarucs, 153 Avenue Maréchal Leclerc, 84510 Caumont sur Durance, France

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ABSTRACT

Electric arc furnace steel slags (EAF-slags) and basic oxygen furnace steel slags (BOF-slags) were used to remove phosphate from synthetic solutions and real wastewater. The main objective of this study was to establish an overview of the phosphate removal capacities of steel slags produced in Europe. The influences of parameters, including pH, and initial phosphate and calcium concentrations, on phosphate removal were studied in a series of batch experiments. Phosphate removal mechanisms were also investigated via an in-depth study. The maximum capacities of phosphate removal from synthetic solutions ranged from 0.13 to 0.28 mg P/g using EAF-slags and from 1.14 to 2.49 mg P/g using BOF-slags. Phosphate removal occurred predominantly via the precipitation of Ca-phosphate complexes (most probably hydroxyapatite) according to two consecutive reactive phases: first, dissolution of CaO-slag produced an increase in Ca^{2+} and OH^- ion concentrations; then the Ca^{2+} and OH^- ions reacted with the phosphates to form hydroxyapatite. It was found that the release of Ca^{2+} from slag was not always enough to enable hydroxyapatite precipitation. However, our results indicated that the Ca^{2+} content of wastewater represented a further source of Ca^{2+} ions that were available for hydroxyapatite precipitation, thus leading to an increase in phosphate removal efficiencies.

1. Introduction

Phosphorus (P) is an essential nutrient for biomass growth. However, 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. Therefore, legislation on P disposal into the surrounding environment is becoming stricter worldwide, including for small wastewater treatment plants (WWTPs). One appropriate technology for improving P removal in small WWTPs is filtration through materials with high affinities for P binding. Since common filter substrates (such as sand and gravel) have limited P removal capacities, research on alternative materials has become a priority. In the last two decades, a large number of potential substrates, including natural materials (rocks, soils and sediments), industrial by-products (steel slag, burnt oil shale and fly ash) and man-made products (light-weight aggregates specifically produced for P removal), have been tested (Vohla et al., 2011). Most of these materials have a high content of Ca, Al, and/or Fe, which are elements with a strong affinity for P binding (Johansson-Westholm, 2006). Batch experiments are commonly performed to evaluate the phosphate removal capacity (PRC) of a potential filter material. In fact, PRC is an important

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* *Corresponding author*. L'UNAM Université, École des Mines de Nantes, CNRS, GEPEA, UMR 6144, 4 Rue Alfred Kastler, B.P. 20722, F-44307 Nantes Cedex 3, France. Tel.: +33 2 51 85 82 53; fax: +33 2 51 85 82 99.
E-mail address: cristian.barca@mines-nantes.fr (C. Barca).

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parameter when comparing and selecting candidate materials to be used as filter media (Drizo et al., 2002). Cucarella and Renman (2009) reviewed a large number of relevant studies that used batch experiments to determine the PRCs of potential filter materials. They observed that there is not a standard procedure for batch experiments and PRCs varied by several orders of magnitude depending on the experimental batch parameters that were arbitrarily established, thus leading to difficulties in comparing the results. The main parameters affecting the results of batch experiments are the size and form of the material, the ratio of material to solution, contact time, agitation mode, temperature, pH and initial phosphate (PO_4–P) concentrations (Cucarella and Renman, 2009).

Since the 1980s, the affinity of steel slag for P binding has been studied with the aim of using a by-product of the steel industry to treat wastewater (first study by Yamada et al., 1986). According to EUROSLAG statistics, more than 16 million tons of steel slag was produced in Europe in 2006: about 80% was used in several fields of application (cement production, road construction) and 10% was recycled internally. However, about 10% was still disposed of in specialised landfill sites. This suggests an interesting potential market for wastewater treatment. The steel industry produces mostly two types of slag derived from two different steelmaking processes: BOF-slag, which originates from the further refining of iron in a basic oxygen furnace, and EAF-slag, which is derived from melting recycled scrap in an electric arc furnace (Proctor et al., 2000). Steel slag is primarily made of iron (Fe) and calcium oxide (CaO), as a result of the use of fluxing agents (mainly lime) during the steelmaking process (Motz and Geiseler, 2001). Several international studies have demonstrated that steel slag is a suitable substrate for PO_4–P removal from wastewater via Ca–P precipitation mechanisms (Drizo et al., 2006; Kim et al., 2006a, 2006b; Bowden et al., 2009). PRCs reported from batch experiments range from less than 1 to up to 80 mg P/g (Drizo et al., 2002; Jha et al., 2008; Xiong et al., 2008; Xue et al., 2009; Bowden et al., 2009). However, the large discrepancy in experimental batch parameters leads to difficulties in comparing the results of different studies (Chazarenc et al., 2008).

Within the framework of a European research project (Research Fund for Coal and Steel (RFCS) research programme under grant agreement n° RFSP-CT-2009-00028 (SLASORB)), our study aimed to evaluate the potential use of steel slag produced in Europe as a reactive medium to treat wastewater.

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

(i) The first large-scale investigation in Europe of the PRCs of steel slag: the same experimental procedures were followed to investigate a selection of samples representative of the European steel slag market. This enabled the results of different experiments to be compared to select the most suitable samples for P removal.
(ii) An in-depth critical investigation of the PO_4–P removal mechanisms: only a few studies in the literature have tried to explain thoroughly the sequence of reactions leading to PO_4–P removal using steel slag (Kim et al., 2006a, 2006b), and many details are still unclear. Our work presents an in-depth study of the main parameters influencing PO_4–P removal. First, the kinetics of Ca^{2+} and OH^- release from slag were studied applying a pseudo-first order model. Then, the influences of pH, Ca^{2+} and initial PO_4–P concentrations on PO_4–P removal were studied in a series of batch experiments of PO_4–P removal from synthetic solutions. Finally, experiments on PO_4–P removal from real wastewater were performed to verify the behaviour of slag when it is used to treat real wastewater.

2. Materials and methods

2.1. *Slag collection and preparation*

The samples of EAF and BOF steel slag tested in this study were collected from 10 production sites throughout Spain, France, Luxembourg and Germany. Since chemical, mineralogical and technical properties of EAF and BOF-slags produced in Europe are generally comparable and independent of their producer (Motz and Geiseler, 2001), we assumed that a sampling of 10 different sites (5 EAF, 5 BOF) was enough to establish an overview of PRCs of European steel slags. The samples were screened on an automatic grinder according to three ranges of granular size (<5, 5–10 and >10 mm). The granular size of 5–10 mm was selected to perform the batch experiments. This enables the results to be compared with the size of field scale filters. Before the experiments, the samples were washed first with tap water to remove fine particles and then dried at 105 °C for 24 h. Energy dispersive X-ray fluorescence analyses (EDX) were performed to determine the semi-quantitative chemical composition of the slag samples (Rayny series EDX-800HS spectrometer, Shimadzu Corporation, Kyoto, Japan).

2.2. *Kinetic experiments on Ca^{2+} and OH^- release*

The kinetics of Ca^{2+} and OH^- release from slag were investigated in a series of batch experiments (adapted from ASTM 4646-87, 1993). The aim of these was to demonstrate that the increase in Ca^{2+} and pH of the solutions depended primarily on CaO-slag dissolution. For each experiment, 40 g of slag was immersed in 1 L of deionised water (conductivity <0.1 μS/cm) contained in a glass bottle, thus leading to a slag to solution ratio of 0.04 g/mL (adapted from Nair et al., 1984). The bottle was placed on an agitation table and shaken at 125 rpm under controlled temperature conditions (20 °C). Samples of solution were taken after 1, 2, 3, 4 and 7 days of agitation. The pH values and total Ca^{2+} concentrations of the samples were measured. The samples were acidified (pH 2–3, using 1 M HCl) to measure the total Ca^{2+} concentrations. The pH values of the solutions were expressed in OH^- concentrations (mg OH/L). The experimental capacities of Ca^{2+} and OH^- release from slag were calculated using equations (1) and (2), where Q_t are the capacities of Ca^{2+} and OH^- release at time t (mg/g), V is the volume of the solution (L), M is the mass of slag (g) and Ca^t and OH^t are the total Ca^{2+} and OH^- concentrations of the solutions at time t (mg/L).

$$Q_t = \frac{Ca^t V}{M} \tag{1}$$