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Continuous-flow of Nanoscale Zero Valent Iron based system for phosphorus removal

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Abstract: In this study, the removal performance of nZVI for phosphorus under different five conditions such as 1) open (with Polishing Unit (1a) and without one (1b)), 2) full aerobic (air flow=1.2L/min. (2a) and 1L/min. (2b)) and 3) full anaerobic conditions (nitrogen flow=3L/min) were analyzed. The initial phosphorus concentration and feeding rate were maintained each approximately 25 mg P/L and 20 ml/min. In each condition, the reactor phosphorus removal rates for initial 3 hours were $77.6 \pm 10.2\%$ (1a), $96.3 \pm 1.7\%$ (1b), $95.6 \pm 1.4\%$ (2a), $95.5 \pm 2.3\%$ (2b) and $96.8 \pm 2.0\%$ (3). From these results, there are no big differences between them. However, all of the rates decreased to about 50 to 80% after 12 hours. The effluent total iron concentration from the reactor was also analyzed and the correlation with the effluent phosphorus concentration was calculated. As a result, correlation coefficient was $R^2=0.963$ (2a), $R^2=0.897$ (2b), $R^2=0.885$ (3) respectively, and it was confirmed that there is positive correlation.

Keywords: Phosphorus removal, nano-scale zero valent iron (nZVI), continuous stirred tank reactor (CSTR)

1. Introduction

Although phosphorus is an essential element to all forms of life on Earth, its excessive amounts lead to eutrophication in natural environments such as reservoirs, lakes, and coastal areas [1]. Eutrophication results in the depletion of oxygen that leads to fish death and effects on aquatic environment. In recent years, due to importance of nano technologies, nano-scale zero-valent iron (nZVI) has been investigated and used in the removal not only phosphorus but also several environmental pollutants from aqueous systems. nZVI has large active surface area and high phosphorus sorption capacities [2]. In particular, several research reports that aimed at elucidating the removal mechanism of phosphorus and phosphate by nZVI have been reported [3-6]. However, these research reports only report short-term processing by batch tests. Therefore, there are not many reports on applying these technologies to actual water treatment systems. In the field of water treatment research, before installing full-scale plant, the Continuous Stirred Tank Reactor (CSTR) is used at laboratory to evaluate about the parameter for designing full-scale one. Because if the reaction rate is higher than the first order, CSTR can be used to reduce the reaction rate and measure it. Since it is operation in a steady state, sampling of the reaction intermediate becomes easier in case of sequential reaction [7]. Also this is widely known as one of the chemical process reactor. In this system, one or more reactants (i.e. In solution or as a slurry) are introduced into a reactor equipped with an impeller (stirrer) and the products are removed continuously. The impeller mixed the chemicals vigorously to ensure well mixing so that there is a uniform composition throughout. The composition at the effluent is the same as in the bulk in the reactor [8].

The objective of this work is to obtain some optimized condition for removing phosphorus by nZVI using CSTR. Five experiments were conducted for different atmospheric by using open, full aerobic and full anaerobic condition.

2. Materials and methods

2.1 Chemicals

The following chemical reagents and materials were used: Sodium borohydride (NaBH₄, 98.0%, Junsei Chemical Co., Japan), ferric chloride hexahydrate (FeCl₃ · 6H₂O, 99.0%, Junsei Chemical Co., Japan), potassium dihydrogen phosphate (KH₂PO₄ 99.5%, Kanto Chemical Co., Japan). Nitrogen gas was purged all prepared solutions for de-oxygenation. All chemicals were applied as delivered without further purification.

2.2 Synthesis of nZVI

nZVI was synthesized as depicted from the following chemical reaction (Eq. (1)) [9]



Solution 1 was prepared by dissolving 21.0 g of sodium borohydride in 1,200 mL of deoxygenated deionized water (DIW). Solution 2 was prepared by dissolving 50.0 g of ferric chloride hexahydrate in 1,200 mL of DIW in separate flask. Then solution 1 was added to solution 2 using a roller pump at a rate of 16 mL/min. with vigorous stirring at 250 rpm under nitrogen atmosphere at constant temperature 25 ± 0.5 °C using water bath. The synthesis was conducted in 5,000 mL four-neck glass flask and left 20 min for aging to complete the reaction. The synthesized iron particles have been filtered by vacuum filter, washed with DIW three times and immediately used in continuous experiments.

2.3 Phosphorus solution quality

The potassium dihydrogen phosphate was used as a phosphorus source and it was diluted with tap water by up to approximately 25 mg P/L. The phosphorus concentration was fixed within whole experiments. And their pH, ORP, DO was 7.0 ± 0.2 , 0.2 ± 3.5 mV, 10.2 ± 2.5 mg DO/L respectively.

2.4 Process of continuous experiment

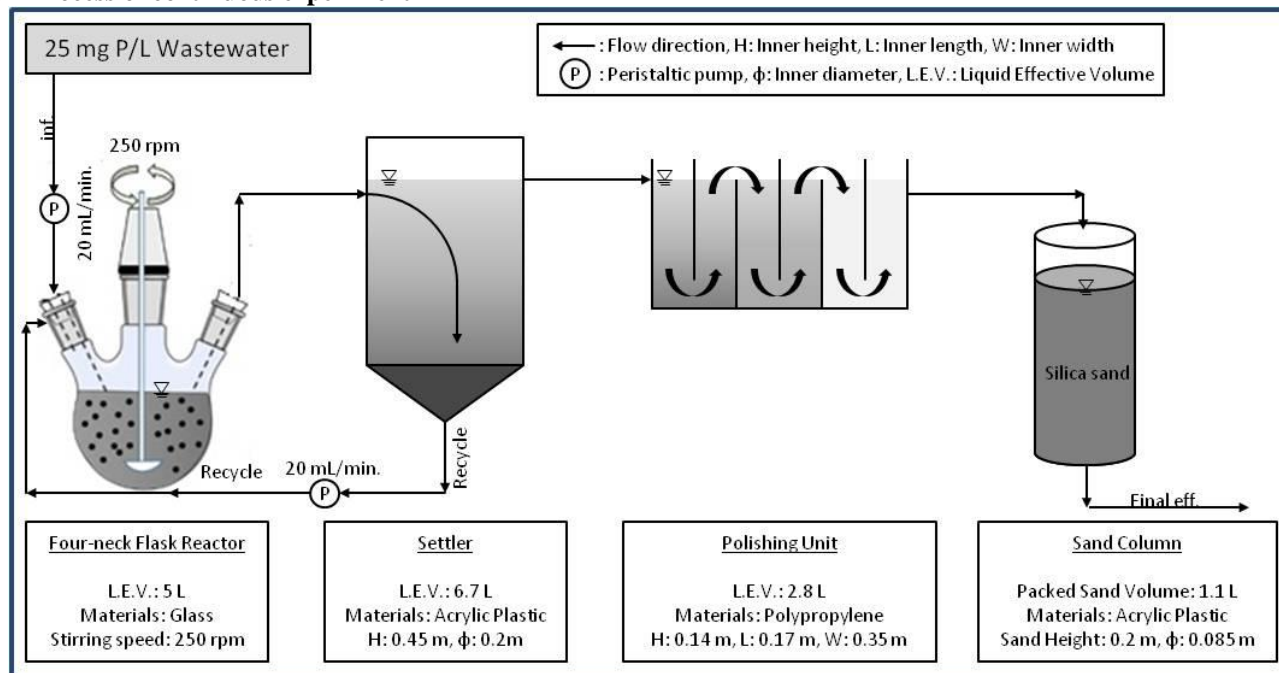


Fig. 1 The flow diagram of the laboratory-scale continuous flow system,

Table 1 Operation condition of continuous system

No.	nZVI Dosage (g)	Condition	Air Flow Rate (mL/min.)	Phosphorus Feeding Rate (mL/min.)	With or Without Polishing Unit	Initial Phosphorus Concentration (mg/L)	Note
1	10	Open	-	40	With	23.5	
2	10	Open	-	20	Without	23.5	
3	10	Full Aerobic	1200	20	With	23.5	
4	10	Full Aerobic	1000	20	With	26.1	
5	10	Full Anaerobic	3000	20	With	26.1	

Pilot process and reactors are illustrated in Fig. 1. The treatment process consisted by Four-neck flask reactor, settler, polishing unit and sand column. The four-neck flask was a glass flask with an effective volume of 5 L. The artificial wastewater was supplied by a peristaltic pump at 20 mL/min, and stirred with an impeller (stirrer) at a speed of 250 rpm to mix the phosphorus solution and nZVI vigorously. Settler was made by acrylic materials with an effective volume of 6.7 L. The settled nZVI was recycled to four-neck flask reactor by a peristaltic pump at 20 mL/min. The polishing unit and was made by polypropylene materials with an effective volume of 2.8 L. Five baffles were installed of this polishing unit. The sand column was made by acrylic materials with an effective volume of 1.1 L. The silica sand (JIS standard sand, Silica sand No.5) was packed with 1.1 L.

The five different condition experiments were conducted in this study (Table 1). In all experiments, nZVI dosage and phosphorus concentration of phosphorus solution were fixed with 10 g and 24.5 ± 1.2 mg/L, respectively. In experiment 1, the atmospheric condition in the reactor was kept an open state, and any aeration operation was not conducted. Phosphorus solution feeding rate was set to 40 mL/min. And a polishing unit was provided after the settler. In experiment 2, the atmospheric condition in the reactor was kept an open state. In this condition, in order to investigate the influence on the treatment due to the change in the phosphorus solution feeding rate, it was 20 mL/min. In addition, it was found that the polishing unit has low phosphorus removal performance under

experiment 1. Therefore, in experiment 2, it was conducted without setting the Polishing Unit. The experiment 3, the atmospheric condition in the reactor was kept with full aerobic by using an air pump (NISSO CHIKARA @4000 SW, NISSO co.ltd. Japan). The air flow rate was 1200 mL/min. In experiment 2, experiments were conducted without installing Polishing Unit. As a result, it did not contribute to the removal of phosphorus, but it was confirmed that it contributed greatly to the removal of total iron, so from the experiment condition 3, the installation of the Polishing Unit was resumed. Experiment 4, the operation was carried out with the air supply amount reduced to 1000 mL/min. This is to investigate a change in the removal performance of phosphorus due to a change in the air flow rate. For the experiment 5, the atmospheric condition in the reactor was kept as a full anaerobic using nitrogen gas. The nitrogen gas flow rate was 3000 mL/min. The experiment was terminated when the phosphorus concentration of the polishing unit was more than 10 mg / L.

2.5 Analysis

Concentration of phosphorus and iron compounds in solution samples were colorimetrically obtained by using an UV-Vis spectrophotometer (DR 3900, HACH Co., USA) via USEPA PhosVer 3 (Ascorbic acid method) at 880 nm and TPTZ (2,4,6-Tri (2-pyridinyl)-1,3,5-triazine) method at 590 nm, respectively.

3. Results and Discussion

3.1 Summary of phosphorus removal

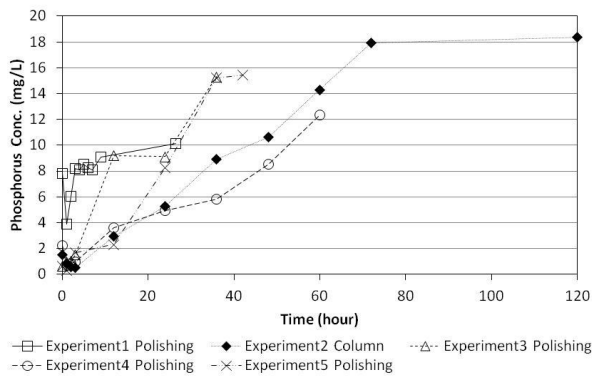


Fig.2 (a) Phosphorus concentration after Polishing Unit

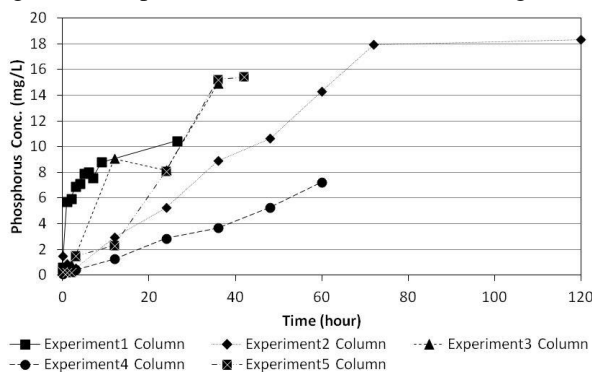


Fig.2 (b) Phosphorus concentration after Sand Column

Fig. 2 (a - b) shows the change in the phosphorus concentration obtained in the continuous experiment. Fig. 1 (a) shows the change the phosphorus concentration after Polishing Unit, Fig. 1 (b) after Sand Column. In Experiment 1, the phosphorus concentration after the Polishing Unit was 3.87 mg/L 1 hour after starting the experiment. However, after 2 hours, the phosphorus concentration was about twice as high. After that, the phosphorus concentration exceeded 10 mg/L after 26.5 hours, so the experiment was terminated. In Experiment 2, Polishing Unit was not installed, so we show the result of sand column only. In Experiment 2, since the flow rate was reduced to half that of Experiment 1, the phosphorus concentration at the 0 hour start of the experiment was 1.51 mg/L. Also, the phosphorus concentration was kept below 1 mg/L until 3 hours after the start of the experiment. In Experiment 1, the phosphorus concentration was more than 10 mg/L 24 hours after the start of the experiment, but in this experiment it was about 5.25 mg/L, which was about half. From these results, it was suggested that the optimal flow rate for this system is 20 mL/min. After that, as a result of continuous experiment, it became 10.65 mg/L after 48 hours, and it was confirmed that it can be used about twice as long as Experiment 1. In Experiment 3, the phosphorus concentration remained below 1.5 mg/L until 3 hours after the start of the experiment, both sand column and polishing unit. However, after 12 hours, both the polishing unit and the sand column showed a phosphorus concentration of near 9 mg/L, which rapidly increased. Oxidation of nZVI is considered as a cause of these phenomena. I would like to describe them in detail in section 3.3. In Experiment 4, the phosphorus concentration was less than 1 mg/L in both cases until 3 hours after the start of the experiment. In Experiment 4,

the phosphorus concentration of the Polishing Unit became 10 mg/L or more after 48 hours from the start of the experiment. In Experiment 5, similar to other conditions, the phosphorus concentration remained at around 1.5 mg/L until 3 hours after the start of the experiment. However, the phosphorus concentration increased to about 8 mg/L 24 hours after the start, and increased to 15 mg/L after 36 hours.

3.2 Phosphorus removal effect of time

Section 3.1 outlined the removal change of phosphorus obtained by continuous experiments. Section 3.2 describes the change in phosphorus concentration up to 12 hours after the start of the experiment. Fig. 3 shows the phosphorus concentration changes until 3 hours after starting the experiment. In the four experiments except Experiment 1, the phosphorus concentration after 3 hours is less than 2 mg/L for both Polishing Unit and Sand Column. Also, the bar graph (Fig. 4) shows the average of the phosphorus removal efficiency up to 3 hours after the start of the experiment. In each condition, the reactor phosphorus removal rates for initial 3 hours were $77.6 \pm 10.2\%$ (Experiment 1), $96.3 \pm 1.7\%$ (2), $95.6 \pm 1.4\%$ (3), $95.5 \pm 2.3\%$ (4) and $96.8 \pm 2.0\%$ (5). From these results, there are no big differences between them.

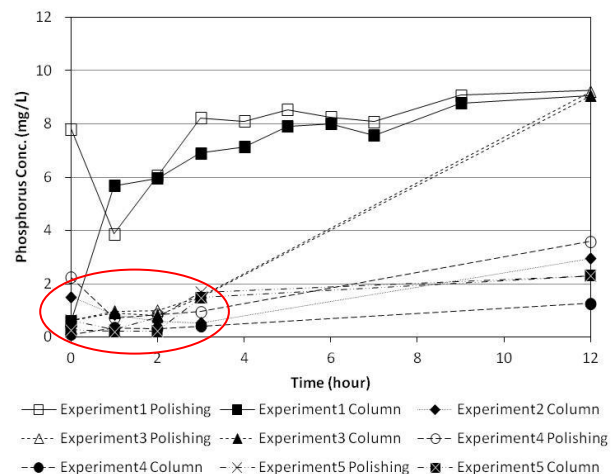


Fig.3 Phosphorus concentration up to 12 hours after the start of the experiment

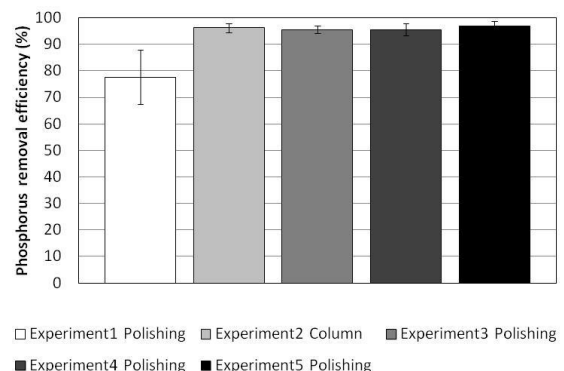


Fig.4 The average of phosphorus removal efficiency up to 3 hours after starting experiment

3.3 Phosphorus removal effect of iron concentration

Fig. 5 shows the change in effluent total iron concentration. Experiment 1, both the Polishing Unit and the Sand Column showed high effluent total iron concentration, showing a maximum of 10 mg/L. In Experiment 2, the effluent of total iron concentration was stable throughout the whole period and was maintained

at about 4 mg/L. Experiment 1 is that the supply wastewater flow rate was larger than Experiment 2. As a result, it was suggested that the effluent total iron concentration was high in Experiment 1. In Experiment 3, the effluent total iron concentration in the Polishing Unit was high, which was as high as about 10 mg/L at the maximum. In Experiment 3, the atmospheric condition in the reactor was maintained as Full Aerobic condition. The air flow rate was too strong, and a lot of total iron flowed out from the reactor. It flowed out to Settler with a large amount of air, so it is thought that all the iron particles flowed out to the Polishing Unit without successful precipitation. In Experiment 4, the flow rate of air was adjusted and the experiment was carried out again. As a result, the effluent total iron concentration compared to Experiment 3 did not exhibit more than 10 mg/L, it was confirmed that 8 mg/L from Polishing Unit is best runoff. In Experiment 5, an experiment was conducted with Full Anaerobic condition. Nitrogen gas supply amount was 3000 mL/min. It was very high compared with Experiment 3, 4. However, compared to Experiments 3 and 4, the effluent total iron concentration of the Polishing Unit was up to 4 mg/L or less. Under anoxic conditions, the core-shell structure of nZVI is well maintained after 72 h. Under oxic conditions, the core-shell structure quickly evolves. The particles may maintain the spherical shape at the initial corrosion stage, and eventually evolve into flaky and/or acicular-shaped structures [10]. For these reasons, Experiment 3 and 4 will collapse the form of particles by oxidation of nZVI, may have a large amount of flow out is pointed out that gradually decreases. From now on, it is necessary to analyze the optimum air flow rate and the surface characteristics of the oxidized particles and consider the method to prevent the outflow of iron particles. The effluent total iron concentration from the reactor was also analyzed and the correlation with the effluent phosphorus concentration was calculated. As a result, correlation coefficient was $R^2=0.963$ (Experiment 3), $R^2=0.89(4)$, $R^2=0.885(5)$ respectively, and it was confirmed that there are positive correlation.

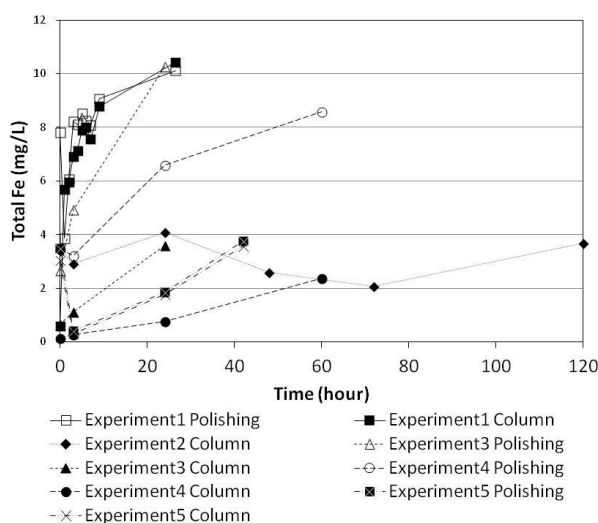


Fig.5 Total iron concentration

4. Conclusion

The objective of this work is to obtain some optimize condition for removing phosphorus by nZVI using CSTR. From the results of Experiment 1 and 2, it was suggested that the phosphorus solution flow rate acceptable for the current system and dosage of nZVI is about 20 mL/min.

In addition, it was confirmed that the removal performance of nZVI was the highest at about 3 hours. Also, about 3 hours after the start of the experiment, no significant change in removal performance was observed under any conditions. However, under aerobic conditions, it was suggested that particle collapse due to nZVI oxidation occurred. It was also found that a large amount of collapsed particles outflow and prevented improvement in removal performance. From now on, it is considered that it is possible to investigate optimal operation conditions by examining nZVI outflow prevention measures and conducting experiment again under the same conditions.

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