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# Enhanced phosphorus removal in a waste stabilization pond system with blast furnace slag filters

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#### ABSTRACT

In this work a tertiary horizontal-flow blast furnace slag (BFS) filter was tested for phosphorus removal under laboratory and field conditions. Laboratory experiments were conducted in a benchscale BFS filter for phosphorus adsorption capacity at equilibrium conditions using P-spiked water. On-site, the performance of a pilot-scale BFS filter was monitored for phosphorus removal from the final effluent of a pilot-scale WSP system located in Esholt (Bradford, UK), which comprises a primary facultative pond and a secondary aerated rock filter (ARF) in series. Adsorption capacity (*q*) results showed that BFS has high affinity for inorganic P species and it can remove up to 30 g P/kg BFS; however, *q* values are strongly dependent on the initial P concentration. The pilot-scale BFS filter tested on-site performed better for longer (<2 mg P/L) than the laboratory-scale filter, even though despite the latter received the same hydraulic and P loadings (1.8 m<sup>3</sup>/m<sup>3</sup> d and 18 g P/m<sup>3</sup> d, respectively). Both the laboratory and field results showed that BFS filters are an appropriate low-cost technology to upgrading small wastewater treatment systems for phosphorus removal.

*Keywords:* Blast furnace slag filter; Domestic wastewater treatment; Phosphorus removal; Waste stabilization ponds

## 1. Introduction

Phosphorus pollution in aquatic environments can be attributed to three major sources: industry, agriculture and wastewater treatment works. The use of phosphates in food processing, detergents and agriculture has resulted in the depletion of this essential plant nutrient, yet its presence in industrial wastes and its persistence in wastewater treatment plant effluents have led to increased concentrations of it in water bodies and have led therefore to widespread concern over its environmental impact. The presence of phosphates in surface water bodies causes a rapid growth of aquatic plants from microscopic (algae) to macroscopic (macrophytes). Excessive growth of these aquatic plants, or 'eutrophication', can seriously interfere with desirable water use; it results in large diurnal variation in dissolved oxygen levels, fish kills and changes in ecosystem function and diversity. Eutrophication has been a serious environmental concern in the developed world over the last 30 years or so and is now a major global concern.

The water industry is facing new challenges as a result of increasingly stringent discharge consents, especially for nutrients (nitrogen and phosphorus). For instance, the EU Urban Waste Water Treatment Directive (91/271/EEC) (UWWTD) and the Water Framework Directive (2000/60/EC) require a total P loading removal of 75–80% in large wastewater treatment plants (WWTP) which discharge into 'sensitive' waters — i.e., those which are eutrophic or which may become eutrophic if protec-

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tive action is not taken. Consequently, large treatment plants have opted for including either biological or chemical nutrient removal processes such as modified activated sludge or chemical precipitation processes; however such processes are expensive in terms of energy consumption and sludge treatment and they also require highly skilled operators. This approach may be reliable and reasonably cost-effective at large WWTP, yet it is almost always technically and financially inappropriate for small communities (<2000 p.e.). The cost per gram of phosphorus removed is much higher for domestic wastewater treatment plants serving small communities since they are unable to achieve the same economies of scale achieved at large WWTP [1].

Comparative cost data suggest that waste stabilization ponds (WSP) should be an attractive option for small communities, yet perceptions relating to land costs, climate and effluent quality have limited their application. Currently very few small domestic wastewater treatment plants in the United Kingdom and other EU Member States are required by the local environmental regulator to remove phosphorus. One example where P removal is required is the Tigh Mor Trossachs WSP system (500 p.e.) in Perthshire, Scotland; its effluent, which discharges into the pristine Loch Achray, is required to have  $\leq$ 3 mg P/L. However, this situation is expected to change and over the next few years and many more small WWTP will be required to remove P.

Reactive sorbent materials have been evaluated for P removal from wastewaters over the past two decades, including early studies with slags [2], sand [3], aluminium and iron oxides [4], limestone [5], shale rocks [6], and wollastonite [7]. Many of these materials have been tested in batch experiments in order to determine sorption equilibrium isotherms, followed by column experiments fed with P-spiked water or wastewater. Some materials have been evaluated in field trials either in constructed wetlands (CW) or in tertiary units following CW; the results from these studies vary, but few substrates appear to be particularly good for P removal with regard to sorption capacity and hydraulics (e.g., wollastonite, slags and, to some extent, light-weight aggregate products [8]). Slag materials are a non-metallic by-product of iron and steel production which floats on the molten metal after raw materials are loaded into and melted in the furnace; blast furnace slag (BFS) is produced by rapid cooling of molten slag [2].

In the work reported herein pilot-scale tertiary horizontal-flow BFS filters were tested under laboratory and field conditions in order to evaluate its potential for P removal at small domestic wastewater treatment plants. In the laboratory bench-scale BFS filter were used to estimate the P-sorption capacity of BFS, and in the field the performance of a pilot-scale BFS filter was monitored for P removal from the effluent of an existing WSP system.

#### 2. Methodology

# 2.1. *P*-sorption capacity under equilibrium conditions in the laboratory

The BFS used in this work was provided by Tarmac Quarry Products Ltd. (Scunthorpe, UK); it has an average grain size of 25 mm, a bulk density of 1.6 kg/L and a bulk porosity of 54%. Its P-sorption capacity was estimated in 14-L bench-scale horizontal-flow filters under laboratory conditions at 20°C. The filters were fed continuously for eight days, until equilibrium conditions were attained, with P-spiked water by pumping from a 25-L feeding tank with a peristaltic pump (model 101UR, Watson Marlow Bredel Inc., Wilmington, USA) at a hydraulic loading of 1.8 m<sup>3</sup>/m<sup>3</sup> d which corresponded to a retention time (~) of 0.25 d; the filter effluent was returned to the feeding tank and recycled during the experiment. P-spiked water solutions were made in 20 L of tap water supplemented with KH<sub>2</sub>PO<sub>4</sub> to give initial P concentrations ( $C_1$ ) of 5, 10 and 100 g P/L to reach the maximum Padsorption capacity as demonstrated by Sakadevan and Bavor [9] and to cover the range of typical P concentrations in domestic wastewaters (5, 10 and 20 mg P/L), as reported by Tchobanoglous and Burton [10]. The phosphorus concentration was determined daily in samples collected from the filter effluents using the ascorbic acid method (method 4500-P [10]). The average equilibrium concentration  $(C_{\rho})$  from duplicate experiments is reported. The laboratory set-up for P-adsorption experiments is shown in Fig. 1.

# 2.1. P-removal at pilot-scale BFS filters

Tertiary horizontal-flow BFS filters were tested under laboratory and field conditions. The laboratory-scale filter was similar to that described above but it was fed continuously with fresh (i.e., unrecycled) P-spiked water (10 mg P/L); samples were collected from the filter effluent and processed for P content as detailed above. In the field the BFS filter was operated for eight months;



Fig. 1. Laboratory set-up for P-adsorption experiments.

it received the final effluent from a pilot-scale WSP system at Esholt WWTP, Bradford, West Yorkshire, UK. The pilot-scale WSP system at Esholt comprises a primary facultative WSP, a secondary aerated rock filter (for ammonia removal) and the tertiary BFS filter for P removal. The primary facultative pond (PFP) is fed with screened wastewater (50% domestic, 50% industrial) and loaded at 80 kg BOD/ha d with an average nominal retention time ( $\theta$ ) of 30 days within the experimental timeframe reported herein. The aerated rock filter (ARF) (4.0×0.5× 0.5 m) was constructed aboveground, lined with a lowdensity polyethylene liner and filled with 40-100 mm limestone aggregate; it was aerated one-third of the way along its length, using an oil-free compressor (Jun-Air, Nørresundby, Denmark) at an air flow rate of 20 L/min. The PFP effluent was pumped into the base of the ARF using a peristaltic pump (Watson Marlow model 504S) at a hydraulic loading rate of 0.6 m<sup>3</sup>/m<sup>3</sup> d ( $\theta$  = 0.8 d). The BFS filter was a 50-L tank filled with BFS and fed with ARF effluent by pumping with a peristaltic pump (Watson Marlow model 504S) at a hydraulic loading rate of 1.8 m<sup>3</sup>/m<sup>3</sup> d ( $\theta$  = 0.25 d). The BFS filter was spiked with a KH<sub>2</sub>PO<sub>4</sub> solution which was pumped from a 25-L container using a peristaltic pump (Watson Marlow model 205S), in order to increase P influent concentration up to 10 mg P/L. Samples from both the BFS filter influent and effluent were collected weekly and processed for P content as described above. The pilot-scale WSP system is shown in Fig. 2.

Surface coating samples from the original BFS medium (Sample A), saturated medium after laboratory experiments (Sample B), saturated medium after on-site experiments (Sample C), and media fully saturated with a 2 M  $H_3PO_4$  solution (Sample D) were processed for X-ray diffraction (XRD) with a X-ray diffractometer equipped with a copper tube (Cu K $\alpha$ ) radiation and a graphite monocromator (model PW1050-Cu K $\alpha$ , Royal Philips Electronics N.V., Amsterdam, The Netherlands). Observations with a scanning electron microscope (SEM) (Stereoscan model 360, Cambridge Instruments Ltd, Cambridge, UK) were also conducted.

## 3. Results and discussion

The results obtained from P-sorption experiments A and B in the laboratory are shown in Table 1; P-sorption capacities (q = mass of P sorbed per mass of BFS) and P-removal values are also included. Results from experiment A show that BFS has a good affinity for inorganic phosphorus species (PO<sub>4</sub><sup>3-</sup>) as q values reached up to 30.2 g P/kg BFS, but at low values of  $C_o$  (experiment B) q de-

Table 1

Results from P-sorption capacity experiments

Experiment	Со,	Ce,	<i>q</i> ,	P removal,
	mg P/L	mg P/L	mg P/kg BFS	%
A – High Co	100,000	177	30,200	99.8
	10,000	104	3,100	98.9
	5,000	94	1,400	98.1
$B - Low C_{o}$	19.5	4.0	18	79.5
	11.2	2.8	10	75.0
	5.1	1.2	5	76.4





(c) BFS filter



(b) Aerated rock filter

Fig. 2. Pilot-scale WSP system at Esholt (Bradford, UK).

creased considerably. This suggests that the sorption process of P species from the bulk of the liquid phase to active points on BFS surface depends on P availability in the liquid. Hence, the surface provided for micropores located in the internal structure of the BFS media could not be reached by P species when tested under low driving force ( $C_o - C_e$ ) conditions, and lower adsorption capacities should be expected. Results at low  $C_o$  values reveal a much more realistic sorption capacity for P removal by adsorption on BFS material as P concentrations in domestic wastewater are typically lower than 20 mg P/L.

The Freundlich model is one of the most widely used expressions for sorption process under equilibrium conditions; it represents the relationship between q (mg P/kg BFS) and  $C_e$  (mg P/L) as an exponential equation. In Eq. (1), the Freundlich model is transformed into a linear equation where  $K_f$  and 1/n are empirical constants which may be used to compare the P-sorption performances of either different sorption media being tested under the same conditions or one sorption medium tested under different conditions.

$$\log_{10} q = (1/n) \log_{10} C_e + \log_{10} K_e \tag{1}$$

Sorption isotherms based on the results from the experiments with high and low  $C_o$  values followed Freundlich model (Fig. 3); corresponding  $K_f$  and (1/n) values were 0.25 and 4.66 for experiment A and 3.89 and 1.04 for experiment B, respectively. The isotherms suggest that BFS would perform better if the P concentration in the influent to a BFS filter was grams of P per litre but this condition is far from the real-life scenario for domestic wastewater treatment. However, these results show that BFS has the potential to produce a final effluent which meets P discharge consents as the aim of P removal from domestic wastewaters is obtain a treated effluent with a low P concentration (e.g., <2 mg P/L).

Results from the continuous-flow pilot-scale filters at Esholt (Fig. 4) show that BFS performed better (<2 mg P/



Fig. 3. P-sorption isotherms at 20°C based on the Freundlich model.

L) for longer than the laboratory-scale filters, even though the latter received the same hydraulic and P loadings (1.8 m<sup>3</sup>/m<sup>3</sup> d and 18 g P/m<sup>3</sup> d, respectively). This may mean that the environment provided by the ARF effluent could have improved the P-sorption capacity of BFS by introducing changes linked to pH, organic matter and dissolved oxygen. For instance, a leachate test carried out previously for our research group showed that Fe is leached from BFS (0.08 mg Fe/kg BFS in 6 weeks) and it could contribute to improved P removal. XRD scans (Fig. 5) from samples B and C did not showed any major change in the mineralogy of the surface coating on the BFS (sample A) which was mostly akermanite (Ca,MgSi,O,), thus indicating that sorbed P species were amorphous. The presence of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) in sample D, confirmed by XRD, suggests that amorphous P forms are linked to Ca/S/O-rich phases as reported by Pratt et al. [12]. SEM images (Fig. 6) confirmed the presence of amorphous forms on BFS after P removal.

In comparison with similar research works with P spiked water under controlled laboratory conditions, the



Fig. 4. Effluent phosphorus concentrations from BFS filters fed with a 10 mg P/L influent.



Fig. 5. XRD scans ( $\theta$ –2 $\theta$ ) from surface coating of BFS samples: original material (A), material from laboratory experiments (B), material from on-site experiments(C) and fully saturated BFS (D).

tested BFS reported higher adsorption capacity and overall P removal efficiency than corresponding figures reported by Sakadevan and Bavor [9], when tested at high initial P concentrations (P > 5 g P/l). Under a more realistic scenario for domestic wastewater treatment ( $P \approx 20 \text{ mg}$ P/L), the tested BFS reported lower adsorption capacities than those reported by Mann [13] which were higher than 380 mg P/kg BFS. Considering that the P adsorption capacity of BFS correlates significantly with media chemical composition (e.g., Ca, Mg, S and Si) and operational conditions (e.g., pH) [13], it seams that P adsorption capacity of the media should be tested for each particular case, in order to determine the longevity of the BFS filters P-removal capacity. However, there is not a reliable laboratory-based method for predicting longevity of filters and further work is needed in this area [14].

On site experiments with domestic wastewater reported that BFS filters performed better for longer than corresponding experiments in the laboratory. The BFS filter tested on site reported a P-retained ratio of 3.2 g P/kg BFS before break-point (P effluent concentration > 2 mg P/L), which is similar to that found at the saturation of a slag material produced in Canada (3.2 g P/kg slag) [15]. Moreover, on site BFS filter had a longer longevity — nearly ten times longer than the lab-based BFS filter. These results are not surprising, particularly considering that the use of laboratory experiments may not be entirely representative of the field systems they are meant to represent [15].

#### 4. Conclusions

P-sorption isotherms showed that BFS has the potential to produce a final effluent which meets P discharge consents (e.g., <2 mg P/L). The sorption capacity of BFS was higher in the field pilot-scale filter than in the laboratory bench-scale filter, possibly due to changes introduced in the aerated rock filter linked to pH and organic matter and dissolved oxygen concentrations. BFS filters are thus an appropriate low-cost technology for



Fig. 6. SEM images from the surface coating of BFS samples: original material (sample A ×500), saturated material from laboratory experiments (sample B ×1300), saturated material from on-site experiments (sample C ×800) and fully saturated BFS (sample D ×300).

upgrading small wastewater treatment systems to remove phosphorus and therefore, further work is required to develop this technology.

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