

Continuous phosphorus removal from water by physicochemical method using zero valent iron packed column

Joo-Young Jeong, Byoung-Min Ahn, Yu-Jin Kim and Joo-Yang Park

ABSTRACT

Excessive phosphorus in aquatic systems causes algal bloom resulting in eutrophication. To treat wastewater including effluent of wastewater treatment plant containing various amounts of phosphorus, a series of continuous experiments on removal of phosphorus from water were performed by using an electrochemical method. The spherical type of zero valent iron (ZVI) and silica sand were packed at appropriate volume ratio of 1:2 in a cylindrical column. An electric potential was applied externally, which can be changed as per the operational requirement. The results indicate that optimum hydraulic retention time of 36 min was required to meet the effluent standards with our laboratory-scale experimental setup. Lower amounts of phosphorus were removed by precipitation due to contact with iron, and additional electric potential was not required. In order to remove high amounts of phosphorus (around 150 mg/L as phosphate), external electric potential of 600 V was applied to the reactor. As the precipitation of phosphate mainly occurs at neutral pH, it is likely that FeHPO_4 will be the main phosphorus-containing compound. Through the results of the large-scale experiments, the ZVI packed reactor can be used as a filter for removal of phosphorus of less than 10 mg/L as phosphate concentration.

Key words | electro-coagulation, electrolytic cell, phosphate precipitation, wastewater treatment plant, zero valent iron

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INTRODUCTION

Phosphorus has a direct impact on eutrophication of both inland and coastal waters. Excessive phosphorus in aquatic systems causes algal bloom that leads to the depletion of the dissolved oxygen, dramatic decreasing of recreational value of water, and appearance of foul tastes in the drinking water (Ivanov *et al.* 2005, 2009; Vasudevan *et al.* 2008). The US Environmental Protection Agency (EPA) has recommended a limit to control eutrophication of 0.05 mg/L for total phosphorus in streams that enter in the lakes and 0.1 mg/L for total phosphorus in flowing streams (US EPA 1986). Various forms of phosphorus in municipal wastewater, such as ortho-, poly- and organic phosphate (Irdemez *et al.* 2006) are usually found in a concentration range of 5 to 20 mg/L (Ivanov *et al.* 2005). If those wastewaters are discharged without an appropriate management, it would lead to a serious loading of the surface water with phosphorus. In this respect, the limit for phosphorus concentration in the

effluent derived from wastewater treatment plant (WWTP), which is discharged in the aquatic systems, varies from 0.1 to 2.0 mg/L (Behbahani *et al.* 2011).

Currently, there are several chemical and biological methods which can be used for the removal of phosphate from wastewater. One of these methods is the precipitation of phosphate with lime ($\text{Ca}(\text{OH})_2$) leading to the formation of low soluble calcium-phosphate compounds. Aluminium or iron salts can also be used (Behbahani *et al.* 2011; Sibrell & Tucker 2012). Biological methods were also developed to remove the phosphate from water. These basically rely on the accumulation of intracellular polyphosphate during the alternating anaerobic and aerobic cycles. A combination of these processes was also applied to maximize phosphorus removal (Kang *et al.* 2003). However, generally, it is difficult to meet the water quality standards for phosphate by using conventional chemical and biological

methods, especially in large-scale installations (Moelants *et al.* 2011).

In this paper, a series of experiments were conducted in order to remove the phosphorus from water up to a value situated below the standard level, by using an electrolytic cell with a zero valent iron (ZVI) packed bed. The major parameters of the process such as the hydraulic retention time (HRT) and the applied external electric potential were investigated in order to determine the best operation conditions.

MATERIALS AND METHODES

Chemicals and materials

To prepare a synthetic wastewater contaminated with 150 mg/L of phosphate, sodium phosphate dibasic (Na_2HPO_4 , >99%, ReagentPlus, Sigma-Aldrich) was used. The sphere type of ZVI (specific gravity: 7.8, diameter: 0.6 mm) with iron content >98.4% (w/w) and silica sand (diameter: <0.3 mm) were supplied from Sanga Co. and Joo-moonjin Silica Sand Co. The volumetric packing ratio (v/v) of silica sand and ZVI is 2:1. A peristaltic pump (Easy-load[®] II, Cole-Parmer Instrument Co.) and tubing (4.8 mm inner diameter, 96410-25, Masterflex[®]) were used to feed the solution uniformly. A direct current power supply (XG600-2.8, Sorensen) was used to apply the electric potential (0–600 V) to the reactor and to measure the electric current consumption. To use the reactor as an electrolytic cell, platinum clad with niobium netting (Pt/Nb) was used as an anode placed at the bottom of the reactor to avoid the electrode corrosion, and stainless steel netting (SUS304) was used as a cathode placed at the top of the reactor. For reactor water tightness, a series of ring-type cork pads (thickness: 2 mm) were inserted between reactor joints, and the joints were connected by flange coupling. All aqueous solutions, including synthetic wastewater, were prepared by using deionized water, and the experiment was conducted at room temperature. The field experiments were carried out during 2 weeks by using wastewater treatment plant effluent with the cooperation of the wastewater treatment plant in Seoul.

Laboratory-scale and large-scale field experiments

The experiments were performed using an effective volume of 1 L laboratory-scale column and 10.2 L large-scale field column reactors (although the effective volume and shape of the reactors between laboratory and field were different, the internal configurations were the same). The ZVI

packed column for laboratory-scale experiment was constructed in a previous research (Jeong *et al.* 2012), and the cross-sectional view of the column reactor is described in detail in Figure 1. An acrylic resin was used to make the reactors, which were 8 cm diameter and 20 cm height for laboratory-scale cylindrical column, and 16 cm length, 16 cm wide and 40 cm height for large-scale field rectangular column (acrylic thickness: 1 cm). Inside of the reactor, an isolating layer of 1 cm thickness of silica sand was placed at the top and at the bottom of the reactor to prevent the contact between electrode and ZVI. After mixing by using a ball mill for around 1 h to get a uniform distribution, the resulting mixture of silica sand and ZVI was packed in the reactor. To improve the up-flow distribution, the spherical glass beads (10 mm diameter) were packed at the bottom of the reactor. The top of the reactor was designed with an open weir to dissipate the unexpected pressure and heat. The ZVI packed bed reactor is not only a physical contactor with iron and silica, but also an electrolytic cell when the electric potential is applied.

Analytical methods

The Hach model DR-2800 spectrophotometer was used to analyse nitrate, nitrite, ammonia, total nitrogen, phosphate, and chemical oxygen demand (COD_{cr}) according to *Standard Methods* (APHA 1998). The pH and electrical conductivity were measured using a pH meter Orion 8156BNUWP (Thermo Scientific, USA) and a conductometer Orion 013010MD (Thermo Scientific, USA).

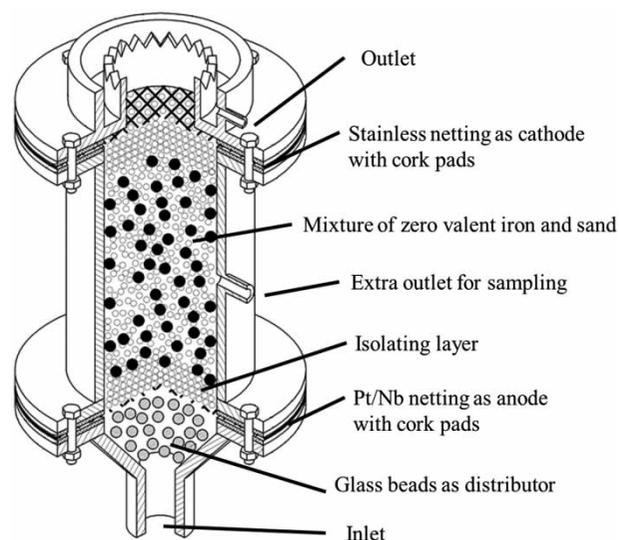


Figure 1 | Schematic view of the cross-section of the ZVI packed column with an effective volume of 1 L unit cell (laboratory scale).

RESULTS AND DISCUSSION

Effectiveness of the hydraulic retention time

To understand the effectiveness of the contact time with ZVI various experiments for different flow rate were carried out. Figure 2 shows the variation of the phosphorus concentration after the treatment of synthetic wastewater (a) and the variation of the electric current (b) at different flow rates (5–30 mL/min). The operation parameters were as follows: phosphorus concentration of 150 mg/L as phosphate, effective volume of reactor: 1 L, mixture porosity: 36% and external electric potential: 600 V (30 V/cm). As can be seen from Figure 2(a), the phosphate concentration in the effluent varies significantly as a function of the flow rate. As the flow rate increases, the electron flux is enhanced, that leads to an increasing electric current. When the flow rate was high, phosphorus removal was decreased because the HRT of wastewater in the reactor becomes shorter. In contrast, when the flow rate was low, phosphorus removal was increased. This indicates that the removal mechanisms such as precipitation and adsorption were greatly affected by the contact (retention) time. Therefore, it seems to indicate a better phosphorus removal from water when small iron particles or good physical mixing was used. In this experiment, the most appropriate flow rate was 10 mL/min (HRT: 36 min). In this case, the phosphorus removal rate was 99.7%.

Effectiveness of the external electric potential

To evaluate the effectiveness of the external electric potential to remove phosphorus from water, experiments were

conducted by varying the external voltage while maintaining a flow rate of 10 mL/min (the reactor configuration and initial concentration are the same as for previous experiments). Figure 3 shows the results regarding the phosphate concentration (a) and pH and electrical conductivity (b) at different external electric potential ranging from 0 (control) to 600 V. As can be seen, phosphorus in water was removed by around 12% by natural iron action induced by corrosion without any external electric potential. When the voltage was increased to 100, 200, 300, 400, 500 or 600 V, the phosphorus removal efficiency was proportionally increased to 27, 43, 68, 75, 89% or more than 99%. It is considered that the pH was reduced to around 4 due to generation of hydrogen ions by electrolysis of water at the anode. Thus, the corrosion of iron was promoted (Jeong *et al.* 2012) and then the generated iron ions were removed by precipitation with phosphate in water (Ikematsu *et al.* 2007). Because it is known that the phosphate and iron combine well each other at neutral pH and form FeHPO_4 (Ivanov *et al.* 2005), the phosphate in the acidic solution is expected to be precipitated and adsorbed (on the iron particle surfaces) at the same time. However, excessive external electric potential will cause safety issues, high operating costs and fast oxidation of iron. Thus, the external voltage should be controlled in relation to the phosphorus concentration in the influent. In the case of the influent phosphate concentration of around 150 mg/L, a maximum 99.8% of phosphate was removed at external voltage of 600 V (30 V/cm).

When the polarity of electrodes was reversed (cathode: bottom of the reactor, anode: top of the reactor), the phosphorus from water was not removed properly (data not shown). It is considered that hydroxide ions generated by

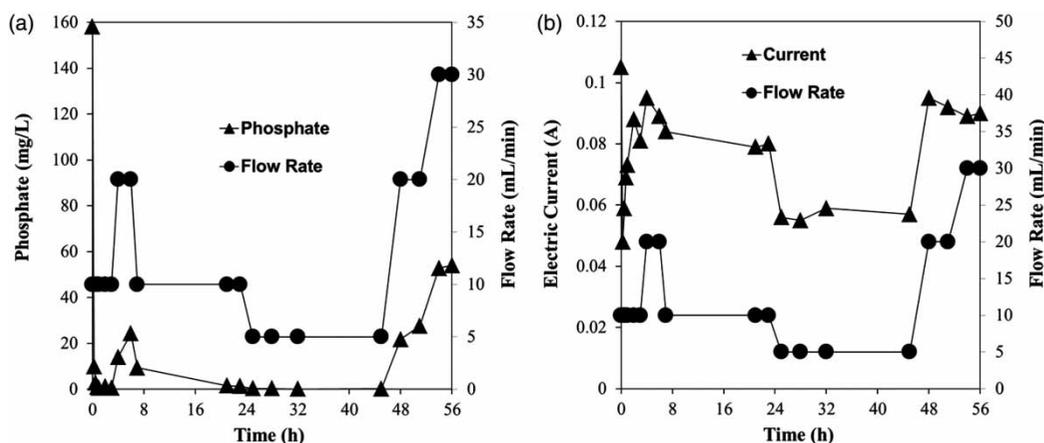


Figure 2 | Variation of the phosphate removal (a) and the electric current (b) at different flow rates (initial phosphorus concentration, 150 mg/L as PO_4^{3-} ; electric potential, 30 V/cm, effective volume of the reactor: 1 L, porosity: 36%).

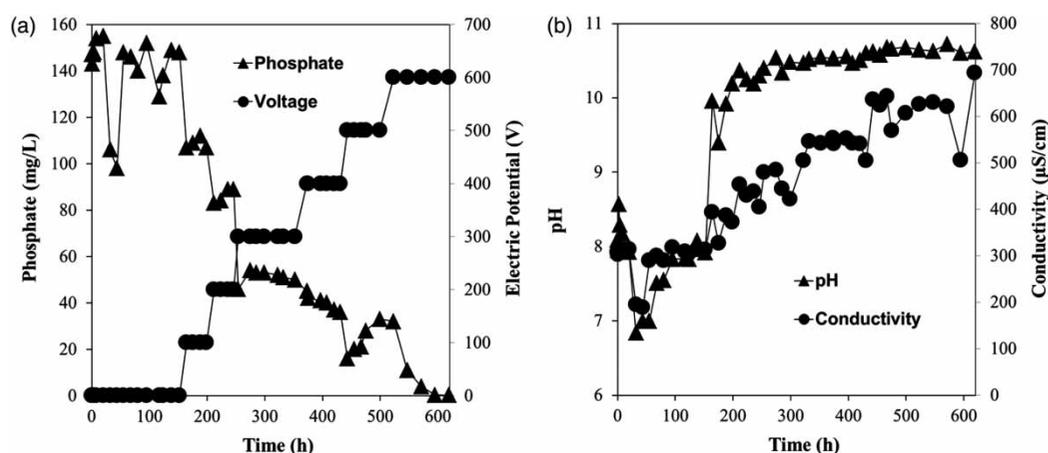


Figure 3 | Variation of the phosphate removal (a) and the pH and electrical conductivity (b) of different electric potentials (initial phosphorus concentration, 150 mg/L as PO_4^{3-} ; flow rate, 10 mL/min).

Table 1 | Characteristics of wastewater treatment plant effluent (August 2012)

Parameter	Value
pH	5.9–6.5
Electrical conductivity ($\mu\text{S}/\text{cm}$)	322–404
Total phosphorus (mg/L as PO_4^{3-})	3.4–7.8
COD_{cr} (mg/L)	23–37
Nitrate (mg/L as N)	6.1–7.8
Nitrite (mg/L as N)	N. D.
Ammonia (mg/L as N)	0.2–0.4
Total nitrogen (mg/L as N)	6.8–9.8

N.D.: not detected.

electrolysis of water at the cathode delayed iron oxidation because of alkalized solution (Jeong *et al.* 2012). Therefore, phosphorus in water was not adequately precipitated and adsorbed. The pH of the effluent was increased to around 10 due to the electrolysis of water at the cathode. The electrical conductivity was increasing constantly due to leaching of iron ions through stepwise increasing of the external electric potential as shown in Figure 3(b). In additional experiments, phosphorus removal efficiency was increased by adding a support electrolyte such as nitrate. It seems to promote iron oxidation because of the higher electrical conductivity related to higher current flows.

Laboratory-scale column test using WWTP effluent

Based on the previous experimental results, a real effluent of a wastewater treatment plant was used to remove its phosphorus content. The characteristics of final clarifier

effluent of the wastewater treatment plant in Seoul which was used in the experiments are shown in Table 1.

Figure 4(a) shows the results regarding the phosphorus and nitrogen removal from wastewater treatment plant effluent at an external electric potential of 600 V and a flow rate of 10 mL/min (HRT: 36 min). In the case of the wastewater treatment plant effluent, the phosphorus in water was removed quickly. After 2 h from the start of the experiment, 0.5–0.8 mg/L of phosphate was still found in the treated water. Denitrification was observed at a magnitude of approximately 30% as the positive effect of electrolysis. This effect is attributed to ammonia, which is the nitrate reduction product stripping phenomenon occurring due to generated oxygen caused by electrolysis and alkaline environment near the cathode.

Figure 4(b) shows the results regarding the variation of the phosphorus and the variation of pH without external electric potential for the same experimental conditions presented in Figure 4(a). When the initial concentration of phosphorus was low enough, like in the wastewater treatment plant effluent, the phosphorus was removed by up to 88% from water through natural iron oxidation, adsorption on its surface and precipitation without external electric potential. In this case, the concentration of phosphate in the effluent could be reduced up to about 1 mg/L. These results indicate that the iron-packed reactor can be used as a ‘filter’ for the treatment of wastewater containing low concentration of phosphorus. As can be seen from Figure 4(b), the pH decreased by approximately 0.4 units compared with the initial one. The hydrogen ions that are generated in the process of phosphate precipitation lead to reduction of the pH value (Stabnikov *et al.* 2004).

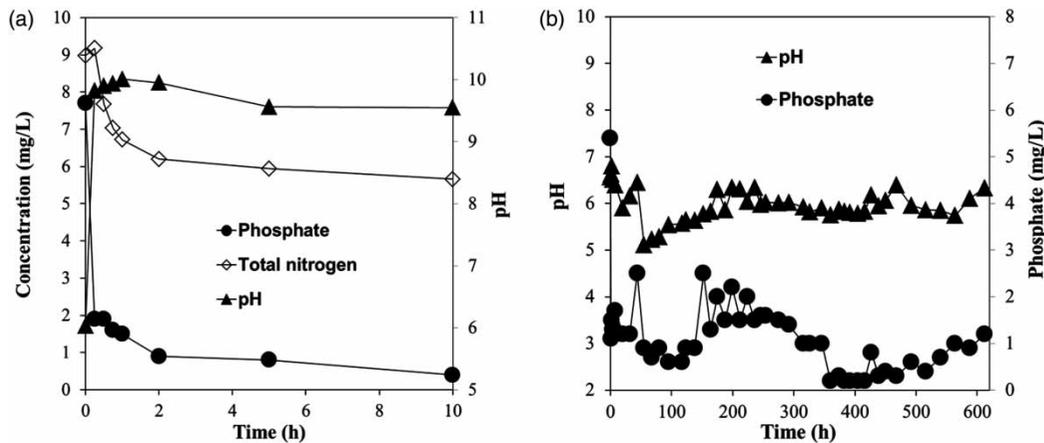


Figure 4 | Variation of the phosphate and total nitrogen removal from wastewater treatment plant effluent in laboratory-scale experiments with external electricity of 600 V (30 V/cm) (a) and without external electricity (b) (flow rate: 10 mL/min; HRT: 36 min).

Large-scale column field test in WWTP

Based on the results of the laboratory-scale experiments, a field test was carried out to evaluate the possibility of applying this method for wastewater containing low concentration of phosphorus such as sewage treatment plant effluent. A reactor with an effective volume of 10.2 L was used (around 10 times bigger than laboratory-scale reactor). The HRT was kept the same as in laboratory experiments (around 36 min) without external electric potential. As is shown in Figure 5(b), the phosphate was removed by more than 90%, and in this respect the concentration in the effluent was maintained at values less than 0.5 mg/L at flow rate of 100 mL/min. However, some channeling phenomena were observed because of

the heterogeneous corrosion of iron. In the reactor, iron corrosion promotes the cementation problems between ZVI and sand by making iron oxides such as magnetite (Fe_3O_4) (Jeong *et al.* 2012). Also, the smaller ZVI will accelerate the channeling phenomenon due to increasing of the reaction surface. In addition, the oxidized iron covered with a passivation film of phosphate may cause obstruction problems because of the greater corrosion resistance (Boshitska *et al.* 2012). As can be seen from Figure 5(a), the pH increased in comparison to its initial values, and this could be the effect of the generation of the hydroxide ions during the oxidation of the iron. In order to prevent channeling and maximize the contact with iron at the same time, a small cross-sectional area and a long-shaped reactor will be much advantageous.

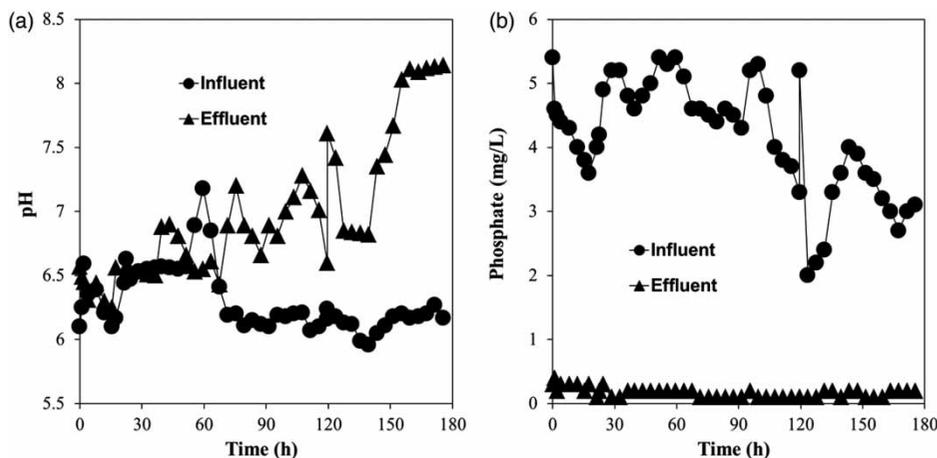


Figure 5 | Variation of the pH (a) and phosphate concentration (b) before/after the treatment without external electricity in large-scale field experiments (flow rate: 100 mL/min; HRT: 35–36 min).

For practical application, a post-treatment is required to neutralize the pH and to remove the excess amount of iron ions of the effluent.

CONCLUSIONS

The HRT of 36 min (10 mL/min at 1 L reactor) and the external electric potential of 600 V (30 V/cm) were required to meet the effluent standards of 0.5 mg/L in the laboratory-scale experiments conducted to treat water with 150 mg/L phosphate. Additionally, the nitrogen in water was removed by around 30% when an external electric potential was applied. In order to remove the high concentration of phosphorus from water, a high HRT and an external electric potential were needed. Lower concentrations of phosphorus (less than 10 mg/L as phosphate) in water were effectively treated (around 90% removal) without external electric potential in the field-scale experiments. This study serves as a background for developing an advanced wastewater treatment technology for the treatment of wastewater polluted with various levels of phosphorus. Wastewater with high phosphorus content such as a specific industrial wastewater or returned activated sludge is expected to show promising results by physical contact with iron and electrochemical reaction in a ZVI packed column.

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