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Phosphate removal in constructed wetland with rapid cooled basic oxygen furnace slag

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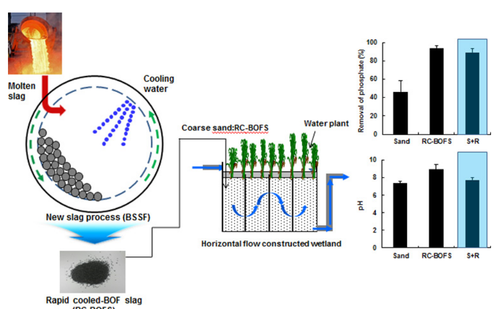
HIGHLIGHTS

- RC-BOFS was an effective adsorbent for phosphate.
- Contact time, initial concentration and pH value affect the adsorption capacity.
- Adsorption mechanisms were well described by SEM-EDS, XRD and FTIR.
- High phosphate adsorption capacity and near-neutral pH was observed in CW with sand and RC-BOFS.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this study was to evaluate adsorption characteristics of phosphate by rapid cooled basic oxygen furnace slag (RC-BOFS) through various conditions and removal rate of phosphate in small-scale constructed wetland with RC-BOFS as filter material. The phosphate adsorption by RC-BOFS was rapid in the first 0.5 h and the pseudo-second-order kinetic model fit the data better than the pseudo-first-order kinetic model. The maximum phosphate adsorption capacities of RC-BOFS under different pH were in the following order: 3.57 mg P g^{-1} (pH 5) > 2.47 mg P g^{-1} (pH 7) > 1.46 mg P g^{-1} (pH 9). Small-size RC-BOFS (0.8–2.3 mm) was more efficient with 23% higher phosphate adsorption than big-size RC-BOFS (2.3–4.6 mm). Characterization of RC-BOFS before and after phosphate adsorption by XRD, FTIR and SEM-EDS indicated that phosphate adsorption by RC-BOFS was dominated by metal oxide and precipitation by calcium and was closely related to the slag chemical properties. The phosphate saturation time in constructed wetland with coarse sand was predicted about 292 days, whereas the longevity of constructed wetland with adding about 25% RC-BOFS to the coarse sand can significantly increase up to 1349 days. It was concluded that the horizontal flow constructed wetland with sand 75%:RC-BOFS 25% ratio could achieve high phosphate removal rate and near-neutral pH for meeting the acceptable water quality discharge standard from water treatment plant.

1. Introduction

Constructed wetland (CW) technology was developed in 1970s as an alternative ecological technology for wastewater treatment

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[1]. This technology has been widely applied to domestic wastewater treatment in rural areas and small village in South Korea [2,3]. It possess several advantages compared with conventional wastewater treatment plants, such as low investment, maintenance and operation cost, utilization of renewable energy sources (wind and solar energy), and tolerance over variation of wastewater volume and level [4].

Constructed wetland design is based on natural components including soil, water plant and microorganism for wastewater treatment [5]. Particularly, the main treatment of nitrogen and organic matter contained in wastewater is by biological reaction. For example, nitrogen is removed through a combination of ammonification, nitrification and denitrification processes by associated bacteria with these in CWs [6,7]. Organic carbon can be removed by both aerobic microbial mineralization and anaerobic microbial methane formation [8,9]. For this reason, the removal of nitrogen and organic matter can be maintained stably even for long-term operation. However, the phosphate treatment mechanisms in CWs are adsorption/precipitation by filter media, uptake by aquatic plant, and immobilization by microbes [10–12]. Overall, phosphate removal occurs mainly as an effect of adsorption and/or precipitation by filter media with minerals based soil such as calcium, iron, magnesium and aluminum [13,14]. In particular, adsorption and precipitation can easily saturate the adsorption sites during pollutant treatment, thereby decreasing the treatment efficiency. Therefore, the selection of filter media with high adsorption capacity is essential to the design of CWs due to the consideration for the longevity of CWs. For this reason, study on new filter media to enhance the phosphate adsorption capacity has become a priority for researchers in the last two decades.

Numerous scientists have evaluated the potential of various filter media such as zeolite, aluminum oxide, limestone, peat, and mesoporous materials for treating phosphate in CWs [15–18]. These filter media however have several disadvantages including insufficient removal rate, high cost requirement, resource depletion, and low applicability for wastewater. Therefore, seeking alternative material for phosphate adsorption in CWs has become the focus for scientists in the past few years.

The slag discharged from the steel industry is one of the industrial wastes, the amount of which is about 27 million tons per year, and it is expected that the amount will be increased every years. Although slag has been used as raw material for cement and fertilizer and for construction and road materials [19,20], its wide use applicability has not been adequately tested. Over the past decades, many studies has reported that slag can be an effective material for the adsorption of phosphate from wastewater [3,21–23]. However, because of the high pH, the most slags studied are limited applicability to the wastewater treatment. Moreover, high pH in water adversely affects aquatic ecosystem such as plants and microorganisms [24,25]. Recently, the rapid cooled basic oxygen furnace slag (RC-BOFS) derived from economical and environmentally friendly new slag process (Baosteel Slag Short Flow) has been developed, which is derived from the molten steel slag and is treated in the roller body with compressed air and cooling water through the tilting device of the slag ladle and cinder scraper [26]. In a very recent study, Park et al. [3] reported that the free CaO content of the slag derived from BSSF is reduced due to the rapid cooling method, which would allow it maintain a lower pH and higher phosphate adsorption capacity than that of conventional slags. However, in the previous study, only phosphate adsorption capacity of RC-BOFS was compared with those of conventional slags, but no investigation under various conditions for application the actual CW was performed. Effects of several parameters such as initial phosphate concentration and pH, particle size and slag dosage, which are important for treating phosphate in CWs were not studied.

Therefore, in this work, we evaluated adsorption characteristics of phosphate by RC-BOFS in detail under various conditions. Then, based on the adsorption experiments, we estimated the saturation time for phosphate removal as RC-BOFS is applied in CW. In addition, adsorption mechanisms of phosphate on RC-BOFS were investigated using X-ray diffractometer (XRD), Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectrometer (EDS), and Fourier transform infrared spectroscopy (FTIR). Finally, the effectiveness of horizontal flow CWs with sand and RC-BOFS was evaluated for treating hydroponic wastewater containing high phosphate.

2. Materials and methods

2.1. Materials

The RC-BOFS was obtained from Gwangyang Iron and Steel Works, POSCO, South Korea. The physicochemical characteristics of the RC-BOFS were analyzed, and the results are shown in Table 1. The bulk density and porosity of RC-BOFS were 1.74 g cm^{-3} and 34%, respectively. The composition of RC-BOFS was mainly CaO (36.7%), Fe_2O_3 (24.2%), SiO_2 (13.4%), MgO (6.4%) and Al_2O_3 (3.3%). The RC-BOFS used in this study contain 1.12% free CaO which is an advantage for maintaining low pH as compared to BOFS (Free CaO = 4–6%) obtained from conventional method [27]. Generally the hydration reaction of free-CaO results in a high pH value in the aqueous phase [28].

2.2. Methods

2.2.1. Batch experiment

To establish the time dependence of phosphate adsorption on RC-BOFS, a series of suspensions in 100 mL glass Erlenmeyer flasks was prepared, each containing 2 g of RC-BOFS and 50 mL of phosphate solution having different concentration (10–200 mg L^{-1}). The initial pH value was adjusted to 7 by drop-wise addition of 0.1 M HCl or NaOH solutions with stirring. After equilibration under shaking for different time internals up to 24 h at 25 °C, the mixture samples were separated by centrifugation at 4000 rpm and the solution was filtered through a Whatman GF/C filter.

The adsorption behavior of the system for the process design and operation control is very important factors. To understand adsorption mechanism well, the pseudo-first-order model and pseudo-second-order model were used to investigate adsorption kinetics of phosphate onto RC-BOFS. These models as described by Lagergren [29] and Ho and McKay [30] respectively were fit to the experimental data to elucidate the phosphate adsorption mechanism onto the RC-BOFS. They are in the form:

Table 1
Physico-chemical characteristics of RC-BOFS.

Physico-chemical characteristics	Content
Porosity (%)	34
Bulk density (g/cm^3)	1.74
d_{10} (mm)	0.8
d_{60} (mm)	1.8
Specific surface (m^2/g)	0.38
Uniformity coefficient (d_{60}/d_{10})	2.25
pH (1:5H_2O)	9.1
SiO_2 (%)	13.4
Fe_2O_3 (%)	24.2
Al_2O_3 (%)	3.3
MgO (%)	6.4
CaO (%)	36.7
Free CaO (%)	1.12