Use of blast furnace granulated slag as a substrate in vertical flow reed beds: Field application

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Abstract

Research was conducted at Middle East Technical University (METU), Ankara, Turkey in 2000 to determine whether a reed bed filled with an economical Turkish fill media that has high phosphorus (P) sorption capacity, could be implemented and operated successfully under field conditions. In batch-scale P-sorption experiments, the P-sorption capacity of the blast furnace granulated slag (BFGS) of KARDEMIR Iron and Steel Ltd., Co., Turkey, was found to be higher compared to other candidate filter materials due to its higher Ca content and porous structure. In this regard, a vertical subsurface flow constructed wetland (CW) (30 m²), planted with Phragmites australis was implemented at METU to treat primarily treated domestic wastewater, at a hydraulic rate of 100 mm d−1, intermittently. The layers of the filtration media constituted of sand, BFGS, and gravel. According to the first year monitoring study, average influent and effluent total phosphorus (TP) concentrations were 6.61 ± 1.78 mg L−1 and 3.18 ± 1.82 mg L−1; respectively. After 12 months, slag samples were taken from the reed bed and P-extraction experiments were performed to elucidate the dominant P-retention mechanisms. Main pools for P-retention were the loosely-bounded and Ca-bounded P due to the material’s basic conditions (average pH > 7.7) and higher Ca content. This study indicated the potential use of the slag reed bed with higher P-removal capacity for secondary and tertiary treatment under the field conditions. However, the P-sorption isotherms obtained under the laboratory conditions could not be used favorably to determine the longevity of the reed bed in terms of P-retention.

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1. Introduction

Excessive phosphorus (P) loading that is contributed by urban runoff, agricultural runoff, erosion from agricultural land and wastewater effluents can disturb the natural balance of the aquatic ecosystem (Brooks et al., 2000) and thus trigger eutrophication of waterbodies (Hillbricht-Ilkowska et al., 1995). In order to prevent the entrance of P-species into receiving waterbodies, recent studies have focused on alternative P-removal technologies that are economically feasible (Brooks et al., 2000). As an ecological engineering alternative to conventional and chemical based wastewater treatment methods, the use of subsurface flow (SSF) constructed wetlands in the removal of P, has been reported in several studies over the last two decades (Reddy and Smith, 1987; Mitsch and Jørgensen, 1989; Mitsch and Cronk, 1992; Moshiri, 1993; Kadlec and Knight, 1996; Pant et al., 2001).

In SSF constructed wetlands, the main P-removal mechanisms are adsorption, complexation and precipitation,
storage, plant uptake, and biotic assimilation (Watson et al., 1989). Even though vegetation, detritus, fauna and microorganisms are important sinks for P in the short term, substrate is the main sink for P in the long term (Sakadevan and Bavor, 1998). The abiotic adsorption of phosphorus (P) to the substrate has also been reported as the major P-removal mechanisms in constructed wetlands by several researchers (Richardson, 1985; Reddy and D’Angelo, 1994; Kadlec and Knight, 1996). Hence, to select specialized substrates with conducive physico-chemical properties to P-removal, while maintaining sufficient permeability (House et al., 1994) is of utmost importance when designing constructed wetlands (Johansson and Gustafsson, 2000). Various physico-chemical properties including pH, redox potential, dissolved ions, calcium content, amorphous and poorly crystalline Al and Fe-oxides content of these substrates influence the P-sorption phenomena onto their surfaces (Froelich, 1988; Zhu et al., 1997; Reddy et al., 1999).

Some of these specialized substrates that were used for P-removal in constructed wetlands were sand, gravel, limestone, shale (Wood and McAtamney, 1996; Drizzo et al., 1999; Johansson, 1997; Mann, 1997; Zuraik et al., 1997), LWA (commercial light weight aggregates, Johansson, 1976; Zhu et al., 1997; Maehlum and Stalnacke, 1999), LECA (a reactive porous media, Zhu et al., 2002), zeolite (natural mineral or artificially produced aluminosilicates, Sakadevan and Bavor, 1998), pelleted clay either alone or in combination with soils (Sakadevan and Bavor, 1998), opaka (a siliceous sedimentary rock, Johansson and Gustafsson, 2000), pumice (natural porous mineral, Njau et al., 2004), wollastonite (a calcium metasilicate, Brooks et al., 2000), fly ash (Jenssen et al., 1993; Mann and Bavor, 1993; Nur Onar et al., 1996; Brooks et al., 2000) alum, dolomite and calcite (Ann et al., 1999; Pant et al., 2001).

Apart from natural substrates, industrial wastes such as blast furnace slag (BFGS), which is a porous nonmetallic co-product produced in the iron and steel industry, has been shown to have a high P-sorption capacity as has been shown earlier in batch and column experiments (Yamada et al., 1986; Mann and Bavor, 1993; Johansson, 1999a,b; Sakadevan and Bavor, 1998; Gruneberg and Kern, 2001; Johansson and Gustafsson, 2000; Korkusuz et al., 2002; Rustige et al., 2003). Even though more detailed knowledge of the removal mechanisms involved in the sorption/release of P with the BFGS are important for practical use and for estimation of the longevity of this material with respect to P, they are not very well known (Johansson and Gustafsson, 2000). Based on this information, BFGS was considered interesting for further investigation, not only because of its potential use in constructed wetlands as substrate, but because of its potential to reduce the solid waste management problems associated with the iron and steel industries (Johansson, 1999a). Sakadevan and Bavor (1998) have also suggested further research to increase the knowledge concerning the use BFGS as a filter material in constructed wetland applications. Moreover, this has only been investigated to a limited extent. Gruneberg and Kern (2001) have pointed out the necessity of long-term studies under field conditions to evaluate the P-sorption capacity of BFGS.

The objective of this paper is therefore to further investigate the P-adsorption characteristics and behaviour of blast furnace granulated slag (BFGS) under field conditions in order to elucidate their potential suitability as a filter medium in SSF constructed wetlands treating domestic wastewater. In this regard, using standard P-solutions, batch scale P-sorption experiments were performed to determine the P-sorption capacity of the BFGS provided from the KARDEMİR Iron and Steel Ltd., Co., Karabük, Turkey, and these were compared to those found in the literature. Moreover, the first-year P-treatment performance of a vertical SSF reed bed (30 m²) implemented in Ankara, Turkey that was filled with BFGS and operated intermittently with primarily treated domestic wastewater, are presented and evaluated. After one year of operation of this constructed wetland, BFGS samples were taken from the filter media of the reed bed. These samples were fractionated for P to characterize the dominant P-sorption mechanism to assess whether laboratory P-sorption results could be used to determine the longevity of BFGS media used in the field applications.

2. Methods

2.1. Site description

A vertical SSF constructed wetland with dimensions of 4.5 m × 6.5 m × 0.60 m (W × L × D) with a surface area of around 30 m² was implemented on the campus of Middle East Technical University (METU), Ankara, Turkey, in the summer of 2001. A slope of 1% was created at the bottom of the wetland to facilitate easier water collection and the bottom was sealed with a nylon sheet. The wetland was first filled with gravel (15 cm of 15/30 mm), then with sieved BFGS (30 cm of grain size <3 mm), and finally with sand (15 cm of grain size <3 mm) as the top layer. Several sizes of PVC pipes were used to distribute the wastewater flow evenly onto the reed bed. Moreover, polyethylene drain-innex pipes were used to collect the treated wastewater. Constructed wetlands were planted with the shoots of the Phragmites australis, which were transferred from the natural reed beds on the campus and transplanted at a density of 9 seedlings m⁻², in May 2002. The primarily treated domestic wastewater was manually diverted from a sedimentation tank (volume = 3 m³) via spherical valves and PVC pipes to the wetlands, once a day for about an hour, yielding an influent discharge rate of 3 m³ d⁻¹ and of a hydraulic loading rate of 0.100 m d⁻¹ (Korkusuz et al., 2002). The plan-view of the vertical SSF constructed wetland implemented on the campus of METU is illustrated in Fig. 1.
2.2. Determination of the physico-chemical characteristics of the BFGS

The information related to the composition of the BFGS of KARDEMİR Iron and Steel Ltd., Co. was provided by the company. The particle density, bulk density and porosity of fresh BFGS sample of KARDEMİR Ltd., Co., were determined using procedures described in the Unit Operations and Unit Processes Laboratory Manual published by Association of Environmental Engineering Professors (1984). The particle size distribution was determined by sieving the BFGS samples through seven different mesh sizes, ranging from 0.149 to 9.5 mm. The pH of the BFGS samples was also measured. The physico-chemical characteristics of the BFGS of KARDEMİR were compared to that of the values reviewed by Johansson (1999a), Grüneberg and Kern (2001), as well as Sakadevan and Bavor (1998).

2.3. Batch-scale P-sorption experiments

The P-sorption capacity of the BFGS produced in KARDEMİR was determined using the procedures described for sorption studies conducted by other wetland researchers (Baker et al., 1998; Zhu et al., 1997; Sakadevan and Bavor, 1998). The sorption capacities were investigated using solutions of potassium phosphate monobasic salt (KH₂PO₄), which is a strong electrolyte and dissociates in solution producing HPO₄²⁻, H₂PO₄⁻ and PO₄³⁻ ions that are immediately available for reactions (Brooks et al., 2000). These ions are the main P-forms that are biologically available and thus contribute to eutrophication in waterbodies. To begin with, BFGS samples (grain size <3 mm) were dried at 105 °C to remove humidity. Afterwards, 8 g samples of BFGS were put in an Erlenmeyer flasks (300 mL) containing 250 mL P-solution of following concentrations: 0, 4, 8, 20, 40, 80, 160, and 320 mg L⁻¹. Additionally, raw domestic wastewater with a concentration of 10 mg P L⁻¹ was placed into one of the Erlenmeyer flasks with 8 g BFGS. Triplicate analyses were conducted for each of the P-concentrations. Although 320 mg L⁻¹ is a much higher concentration than that of the concentrations of domestic wastewater (6–20 mg L⁻¹) reported by Metcalf and Eddy (1991), higher P-concentrations were necessary to establish a sorption isotherm (Zhu et al., 1997).

The Erlenmeyer flasks were placed into the shaker, which was maintained at 22 °C and at 200 rpm for 24 h. The supernatant was filtered through 0.45 μm Millipore membrane filter and decanted into a vial. The concentrations of the filtrates were analyzed according to the Ascorbic Acid Spectrophotometric Method (APHA, 1999). The amount of P removed by BFGS was calculated according to following equation:

$$q = \frac{(C_i - C_f) \times V}{M}$$

(1)
where

\[
q = \text{amount of P-sorbed per unit of BFGS (mg P kg}^{-1}\text{ BFGS sample),} \\
C_i = \text{initial concentration of P (mg L}^{-1}\text{),} \\
C_f = \text{final concentration of P or equilibrium concentration (mg L}^{-1}\text{),} \\
V = \text{volume of phosphate solution added to flask (0.250 L),} \\
M = \text{Mass of dry weight of the BFGS (0.008 kg of BFGS)}.
\]

2.4. Monitoring and measurements of the water quality parameters

The operation and monitoring of the wetlands of METU were conducted between July 2002 and July 2003. The influent and effluent water samples of the constructed wetland were taken periodically and brought to the Chemistry Laboratory of the Department of Environmental Engineering of METU within 15 min. Chemical analyses were performed on the same day according to the Standard Methods (APHA, 1999). Temperature, conductivity, pH, chemical oxygen demand (COD), total suspended solids (TSS), ortho-phosphate phosphorus (PO$_4^{3-}$–P), total phosphorus (TP), ammonium nitrogen (NH$_4^+$–N), nitrate nitrogen (NO$_3^-$–N), and total nitrogen (TN) were monitored. For each of these parameters, samples were analyzed in duplicates or triplicates.

Although this paper focused on the P-retention capacity of the main BFGS layer in the reed bed, the characteristics of the primarily treated domestic wastewater that was applied to the reed bed of METU (July 2002–July 2003) were also provided. Moreover, for the monitoring period, the P-loading rate (g m$^{-2}$ d$^{-1}$) vs. effluent P-concentrations (mg L$^{-1}$) of the reed bed of METU were presented and discussed.

2.5. Chemical extraction experiments for phosphorus

The substrate samples were taken randomly from several points throughout the vertical SSF constructed wetland of METU at the beginning (in May 2002; used as blank) and end of the operation period (in July 2003). In the Chemistry Laboratory of the Department of Environmental Engineering of METU, P-extraction experiments were conducted.

Fractionation of P-forms in the filter media can provide an opportunity to understand which forms of ions in the filter media sorbed the P and what type of transfer processes occurred between these ions and P (Zhu et al., 2002). Identification of the P-forms in soils/sediments/wetland substrates may be achieved by chemical extraction, using procedures, which have been proposed in the literature (e.g. Chang and Jackson, 1957; Hiltjes and Lijklema, 1980; Williams et al., 1971; Hartikainen, 1979; Stuanes and Nilsson, 1987 cited in Zhu et al., 2002). These procedures are based upon the assumptions that certain reagents will extract discrete forms of inorganic P (Sovik and Klove, 2002). In this study, the chemical extraction methodology to fractionate the inorganic P-forms retained by BFGS layers of the reed bed of METU was carried out according to a method developed by Chang and Jackson (1957) and modified by Hartikainen (1979), which was a suitable method for media with high Ca content (Zhu et al., 2002).

All the substrate samples were brought to the laboratory and stored in the dark at 4 °C until analysis. BFGS samples were firstly dried at 105 °C for 12 h, and then weighed. Afterwards, 1 g of each sample was put into the Erlenmeyer flasks (50 mL). The extractant (NH$_4$Cl) was also added to the flasks and the flasks were placed into the shaking machine (at 200 rpm). The extraction scheme is shown in Table 1. For each of the extraction step, five replicates were used.

The extractant from each extraction step was centrifuged. The supernatant was filtered through 0.45 µm Millipore membrane filter and decanted into a vial. The BFGS samples were washed twice with 25 mL saturated NaCl solution between extraction steps to get rid of any phosphorus that had re-adsorbed back onto the soil from the solution (Headley et al., 2003). The amount of P in the supernatant was measured using the Ascorbic Acid Method (APHA, 1999). The sample blank P values were then subtracted from the measured P values of the BFGS samples to take into account any pre-existing P on the raw slag, or that was dissolved from the internal structure of BFGS during extraction.

<table>
<thead>
<tr>
<th>Phosphorus fraction</th>
<th>Extractant</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loosely bounded P</td>
<td>1 M NH$_4$Cl</td>
<td>50 mL extractant, shaken for 1 h</td>
</tr>
<tr>
<td>Al-Bounded P</td>
<td>0.5 M NH$_4$F</td>
<td>50 mL extractant, shaken for 1 h</td>
</tr>
<tr>
<td>Fe-Bounded P</td>
<td>0.1 M NaOH</td>
<td>50 mL extractant, shaken for 18 h</td>
</tr>
<tr>
<td>Ca-Bounded P</td>
<td>1 M H$_2$SO$_4$</td>
<td>50 mL extractant, shaken for 1 h</td>
</tr>
<tr>
<td>Occluded P</td>
<td>KCl–C$_6$H$_5$O$_2$–EDTA</td>
<td>50 mL extractant, shaken for 1 h</td>
</tr>
</tbody>
</table>


3. Results and discussion

3.1. Physico-chemical characteristics of the BFGS

In the production of iron; iron ore, iron scrap, and fluxes (limestone and/or dolomite) are charged into a blast furnace at temperatures above 1500 °C along with coke for fuel. The coke is combusted to produce carbon monoxide, which reduces the iron ore to a molten iron product. Blast furnace slag is a nonmetallic co-product produced in this
process. The physical structure and gradation of granulated slag depend on the chemical composition of the slag, its temperature at the time of water quenching, and the method of production. Treatment with controlled quantities of water during the cooling increases the vesicular nature of slag, producing a light-weight, porous medium (Mann and Bavor, 1993). In recent years, the use of slag in constructed wetlands for removal of P has been questioned by some of the wetland researchers (Mann and Bavor, 1993; Sakadevan and Bavor, 1998; Johansson, 1999; Grüneberg and Kern, 2001).

The chemical composition of the BFGS (KARDEMİR Iron and Steel Ltd., Co.) for this study and of the blast furnace slags used by other wetland researchers in other countries (Sakadevan and Bavor, 1998; Johansson, 1999a; Grüneberg and Kern, 2001) is presented in Table 2. All of the slag samples presented in Table 2 are rich in SiO$_2$ and CaO, followed by Al$_2$O$_3$ and MgO. The BFGS of KARDEMİR have slightly lower CaO content (33.53%) and slightly higher SiO$_2$ content (41.79%) than other BFGS samples. The particle density, bulk density and the porosity values of the slag used in the wetland of METU were comparable to the literature values. However, the pH of the BFGS of KARDEMİR was lower than the literature values.

According to the particle-size distribution of BFGS of KARDEMİR, 50% of the cumulative weight of BFGS samples could pass through the sieves with mesh sizes smaller than 1 mm (Korkusuz, 2004), which indicated that BFGS of KARDEMİR had a finer texture. The smaller the particles of the filter media, the lower the hydraulic conductivity is in the reed bed (Johansson, 1997). Materials with lower permeability (hydraulic conductivity) retard the movement of water, hence allowing longer periods of time for sorption to occur (Johansson, 1999a). In this study, the hydraulic conductivity could be measured neither in the field, nor in the laboratory. However, during the operation period (12 months), there were no clogging problems or surface overflow in the reed bed of METU, which would be the indicators of inappropriate selection of the filter material (Vymazal et al., 1998).

### 3.2. Phosphorus sorption isotherm studies

In the literature, other P-sorption studies on the use of slag as filter medium in filters and constructed wetlands for P-removal (Mann and Bavor, 1993; Sakadevan and Bavor, 1998; Baker et al., 1998; Johansson, 1999a,b; Johansson and Hylander, 1998; Johansson and Gustafsson, 2000) have been conducted. Mann and Bavor (1993) reported a P-sorption capacity of 420 mg P kg$^{-1}$ for a BFGS that was considered to have good potential for application in a CW, while Sakadevan and Bavor (1998) reported a P-sorption capacity of 44,000 mg P kg$^{-1}$ for their BFGS. Crolla et al. (2000) reported P-sorption capacities ranging from 3900 to 17,000 mg P kg$^{-1}$ for a number of slags tested, whereas Johansson (1997, 1999a) and Johansson and Hylander (1998) reported P-sorption capacities of the slags produced in Oxelösund, Sweden ranging from 100 to 600 mg P kg$^{-1}$.

The initial and final (equilibrium) P-concentrations, as well as the P-sorption capacities for BFGS produced in

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>Blast furnace granulated slag (BFGS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KARDEMİR Iron Steel Ltd., Co., Turkey$^a$</td>
</tr>
<tr>
<td>FeO</td>
<td>0.64</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>–</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>41.79</td>
</tr>
<tr>
<td>MnO</td>
<td>2.35</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>12.47</td>
</tr>
<tr>
<td>CaO</td>
<td>33.53</td>
</tr>
<tr>
<td>MgO</td>
<td>6.55</td>
</tr>
<tr>
<td>S</td>
<td>0.81</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>–</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.24</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.45</td>
</tr>
<tr>
<td>Bazite</td>
<td>0.75</td>
</tr>
<tr>
<td>Particle density (g cm$^{-3}$)</td>
<td>2.112</td>
</tr>
<tr>
<td>Bulk density (g cm$^{-3}$)</td>
<td>1.07</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>50</td>
</tr>
<tr>
<td>pH</td>
<td>8.40</td>
</tr>
</tbody>
</table>

$^a$ See KARDEMİR (2001).

$^b$ See Johansson (1999a).


KARDEMIR (particle diameter <3 mm) are summarized in Table 3. In this study, as the initial P-concentrations of the solutions changed between 0 and 320 mg L\(^{-1}\), the P-sorption capacities of BFGS have varied between 0 and 9153 mg P kg\(^{-1}\) (Table 3). The higher P-sorption capacities were obtained for higher initial P-concentrations. This can be explained by a more efficient utilization of the adsorptive capacities of the slag samples due to greater driving force of a higher concentration gradient pressure (Bharda and Sheldarkar, 1993).

Moreover, the relationship between the P-concentrations and the P-sorption capacities of BFGS samples could be explained by examining the prevailing reactions of the adsorption and precipitation mechanisms (McDowell et al., 1977; Nichols, 1983; Brady, 1990). Adsorption may actually be considered as a unique form of precipitation, where phosphates anions and cations combine to form a solid (Nichols, 1983).

Under basic to neutral conditions (7 < pH < 14), adsorption of phosphates to calcium occurs, in which the P is precipitated as insoluble Ca–P. Reaction between calcium and dihydrogen-phosphate to produce tricalcium phosphate, Ca\(_3\)(PO\(_4\))\(_2\), is presented below (Brady, 1990):

\[
3\text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^- \rightarrow \text{Ca}_3(\text{PO}_4)_2 \downarrow + 4\text{H}^+ \quad (2)
\]

Although this compound is quite insoluble, it may be converted further to even more insoluble products such as hydroxyapatite (HAp) [3Ca\(_3\)(PO\(_4\))\(_2\) \cdot \text{Ca(OH)}_2] over time (Brady, 1990). Phosphates can also react with some other soluble metals (Al, Fe, Mn, etc.) to form insoluble hydroxy-phosphates (McDowell et al., 1977). Moreover, Johansson (1999) described another reaction with calcium and monohydrogen phosphate

\[
5\text{Ca}^{2+} + 3\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{Ca}_5(\text{PO}_4)_3 \cdot \text{OH} \downarrow + 4\text{H}^+ \quad (3)
\]

According to these reactions, as the P-concentration in the solution increases, the reactions move to the right to restore equilibrium (Stober et al., 1997) and the P that is readily removed from the solution is converted further to insoluble products such as hydroxyapatites (HAp) (Brady, 1990).

The differences in the P-sorption capacities of BFGS of KARDEMIR and other studies could be related to the differences in the chemical composition and physical properties (such as surface area and surface structures) resulting in different amounts of reactive Ca, Fe, Al (Zhu et al., 2002) and different pH values. Moreover, differences in the experimental approach (batch or column studies, intermittent flow or continuous flow, wastewater or P-solution, P-concentrations, mass of the substrate used in the sorption study, pH of the solution, shaking time, temperature, etc.) used in the above-mentioned studies have resulted in such variations. However, these studies indicated that coarse-grained blast furnace slag (diameter <4 mm) could be considered as a suitable material in ecologically engineered treatment systems like constructed wetlands for enhanced P-sorption due to its physical and chemical properties conducive to P-removal (House et al., 1994).

### 3.3. Monitoring study

The characteristics of the primarily treated domestic wastewater of METU (July 2002–July 2003) was presented in Table 4. Generally, the average concentrations of the pollutants of the raw domestic wastewater of METU were lower than that of the literature values given by Vymazal et al. (1998); but similar to that of the typical values for domestic wastewater given by Metcalf and Eddy (1991). However, the COD:BOD\(_5\) ratio of the primarily treated wastewater of METU was about 4.6, which is considerable higher than the literature value of 1.14 (Metcalf and Eddy, 1991). Thus, it can be concluded that the domestic wastewater of the METU had a low biodegradability and could be therefore classified as “weak” wastewater. The weak characteristic of the wastewater was due to the water usage habits of the inhabitants of the METU campus and due to

### Table 3

<table>
<thead>
<tr>
<th>C(_i)</th>
<th>0</th>
<th>4</th>
<th>8</th>
<th>9.14(^{a})</th>
<th>10</th>
<th>20</th>
<th>40</th>
<th>80</th>
<th>160</th>
<th>320</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_f)</td>
<td>0.03</td>
<td>0.69</td>
<td>2.11</td>
<td>2.70</td>
<td>2.89</td>
<td>2.15</td>
<td>4.78</td>
<td>9.99</td>
<td>17.88</td>
<td>27.1</td>
</tr>
<tr>
<td>q</td>
<td>0</td>
<td>103</td>
<td>184</td>
<td>201</td>
<td>222</td>
<td>558</td>
<td>1101</td>
<td>2188</td>
<td>4441</td>
<td>9153</td>
</tr>
</tbody>
</table>

\(C_i = \) initial P-concentration of the solution (mg L\(^{-1}\)), \(C_f = \) final (equilibrium) P-concentration of the solution (mg L\(^{-1}\)), \(q = \) sorbed P capacity of the BFGS sample (mg P kg\(^{-1}\) of BFGS).

\(^{a}\) Raw domestic wastewater of METU, P-concentration of this sample was 9.14 mg L\(^{-1}\).

### Table 4

The characteristics of the primarily treated domestic wastewater of METU

<table>
<thead>
<tr>
<th>Concentration</th>
<th>BOD(_5)</th>
<th>COD</th>
<th>TSS</th>
<th>PO(_4^{3-})–P</th>
<th>TP</th>
<th>NH(_4^+)–N</th>
<th>NO(_3^–)–N</th>
<th>TN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average (mg L(^{-1}))</td>
<td>50</td>
<td>227.87</td>
<td>48.27</td>
<td>4.59</td>
<td>6.61</td>
<td>24.56</td>
<td>1.21</td>
<td>30.32</td>
</tr>
<tr>
<td>St. Dev. (mg L(^{-1}))</td>
<td>35</td>
<td>67.61</td>
<td>32.38</td>
<td>1.47</td>
<td>1.78</td>
<td>6.51</td>
<td>1.08</td>
<td>12.36</td>
</tr>
<tr>
<td>Min (mg L(^{-1}))</td>
<td>40</td>
<td>108.00</td>
<td>24.00</td>
<td>2.25</td>
<td>3.59</td>
<td>15.05</td>
<td>0.00</td>
<td>12.38</td>
</tr>
<tr>
<td>Max (mg L(^{-1}))</td>
<td>100</td>
<td>307.33</td>
<td>140.00</td>
<td>8.03</td>
<td>9.47</td>
<td>34.53</td>
<td>3.22</td>
<td>52.10</td>
</tr>
</tbody>
</table>

Sample size (\(n\)) = 100.
the dilution of the wastewater with the precipitation as typical of a combine sewerage system.

For the monitoring period of July 2002–July 2003, average (±St. Dev.), minimum and maximum influent and effluent P (PO$_4^{3-}$–P and TP) concentrations from the slag reed bed of METU, as well as the concentration-based removal efficiencies (RE%) are given in Table 5. Concentration based percent removal efficiencies (RE%) were calculated according to the following equation:

$$RE\% = \frac{C_{in} - C_{out}}{C_{in}} \times 100$$

The P-loading rates were calculated for a HLR of 100 mm d$^{-1}$ and were plotted against effluent concentrations for PO$_4^{3-}$–P and TP in Figs. 2 and 3, respectively. The effluent P-concentrations of the reed bed with BFGS were almost constant and very low at the beginning of the operation period (independent of the influent concentrations). However, they rose with increasing P-loading rates and time. The constant effluent concentrations of the slag reed bed at the beginning of the operation was mainly due to the higher P-sorption capacity, when the slag substrate was fresh and the sorption sites were free of P. Prior to performing chemical extraction experiments for P, it was surmised that the P-removal was mainly due to calcium precipitation since BFGS of KARDEMIR had higher calcium content (33.53%) compared to its lower Al (12.47%) and Fe (0.64%) content. Moreover, since the pH of the slag reed bed (Fig. 4) did not fall below 7.11 (7.67 ± 0.37), it was believed that the Al–P and Fe–P oxides were the less available forms when compared to the calcium bounded-P at near neutral and higher pH levels (Brady, 1990; Richardson and Craft, 1993). Hence, the increase in the effluent P-concentrations of the reed bed of METU could be related to a possible decrease in the free calcium ion concentrations.

Additionally, the effluent P-concentrations responded to precipitation events as the influent P-concentrations did. The decrease in P-removal efficiencies of the slag reed bed after rainfall events could be explained as a combination of dilution and flushing effect by the precipitation. The already adsorbed P in the BFGS matrix might have been “flushed out” when the P-concentrations in the bulk solution were low, and thus caused an equilibrium shift and resulting in desorption. Also, additional P might have

Table 5

<table>
<thead>
<tr>
<th>PO$_4^{3-}$–P</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Influent (mg L$^{-1}$)</td>
<td>Effluent (mg L$^{-1}$)</td>
</tr>
<tr>
<td>---------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Average</td>
<td>4.59</td>
</tr>
<tr>
<td>St. Dev.</td>
<td>1.47</td>
</tr>
<tr>
<td>Min</td>
<td>2.25</td>
</tr>
<tr>
<td>Max</td>
<td>8.03</td>
</tr>
<tr>
<td>Median</td>
<td>4.33</td>
</tr>
<tr>
<td></td>
<td>6.61</td>
</tr>
<tr>
<td></td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>3.59</td>
</tr>
<tr>
<td></td>
<td>9.47</td>
</tr>
<tr>
<td></td>
<td>6.81</td>
</tr>
</tbody>
</table>

Fig. 2. Influent and effluent PO$_4^{3-}$–P concentration values of the slag reed bed of METU.
leached to the wetland cell (Vymazal et al., 1998) from decaying vegetation and microorganisms, resulting in negative removal efficiencies. In vertical flow wetlands older than one year, effluent P-concentrations might exceed influent concentrations with changes in oxidation–reduction behavior and reverse adsorption–precipitation mechanisms (Lantzke et al., 1999). Another explanation for the P releases could be the decrease in the pH values of the wetland bed with time (Fig. 4). Since the affinity of the fill medium for P depends on its contents and on the pH of the
environment, changes in pH values might have negatively affected the P-retention. It is known that the emergent plants can change the pH values of the fill media by proton release during nutrition, exudation of organic acids and production of carbohydrates, and CO₂ release by roots (Olsen et al., 1981).

Nevertheless, the TP influent and effluent values of the slag reed bed of METU (influent 6.6 mg L⁻¹, effluent 3.2 mg L⁻¹) were comparable with the TP performance results of some of the vertical flow wetlands in Belgium (influent 6.8 mg L⁻¹, effluent 3.6 mg L⁻¹); Austria (influent 10.7 mg L⁻¹, effluent 4.0 mg L⁻¹); and Germany (influent 15.9 mg L⁻¹, effluent 4.8 mg L⁻¹) (Vymazal et al., 1998). Lee and Lin (1999) reported that it is very difficult to reduce the TP effluent concentrations to below 8 mg L⁻¹ after secondary treatment in a conventional treatment system. The slag reed bed of METU used to provide secondary treatment in METU showed a promising TP removal performance for the first year of operation under the prevailing conditions of Ankara.

It was also found that for the monitoring period, the PO₄³⁻–P loading rates for the reed bed of METU varied between 0.21 and 0.80 g m⁻² d⁻¹ (0.47 ± 0.15 g m⁻² d⁻¹) and ranged from 0.34 g m⁻² d⁻¹ to 0.97 g m⁻² d⁻¹ (0.65 ± 0.18 g m⁻² d⁻¹) for TP loading rates (Figs. 5 and 6). The slag system could remove PO₄³⁻–P and TP efficiently even as the loading rates increased. From the linear regression analysis (Figs. 5 and 6), it could be stated that for the slag reed bed of METU, a good correlation was not evident between the P-loading rate and the effluent values, because of the variable P-treatment performance of the slag system during the whole monitoring period. The weak correlation between loading rate and removal rate at any given moment in time was likely due to the response lag.

### 3.4. Phosphorus fractionation experiments

The results of the P-fractionation experiments to investigate the amount and how the inorganic P was sorbed to the BFGS media in the reed bed of METU, are given in Table 6. The average P amount available for plants (TIP) and TP sorbed by the BFGS samples in 12 months (July 2002–July 2003) were found to be around 10 mg kg⁻¹ (Korkusuz, 2004) and 70 mg kg⁻¹ (difference between 85.68 and 18.79 mg kg⁻¹), respectively (Table 6).

Chemical P-fractionation experiments showed that the loosely bound P and Ca–P were the predominant forms of P mineral for the slag samples taken in July 2003; whereas for the fresh BFGS samples the dominant P-forms were Ca–P, loosely bound P and Fe–P, respectively (Table 6). With the methods applied in this work, Al-bound P and occluded-P could not be observed for slag samples. As P is known to bind with Ca at high pH, formation of calcium phosphates was believed to be a major mechanism of P-removal by slag systems (Baker et al., 1998). Hence, it was thought that the slightly basic conditions in the slag reed bed during the whole monitoring year (average pH of the effluent = 7.67 ± 0.37) might have favored the formation of loosely bound P and Ca–P compounds over Fe–P, Al–P products (Fig. 4).

Similarly, calcium-containing alkaline slag has proven to have a high P-sorption capacity as shown earlier in batch, column experiments but also in some field investigations (Yamada et al., 1986; Mann and Bavor, 1993; Johansson, 1999a,b; Sakadevan and Bavor, 1998). The higher P-removal capacity was probably obtained for slags, which were high in easily leached Ca and for slags that already contained seeds of HAp or related apatites (carbonate apatite, fluorapatite) that might have functioned...
as seeds. Johansson and Gustafsson (2000) studied P-removal by slag and showed that calcium concentration decreased with increasing P addition. In support, they performed an ion activity determination to show that the removal mechanisms for BFGS were precipitation of HAp, not other calcium phosphates. The results of the investigations by Johansson and Gustafsson (2000) showed that direct HAp formation was the predominant P-removal mechanism when a model P-solution was added to slag materials. Moreover, Joko (1984) and Van Dijk and Braakensieck (1984) showed that HAp was precipitated directly from solution when hydrated lime was added to wastewaters. The critical supersaturation limit in these earlier studies ranged from 10^2 to 10^2.5 times the HAp solubility, similar to that found in the study conducted by Johansson and Gustafsson (2000). Johansson and Gustafsson (2000) also showed that the alkalinity may be important in limiting the extent of HAp precipitation, as CO_3^{2-} ions may remove Ca^{2+} through calcite precipitation. Thus, Ca-containing materials may be less efficient P-retainers at higher alkalinites.

In this regard, the higher CaO content (33.53%) of the fresh slag samples (Table 2) also supported the idea that there were already seeds of HAp in the slag produced in KARDEMIR so that P was easily precipitated with calcium. The pH values of the effluent of the slag wetland system (maximum and minimum pH of the effluent = 8.56–7.11) decreased with time (Fig. 4) which might be due to the removal of Ca^{2+} by CO_3^{2-}. A possible decrease in the free calcium ions might have resulted in a decrease of the P-retention capacity of the slag system with time. However, Vymazal et al. (1998) emphasized that the sorption capacity in artificial wetlands is not generally limited because of the input of Ca, Fe, and Al by wastewater. In this regard, calcium ions contained in the wastewater might have also contributed to Ca content of the slag material.

The loosely-bounded P fraction could consist mainly of adsorbed P that is available for plant uptake. Adsorption of P occurs rapidly and is potentially reversible if a change takes place in the pH, redox potential or equilibrium P-concentration (Grobbeelaar and House, 1995; Hillbricht-Ilkowska et al., 1995). Therefore, the weakly bound P fraction did not represent a permanent sink. However, once P was held at the filter media surface by adsorption, it might become more permanently bound through inner-sphere complexation and precipitation reactions (Frossard et al., 1995; Sparks, 1995). In this way, weakly bound P might gradually progress into the Ca-associated P fraction to be more permanently removed (Headley et al., 2003).

Table 6
Chemical P-fractionation of the slag samples (analyzed in the Chemistry Laboratory of the Department of Environmental Engineering of METU, July 2003)

<table>
<thead>
<tr>
<th>Phosphorus forms (mg P kg^{-1})</th>
<th>Fresh BFGS (blank)</th>
<th>BFGS taken from slag reed bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loosely bounded P</td>
<td>4.92 ± 0.68^a</td>
<td>42.17 ± 7.28</td>
</tr>
<tr>
<td></td>
<td>[4.06–5.60]^b</td>
<td>[34.73–54.19]</td>
</tr>
<tr>
<td>Al-Bounded P</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fe-Bounded P</td>
<td>1.97 ± 0.68</td>
<td>6.58 ± 3.25</td>
</tr>
<tr>
<td></td>
<td>[1.33–3.08]</td>
<td>[3.08–11.70]</td>
</tr>
<tr>
<td>Ca-Bounded P</td>
<td>11.90 ± 0.81</td>
<td>36.93 ± 12.30</td>
</tr>
<tr>
<td></td>
<td>[11.20–12.60]</td>
<td>[18.90–44.80]</td>
</tr>
<tr>
<td>Occluded-P</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Total</td>
<td>18.79</td>
<td>85.68</td>
</tr>
</tbody>
</table>

^a Average values (mg P kg^{-1}) ± standard deviations (mg P kg^{-1}) for a sample size of n = 5.

^b Minimum – maximum values (mg P kg^{-1}) found in the extraction experiments.

Fig. 6. TP loading rate (g m^{-2} d^{-1}) vs. removal rate (g m^{-2} d^{-1}) of the slag reed bed of METU.
To determine if P-loaded slags might be efficient agricultural fertilizers, Johansson and Hylander (1998) conducted some experiments and reported that P retained by slag could be recovered to some extent. Hylander et al. (1998) also showed, in pot experiments with barley that P retained by slag was available for uptake by plants. However, further investigations are required to understand the P uptake mechanisms of the plants and the required conditions.

3.5. Questioning the use of the P-sorption isotherms to estimate the longevity of the reed bed filled with BFGS

According to the results of the P-fractionation experiments that were performed for the BFGS samples taken from the slag reed bed of METU after an operation period of 12 months, TP-remaining in the slag material was approximately 70 mg kg\(^{-1}\) (Table 3). However, for an initial P-concentration \(C_p\) of \(\sim 7\) mg L\(^{-1}\) that corresponded to an average P-concentration of the domestic wastewater applied to the wetlands of METU over 12 month (Table 3), the P-sorption capacity was determined to be approximately 150 mg kg\(^{-1}\) (Table 3).

There might be several reasons which might have caused this considerable difference between these two sorption capacities (\(\sim 150\) mg kg\(^{-1}\) and \(\sim 70\) mg kg\(^{-1}\)). It has been stated that a reduction in the concentration of P in the filter media due to biological uptake (microorganisms and reed plants), flushing or dilution via precipitation could cause a release of P that has been adsorbed by the filter media (Syers et al., 1973). The amount of P-released would depend on the age and the solubility of the precipitate. It would be released most easily from freshly precipitated crystals and adsorbed-P that had not yet penetrated particles (Brady, 1990). This may have significance for outdoor wetland systems like the reed bed of METU, especially during precipitation and snow-melt events, and also when the influent P-concentrations fluctuate. Although the influence of organic matter (OM) on P-sorption is not well known, a negative relationship might have developed due to physical blockage of adsorption sites, or competition for sites by organic ions (Sakadevan and Bavor, 1998). On the other hand, some retention of P had been observed in association with organic matter, although most likely due to its Fe, Al and Ca content (Nichols, 1983; Reed and Brown, 1995; Sakadevan and Bavor, 1998).

4. Conclusions

This study aimed to assess whether a reed bed filled with blast furnace granulated slag, which is co-produced by KARDEMİR Iron and Steel Ltd., Co., Turkey, and has high phosphorus (P) sorption capacity, could be operated successfully under field conditions for P-removal. Thus, a vertical subsurface flow reed bed (30 m\(^2\)), planted with Phragmites australis was implemented at METU to treat primarily treated domestic wastewater and batch-scale P-sorption experiments were conducted.

The physico-chemical properties of blast furnace slag samples used in this study and in other studies given in the literature were found to be different from each other. The differences in those properties were thought to be due to the differences in the chemical and physical compositions of the slags produced in different places with different methods, due to differences in temperature at the time of water quenching and due to the variations in the experimental methodologies. Chemical P-fractionation experiments showed that the loosely bound P (49.22%) and Ca–P (43.10%) were found to be the predominant forms of P-mineral for the BFGS samples taken from the slag reed bed. Loosely-bounded P was due to the high metal content and large surface area of the BFGS, whereas Ca-bound P was due to high Ca content and basic conditions (pH > 7.7).

In the P-sorption isotherm studies conducted in this work, while the initial P-concentrations of the solutions changed between 0 and 320 mg L\(^{-1}\), the P-sorption capacities for the blast furnace granulated slag (BFGS) provided from the KARDEMİR Iron and Steel Company, Karabük, Turkey, have varied between 0 and 9150 mg P kg\(^{-1}\), respectively. For an initial P-concentration of \(\sim 7\) mg L\(^{-1}\), which corresponded to the average influent TP concentration of the primarily treated domestic wastewater, the P-sorption capacity was found to be \(\sim 150\) mg kg\(^{-1}\). However, according to the P-extraction and P-fractionation experiments performed for the BFGS samples, which were taken from the slag reed bed of METU after 12 months of operation, the P-remained in the slag material was \(\sim 70\) mg kg\(^{-1}\). Therefore, it can be concluded that the P-sorption isotherms may not be used to estimate the longevity of the reed bed of METU in terms of P-removal. The reed bed of METU was operated under field conditions with real primarily treated domestic wastewater for a 12-month monitoring period. During this period, \(\text{PO}_4^{3-}\)–P and TP concentrations fluctuated from 2.25 to 8.03 mg L\(^{-1}\) and from 3.59 to 9.47 mg L\(^{-1}\), respectively. The change of P-concentration resulted in varying P-sorption capacities. Moreover, the reed bed of METU received snow and rain, had dry and rest periods and fluctuating water levels, which could have influenced the Ca concentration in the treated wastewater in the bed and thus affected the lifetime of P-retention of the filter media. Nevertheless, the sorption isotherms can be used to select the most suitable filter material among several candidate filter materials in terms of P-sorption. However, further and longer investigations on P-removal of the slag in the reed beds are needed both in laboratory-scale and field applications.

References


