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# Application of steel slag coated with sodium hydroxide to enhance precipitation-coagulation for phosphorus removal

Taejun Park [a], Vanvimol Ampunan [a], Sungkyu Maeng [b], Eunhyea Chung [a, *]

[a] Department of Energy System Engineering, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul, 08826, Republic of Korea
[b] Department of Civil and Environmental Engineering, Sejong University, Neungdong-ro 209, Gwangjin-gu, Seoul, 05006, Republic of Korea

## HIGHLIGHTS

- Phosphorus removal was demonstrated using sodium hydroxide coated slag.
- Coated slag caused high pH of the solution and increased the removal efficiency.
- When pH dropped below 8.0, phosphorus removal efficiency rapidly decreased.
- Ca, Mg, Al, and Na ions were consumed in the precipitation-coagulation process.
- Enhanced removal efficiency was obtained by recycling the initial effluent.

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## ABSTRACT

Phosphorus removal has been studied for decades to reduce the environmental impact of phosphorus in natural waterbodies. Slag has been applied for the phosphorus removal by several mechanisms. In this study, sodium hydroxide coating was applied on the slag surface to enhance the efficiency of precipitation-coagulation process.

In the batch test, it was found that the capacity of the slag to maintain high pH decreases with increasing its exposure time to the aqueous solution. In the column test, the coarse-grained coated slag showed higher phosphorus removal efficiency than the fine-grained uncoated slag. The coated slag maintained pH higher than uncoated slag and, accordingly, the removal efficiency of phosphorus was higher. Especially, when pH was less than 8, the removal efficiency decreased significantly. However, coated slag provided an excess amount of aluminum and sodium. Thus, a return process to reuse aluminum and sodium as a coagulant was introduced. The return process yields longer lifespan of slag with higher phosphorus removal and lower concentration of cations in the effluent. With the return process, the phosphorus removal efficiency was kept higher than 60% until 150 bed volumes; meanwhile, the efficiency without return process became lower than 60% at 25 bed volumes.

## 1. Introduction

Phosphorus plays a significant role for living creatures. However, an excess supply of phosphorus to the natural water systems can cause environmental problems such as eutrophication and algae bloom (Smith, 2003). Therefore, the regulation of the disposed phosphorus to the natural water system has been discussed for decades. Accordingly, numerous technologies and processes to reduce the phosphorus concentrations in wastewater have been developed.

Several researchers focused on a cost reduction by recovering useful minerals or using industrial byproducts in the process. Crystallization processes were designed to recover phosphate minerals in the form of hydroxyapatite or struvite (Morse et al., 1998; Claveau-Mallet et al., 2012; Kruk et al., 2014). Slag, red mud and fly ash were studied as a byproduct material to remove phosphorus (Koumanova et al., 1997; Li et al., 2006; Bowden et al., 2009). Especially, the steel slag has been studied by many researchers due to its sufficient ionic contents that can be utilized in the process and its high adsorption capacity (Yamada et al., 1986; Kostura et al., 2005; Gong et al., 2009). For the adsorption process, slag had been ground into fine size to increase the surface area

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* Corresponding author.
*E-mail address:* echung@snu.ac.kr (E. Chung).

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and treated with acid to lower pH for better adsorption efficiency (Xue et al., 2009).

Most of the previous studies focused on the adsorption capacity of the slag. However, the slag contains a large number of chemical species, which makes it suitable for the precipitation of calcium phosphate. Slag contains calcium and free limes (Shi, 2004) and they cause high pH (Azizi, 2014) and calcium-rich solution that would be an optimal condition for calcium phosphate precipitation (Jenkins et al., 1971).

There are mainly three kinds of steel slag mostly produced from steel manufacturing industry. Basic oxygen furnace uses melted metals from other furnaces and oxygen is blown to remove the impurities. In contrast, electric arc furnace melts several kinds of metals in the furnace such that alloy or stainless can also be added to the process. After the slag is moved from the two furnaces to ladle furnace, the ladle furnace slag is generated in the secondary process (Shi, 2004). The chemical composition of the steel slag varies by the slag type.

Several studies have shown the potential of phosphorus removal by precipitation-coagulation using the slag through lab-scale column tests (Drizo et al., 2006; Barca et al., 2014) and in constructed wetlands studies (Shilton et al., 2006; Pratt et al., 2007). Coagulation generally occurs in less than 10 s (Crittenden et al., 2005) and efficient removal of phosphorus is performed with a short hydraulic retention time (HRT).

The factors controlling the precipitation-coagulation process include pH, calcium ion concentrations, and coagulant types. Slag can provide sufficient calcium ions to a solution since more than 50% of slag is consisted of calcium containing minerals (Shi, 2004). However, the amount of lime in the slag is not sufficient to maintain high pH for a long time. Also, the elements that can play a role of the coagulants is not released enough to remove phosphorus in the solution. Therefore, the slag is easily exhausted and should be treated for reuse or replaced by new slag. Consequently, modification of the substances to maintain high pH for a longer time and to provide the consistent coagulation of phosphate precipitates is expected to extend the slag replacement period.

Sodium hydroxide coating is applied on the surface of the slag in this study. Sodium hydroxide can increase pH of the solution effectively. At the same time, a large number of sodium ions dissolved into the solution as an electrolyte will promote coagulation by destabilizing the system (Shaw, 1992). Therefore, the sodium hydroxide coating is expected to improve the phosphorus removal efficiency of the slag, especially through the precipitation-coagulation process.

## 2. Materials and methods

### 2.1. Wastewater sampling procedure

Flow back wastewater after the sludge treatment process was collected as a wastewater sample for the experiment. Since the flow back wastewater was generated by squeezing the spent sludge to obtain solid sludge for disposal, the water contains the high concentrations of many elements including phosphorus. Therefore, removal of phosphorus in this type of wastewater can lead to the reduction of phosphorus in the whole wastewater treatment system. The flow back wastewater was collected in a plastic bottle from the pipe connected to the sludge treatment process at the wastewater treatment plant in Suwon, South Korea. The samples were sealed and kept at 4 °C to maintain the condition of the samples.

### 2.2. Slag preparation

Ladle furnace (LF) slag was obtained from Dongbu Steel, Chungcheongnam-do, South Korea. The slag was ground and sorted into four grain sizes: 0.5–1, 1–2, 2–4, and 4–6 mm. The slag samples were kept in a zipped plastic bag to minimize contact with the atmosphere in order to minimize reactions with air including slag carbonation. The slag larger than 4 mm is used for the batch test, and smaller than 4 mm is used for the column test. The slag larger than 4 mm was chosen to see the dissolution trends in a short period of time as a basic study because the smaller slag would show better performance for a longer time. The slag samples were abbreviated by the coating (coated (C) and uncoated (U)) and grain sizes (0.5–1 mm (1), 1–2 mm (2), 2–4 mm (3), and 4–6 mm (4)). Six types of samples (U1, U2, U3, U4, C3, and C4) were tested in the study.

### 2.3. Slag coating process

The coating process is referred from the literature of Zhang and Itoh (2005). Sodium hydroxide was coated on the surface of slag whose particle size was 4–6 mm (C4) for the batch test and 2–4 mm (C3) for column test. After the slag had been dried in an oven at 105 °C, the 500 g of slag was stirred in1 L beaker of 1 M sodium hydroxide solution for two hours. The slag in the solution was aged at 80 °C for 48 h in an oven. Afterward, the slurry of the slag was heated at 105 °C for two hours in an oven and 550 °C for one hour in a furnace. Then, the slag was cooled down in room temperature and finally dried at 105 °C for 24 h.

### 2.4. Batch test

Batch test was designed to determine the factors affecting the slag exhaustion. 5 g of 4–6 mm grained slag (U4 and C4) samples were placed in 500 mL of distilled water and stirred at 100 rpm at room temperature. pH of the solution was measured over time. When pH of the solution reaches to 10.5, the time was recorded, and the water was replaced by fresh distilled water. A target pH was set as 10.5 because it is the preferable pH for the calcium phosphate formation using lime in conventional wastewater treatment (Jenkins et al., 1971; Tchobanoglous et al., 2004). The experiment was terminated when the time required to reach pH 10.5 exceeds one hour.

### 2.5. Column test

Diameter and height of the column were 3.7 mm and 2000 mm, respectively and the total volume of the column was 2 L. 200 mL of the slag was placed in the column, and the wastewater sample was fed upward from the bottom of the column at room temperature. The column HRT was 15 min and the flow rate was 8 L/h. The water sample for analysis was collected at the top of the column. After the column tests, the spent slag and the precipitates generated inside the column were collected for analysis. The collected slag and precipitates were dried at 30 °C in an oven and sealed in a petri dish to avoid the contact with air before analysis. The column tests were performed using different types of the slag (U1, U2, U3, and C3) to observe the effect of particle size and the coating. The sample was collected by a unit of bed volumes (BV) which was 200 mL in this study.

### 2.6. Analytical procedure

The pH and conductivity of the samples were measured by a multi-meter (Orion, STAR A329) and the cations were detected by