室内カラム試験におけるナノ粒子ゼロ価鉄を用いたリン除去

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Investigation on Phosphorus Removal from Water
Using Nanoscale Zero Valent Iron:
Column Experiments

室内カラム試験における
ナノ粒子ゼロ価鉄を用いたリン除去

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Abstract

In recent years, the interest in permeable reactive barriers (PRBs) as in-situ groundwater purification technologies has risen. Nanoscale Zero Valent Iron (NZVI) is one of the most promising material used in PRBs due to its applicability and low cost. Although several studies have proved efficiency of NZVI on phosphorus removal in batch experiment, little study has been done to examine under environment close to actuality such as column experiment. The present study was undertaken in order to investigate a rational design on phosphorus removal by NZVI for PRBs application. Research on the laboratory-scale column (100 cm length, 10 cm inner diameter) was conducted under ten different conditions. Effect of modified NZVI (Fe/Cu), support material, pore water velocity through the column and various state of NZVI were examined on phosphorus removal. Also, multi-layer design was proposed as a new method in PRBs and evaluated. Results indicated that the addition of copper onto surface of NZVI enhanced phosphorus removal in porous media. It seems possible that this result is due to low pH values caused by the addition of copper. Efficient removal of phosphorus was observed with low flow rate condition. Also, the results signified that proposed multi-layer design had a possibility to be contribution on removing phosphorus, however, pH values and characteristics of support material might be key parameters in case of using modified NZVI (Fe/Cu).

Contents

Chapter 1

Introduction

1.1   Background

There has been a significant concern about water pollution caused by many sources such as untreated human wastewater, industrial waste and fertilizer. Water is indispensable to sustain human life and social life. In recent years, demand for water has been growing due to population increase and economic development. According to an OECD* report [1], water scarcity may affect more than 40 percent of people in the world by 2050. Even in the present situation, some people worldwide lack access to water, particularly in developing countries. Polluted water is utilized as drinking and daily life water because of the lack of wastewater purification facilities. Substances which induce water pollution are harmful to human bodies and ecological system. Therefore, wastewater treatment has become one of the most crucial topics.

Above all, treating groundwater is a matter requiring immediate attention. It requires a long period of time to replace polluted water with clean water since underground water flows slowly [2]. Hence, a groundwater pollution needs immediate action. Groundwater purification facilities have been becoming pervasive these days in developed countries, including Japan. However, the problem remains unsolved in developing countries due to economic reasons. From these viewpoints, it is important that groundwater treatment application which is low cost and can be widely spread is discussed.

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*OECD: Organisation for Economic Co-operation and Development

1.2   Technologies of treating groundwater

Many technologies have been applied to solve the groundwater pollution. These technologies can be classified as above ground methods (ex-situ), such as reverse osmosis and ultrafiltration or below ground methods (in-situ). Both technologies have their advantages and disadvantages in treating groundwater. Over the past decades, in-situ remediation has attracted a great deal of attention owing to its low cost. In particular, researchers have shown an increased interest in permeable reactive barriers (PRBs).

1.3   Permeable Reactive Barriers

PRBs is considered to be one of the most promising in-situ technologies. This technology has expectations of the dissemination and more development due to its low cost and easiest of maintenance. A schematic diagram of PRBs is shown in Figure 1.1. PRBs is a wall placed below ground and allows groundwater to pass through it. Reactive material inside the barrier removes contaminants from groundwater while water flows through the wall. Additionally, PRBs is responsible for preventing diffusion of polluted zone.

In order to remove contaminants effectively, it is important to select the appropriate reactive material. Many reactive materials have been used in PRBs such as granular zero-valent iron, zeolite and marble. Among them, the most common material in PRBs is considered to be zero-valent iron (ZVI). To date, ZVI has been applied in the construction of more than 200 PRBs worldwide [3]. Several researchers [4, 5] have reported that PRBs using ZVI can remove various contaminants and remain effectiveness for a period of 15 years.
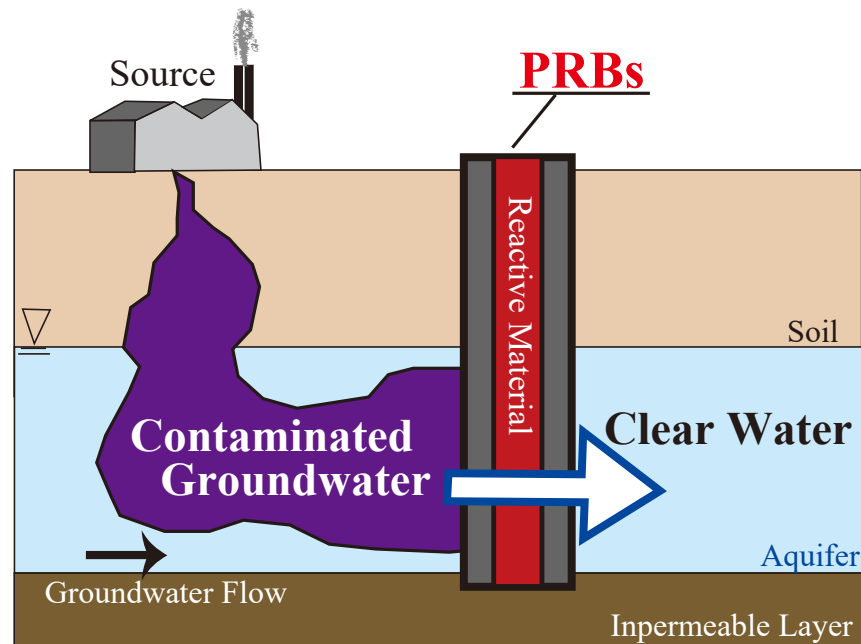
Fig. 1.1 Schematic diagram of Permeable Reactive Barriers.
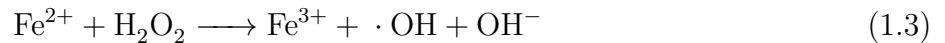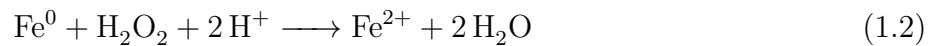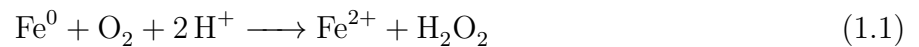
1.4 Zero-Valent Iron

Recently, researchers have shown an increased interest in method for removing contaminants by ZVI. ZVI (Fe^0) is a zero form of iron in micro-scale granular and has core-shell structure. ZVI is abundant as iron is the fourth most common element in the crust of Earth. Besides, ZVI is cheap, non-toxic, easy to produce, and its reduction process requires little maintenance.

ZVI has been used successfully to remove various contaminants in aqueous such as azo dye [6], heavy metal ions [7], phosphorus [8] and organic compounds [9]. Main removal mechanisms by ZVI are shown in Figure 1.2. Chemical and physical removal occur simultaneously including reduction, adsorption, precipitation and co-precipitation. Tokumura et al. [10] has reported that ZVI provides four forms of iron, which contributes to the contaminants removal directly or indirectly. First, the core zero valent iron acts as an electron source. Second, the oxide shell facilitates adsorption of contaminants via electrostatic interactions. Third, the separating iron ions (Fe^{2+}, Fe^{3+}) cause precipitation and co-precipitation as flocculants. Finally, the Fe complex removes contaminants by sedimentation. The important redox reactions are provided below.
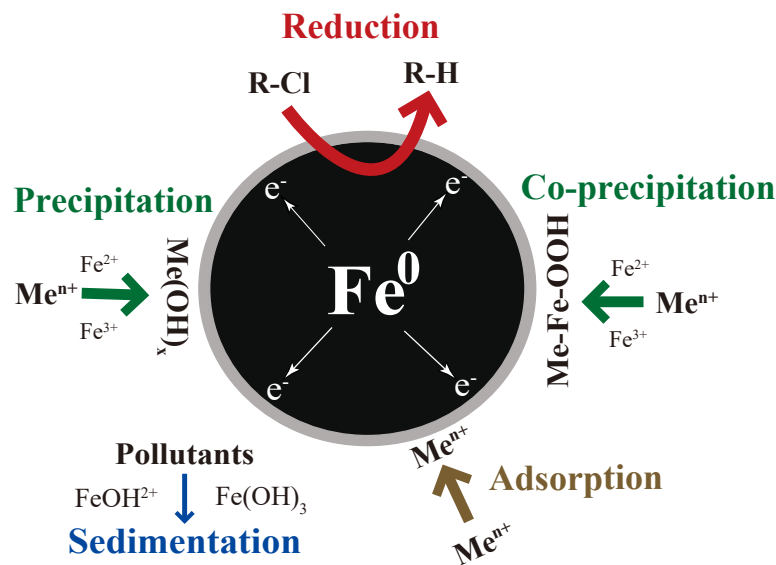
Fig. 1.2 Core-shell structure of ZVI depiciting main mechanisms for pollutants removal.

$$Fe^0 + O_2 + 2\,H^+ \longrightarrow Fe^{2+} + H_2O_2 \tag{1.1}$$

$$Fe^0 + H_2O_2 + 2\,H^+ \longrightarrow Fe^{2+} + 2\,H_2O \tag{1.2}$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot\,OH + OH^- \tag{1.3}$$

Many studies have been conducted on water treatment by ZVI due to its applicability and advantages. Additionally, there have been several attempts to enhance the reactivity of ZVI.

1.5 Modifying ZVI

One approach that has been proven effective is reducing particle size. Nanoscale Zero Valent Iron (NZVI) is more effective compared to micro-scale ZVI in removing contaminants as it provides larger specific surface area and higher reactivity. According to Almeelbi [11], nano-scale ZVI was 13.9 times more efficient than micro-scale ZVI in removing aqueous phosphate. Additionally, reducing the particle size improves mobility. However, a major problem with NZVI is agglomeration due to strong intermolecular forces as shown in Figure 1.3. The agglomeration causes small surface area of iron particles, which leads decline of adsorption capacity. Besides, it induces the loss of its mobility in porous media. Hence, many attempts have been performed to prevent from particles gathering.

One of the approved methods is addition of other metals onto the surface of NZVI (known as Bimetallic-NZVI). Bimetallic-NZVI are composed of the iron along with a noble metal such as palladium (Pd), platinum (Pt) and copper (Cu). This noble metal serves the role as a catalyst and increases a rate of reduction. Above all, a previous study [12] has reported that the addition of copper (Cu) enhances the reactivity of NZVI remarkably and is relatively inexpensive. The structure of Bimetallic-NZVI (Fe/Cu) is shown Figure 1.4.
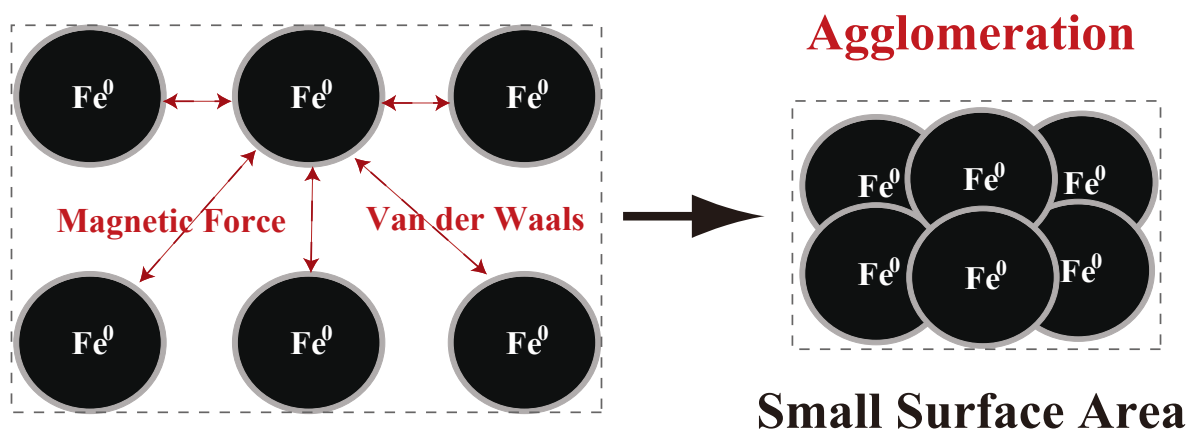

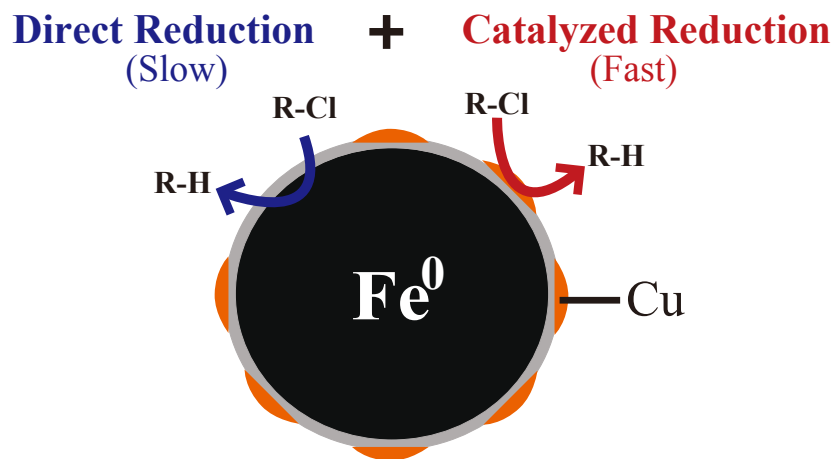**Fig. 1.3** Conceptual model of NZVI agglomeration.

Fig. 1.4 Schematic presentation of NZVI modification method by copper doping.

1.6 Previous research

As mentioned so far, many studies have conducted to investigate the efficiency of ZVI or NZVI on treatment in batch experiments. However, there is a great gap between the situation of batch experiments and practical application such as PRBs. Batch experiments are mainly conducted in a short period and under a circumstance of non-flowing solution. Therefore, in order to develop the results of batch experiments into practical application, it is important to be conducted under environment close to actuality such as column experiments.

Several researchers have focused on evaluating the efficiency and mechanism of water treatment by iron particles in porous media for a much longer period. Wan et al. [13] studied arsenic sorption in a ZVI/sand column. Hosseini et al. [14] assessed nitrate removal in packed column by nano-Fe/Cu particles. Han et al. [15] reported the optimum conditions for the removal of different heavy metal ions using Fe/Al in a laboratory-scale PRBs system. Taking these previous studies into account, it is also important to focus on a certain pollutant.

1.7 Phosphorus

There is a variety of contaminants in groundwater, depending on the different combination of source, vegetation and soil. Among them, this study focused on phosphorus removal for the following two reasons. The first reason is that many column experiments on other contaminants removal by NZVI have been conducted as mentioned above, while that on phosphorus removal have been little investigated. Although a few studies have targeted phosphorus removal in column experiments [16, 17], these studies have used micro-scale ZVI as reactive material. To the best of the author's knowledge, no previous study has investigated the phosphorus removal by NZVI and Bimetallic-NZVI in column experiments. Phosphorus do not have a great harm to human directly. However, excessive phosphorus in water causes unusual increase of microorganisms and eutrophication. Therefore, it is necessary to investigate phosphorus removal by NZVI.

The second reason is that the mechanism of removing phosphorus by NZVI is considered to be mainly adsorption, which is worthy of investigation due to adsorption is principal removal mechanism of NZVI. The optimum condition of treatment by oxidation-reduction does not necessarily correspond to the optimum removal condition by adsorption. Therefore, it is essential to clarify the rational conditions on removing phosphorus by adsorption using NZVI.

1.8   Research objectives

The major objective of this study was to investigate a rational design on removing phosphorus by NZVI for PRBs application through the laboratory-scale column experiments. Our previous study [12] have reported that Bimetallic-NZVI (Fe/Cu) is more effective on removing phosphorus compared with NZVI in batch experiments. The column experiments were conducted in order to evaluate the performance of Bimetallic-NZVI in porous media for a much longer period. Furthermore, this paper was undertaken to investigate a reasonable design on removing phosphorus by NZVI for PRBs application when not using Bimetallic-NZVI due to economic reasons. The effect of multi-layer system, support material, pore water velocity through the column and various state of NZVI were examined using the laboratory-scale columns under different configurations.

1.9   Framework

The overall structure of the study takes the form of four chapters, including this introductory chapter. Chapter 1 presents information about water pollution, wastewater treatment technologies, and current researches about ZVI. The goals of this study are also identified in the chapter. Chapter 2 introduces common materials and operation procedures in this study. Chapter 3 is concerned with the column experiment in order to reveal the rational design of PRBs. Proposal of new design for PRBs, experimental details, results and findings are presented. Finally, Chapter 4 displays summary of this study.

Chapter 2

Materials and Methods

This chapter introduces common materials and operation procedures of this study involving chemical preparation, synthesizing method of NZVI and Bimetallic-NZVI, column system, analytical inspections. Details of the column experiments will be described in later chapter.

2.1 Materials

Sodium borohydride (NaBH$_4$, 98.0%, Sigma-Aldrich Inc., USA) and ferric chloride hexahydrate (FeCl$_3$·6H$_2$O, 99.0%, Junsei Chemical Co., Japan) were purchased for NZVI synthesis. Anhydrous copper chloride (CuCl$_2$, 99.0%, Sigma-Aldrich Inc., USA) was used for Bimetallic-NZVI synthesis. Potassium dihydrogen phosphate (KH$_2$PO$_4$, 99.5%, Kanto Chemical CO., Japan) was used to prepare phosphorus solution. Sodium sulfate (Na$_2$SO$_4$, 99%, Wako Co., Japan), magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O, 97%, Wako Co., Japan), sodium bicarbonate (NaHCO$_3$, 99%, Wako Co., Japan) and calcium chloride dihydrate (CaCl$_2$·2H$_2$O, 70–79%, Junsei Chemical Co., Japan) were purchased to prepare simulated groundwater. Hydrochloric acid (HCl, 35–37%, Wako Co., Japan), sodium hydroxide (NaOH, 97%, Wako Co., Japan) and pH buffer solution (Sansyo Co., Japan) were used for pH adjustment. All aqueous solutions were prepared using deionized water and purged with nitrogen gas for 20 minutes for preventing oxidation. Standard sand (As one Co., Japan) and river sand (Kobaya, Miyazaki, Japan) were used as porous medium. All chemicals were used as received without any pretreatment.
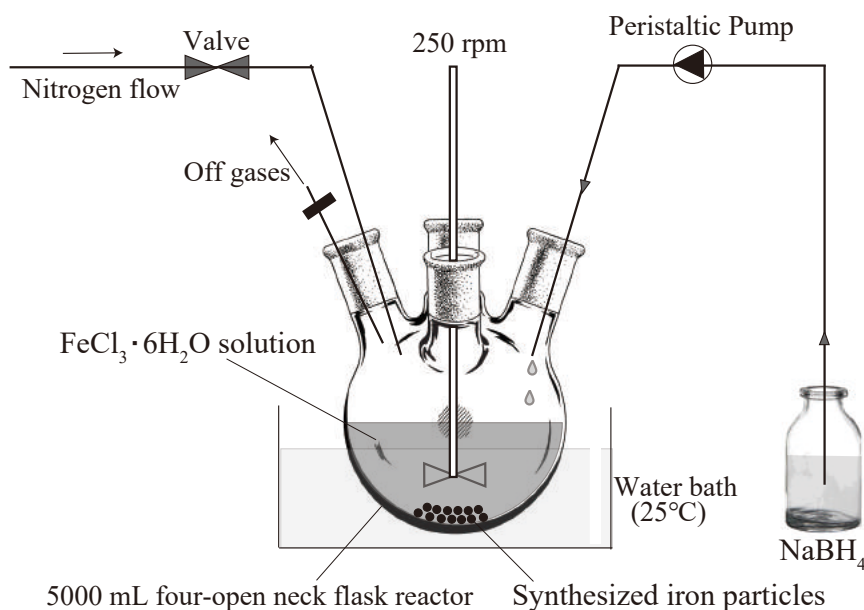
2.2 Synthesis

2.2.1 Synthesis of NZVI

NZVI was synthesized according to the bottom-up approach in the following chemical reduction reaction (2.1) [18].

$$4\,Fe^{3+} + 3\,BH_4^- + 9\,H_2O \longrightarrow 4\,Fe^0 + 3\,H_2BO_3^- + 12\,H^+ + 6\,H_2 \tag{2.1}$$

10 g NZVI was synthesized at once. Sodium borohydride solution (NaBH$_4$, 98%, 0.74 M) was added drop wise to ferric chloride hexahydrate (FeCl$_3$·6 H$_2$O, 99%, 0.15 M) using a peristaltic pump at a rate of 1 L/h in 5000 mL four-neck glass flask. The synthesis was conducted under nitrogen atmosphere to maintain anaerobic condition. The mixed solution was vigorously stirred at 250 rpm, kept at constant temperature ($25 \pm 0.5°C$) using water bath and left 20 minutes as aging time to complete the reaction. After complete reaction, the resultant black precipitates (NZVI) were collected by vacuum filtration and washed with deoxygenated deionized water (DIW) three times. The synthesized NZVI in slurry form was dried under nitrogen atmosphere and immediately used in column experiments. Schematic drawing of NZVI synthesis process is presented in Figure 2.1.

Fig. 2.1 Schematic of NZVI synthesis process.
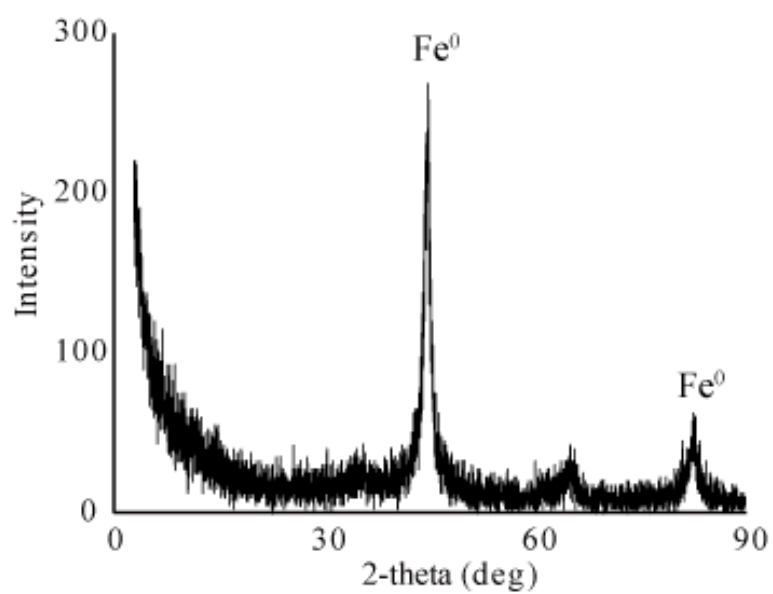
2.2.2   Synthesis of Bimetallic-NZVI

Bimetallic-NZVI (Fe/Cu) was prepared in a similar method except for addition of $CuCl_2$ to ferric chloride hexahydrate before dropping sodium borohydride. According to Khalil et al. [19], a ratio of $0.5\!:\!10$ of $CuCl_2$/NZVI was optimum for the improvement of efficiency. Bimetallic-NZVI (Fe/Cu) was synthesized in the following redox reaction (2.2).

$$Fe^0 + Cu^{2+} \longrightarrow Fe^{2+} + Cu^0 \tag{2.2}$$

2.3   Characterization of NZVI and Bimetallic-NZVI

This section presents a characterization of NZVI and Bimetallic-NZVI synthesized above method. In order to obtain the properties of synthesized iron particles, X-ray diffraction (XRD), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area and particle size were analyzed in our previous study.

XRD patterns of NZVI is shown in Figure 2.2. Compositions of the iron products were analyzed by XRD (TTR, Rigaku, Tokyo, Japan). Samples were analyzed using Cu K_a radiation ($\lambda = 1.5418\mathring{A}$) with a scan rate of $2°$ min^{-1} and scanning range between $3°$ and $90°$. The peak at $44.8°$ in XRD spectrum indicates the presence of zero-valent iron in the synthesized particles. The particle size of synthesized particles was estimated by laser diffraction particle size analyzer (SALD-2300, Shimadzu Co., Japan). The average particle size of NZVI is 42 nm. The BET specific surface area of synthesized particles was determined by a specific surface area analyzer (Micromeritics 3Flex, USA). The BET surface area of NZVI is 43 m^2/g. TEM images of synthesized particles are depicted in Figure 2.3. The surface morphologies of synthesized particles were obtained on TEM (JEM-ARM 200F, JEOL Co., Japan). NZVI particles show the chain-structure form due to the agglomeration. By contrast, Bimetallic-NZVI particles relatively distribute separately owing to the coating by copper. Additionally, TEM images indicate that both synthesized particles are generally spherical and nano-scale.

Fig. 2.2 XRD patterns of synthesized NZVI.
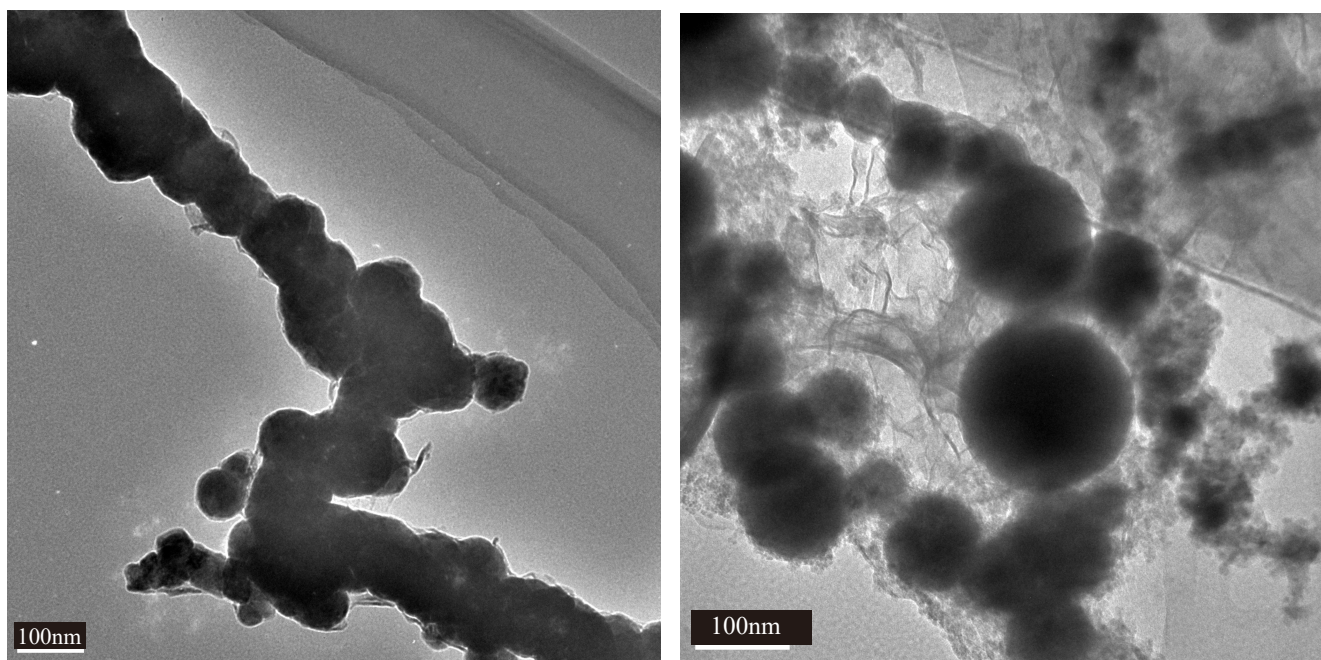
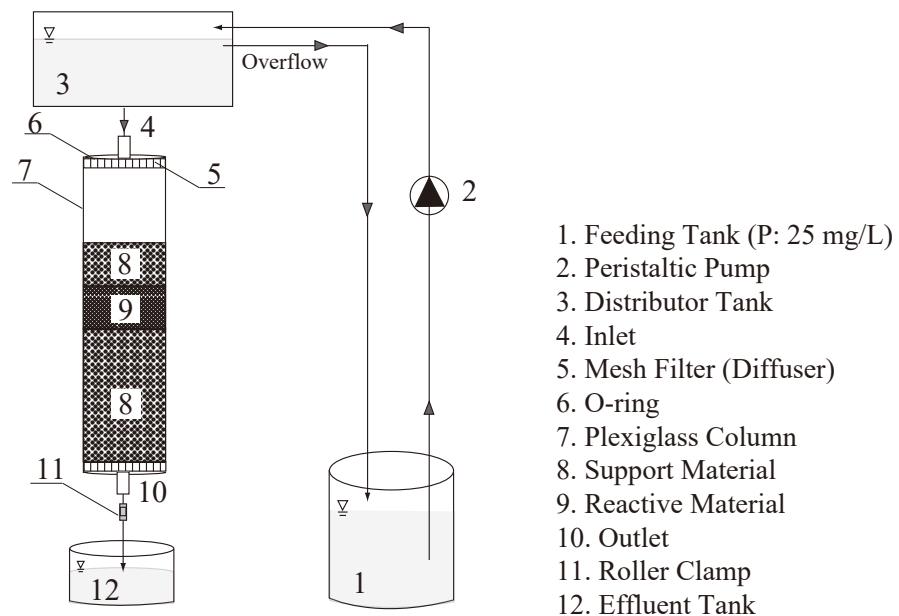

(a) NZVI   (b) Bimetallic-NZVI

Fig. 2.3 TEM images of (a) NZVI and (b) Bimetallic-NZVI.

2.4 Column experimental setup

Laboratory-scale column experiments were conducted using a plexiglass column with 100 cm length and 10 cm internal diameter. In this study, 65 cm of the column was actually used in packing materials. Figure 2.4 and Figure 2.5 present a schematic diagram and picture of the column system, respectively. A river sand and standard sand were used as support material on the top and bottom of the column. The middle of the column was filled with reactive material. The columns were pumped with downflow mode by a peristaltic pump and effluents were collected at predetermined time intervals for measurement. Mesh filters were used in order to prevent the inflow of impurities into the column and the flow out of the soil on both sides. Additionally, the upper mesh filter served as a diffuser. O-rings were used to seal the column on both sides. The column experiments were conducted under ten different conditions. The column system was operated at room temperature. Water samples were collected from outlet and analyzed for phosphorus concentration. pH, oxidation reduction potential (ORP) and dissolved oxygen (DO) of outlet were analyzed every day.

1. Feeding Tank (P: 25 mg/L)
2. Peristaltic Pump
3. Distributor Tank
4. Inlet
5. Mesh Filter (Diffuser)
6. O-ring
7. Plexiglass Column
8. Support Material
9. Reactive Material
10. Outlet
11. Roller Clamp
12. Effluent Tank

Fig. 2.4 Schematic diagram of the column experimental system.

2.5 Analysis

Concentration of phosphorus was measured using an UV-Vis spectrophotometer (DR 3900, Hach Co., USA) via USEPA PhosVer 3 (Ascorbic acid method) at 880 nm. The values of pH and ORP were obtained using a pH/ORP digital meter (D-72, Horiba Co., Japan). DO was measured by using a DO digital meter (HQ30d, Hach Co., USA).

Fig. 2.5 Image of the column experiment.

Chapter 3

Results and Discussion

Chapter 3 presents the column experiment in order to reveal the ideal design of PRBs using NZVI as reactive material on phosphorus removal. First, Section 3.1 shows the objectives in this experiment. Additionally, the mechanisms and challenging on phosphorus removal by iron particles argued in previous studies are arranged. A new method for solving the problems are proposed. Next, Section 3.2 displays column configurations and flowchart of the experiments. Section 3.3 introduces the procedures and details of each experiment. Section 3.4 shows obtained results from each experiment. Finally, Section 3.5 presents discussion from the results.

3.1　Purpose of the experiment

This experiment was conducted with two objectives. The batch study by Eljamal et al. [12] reached a conclusion that Bimetallic-NZVI (Fe/Cu) is more efficient than NZVI on phosphorus removal. In this connection, the first purpose is to verify the performance of Bimetallic-NZVI (Fe/Cu) on removing phosphorus in the porous media for a longer period. The second purpose is to explore a reasonable and highly effective design for PRBs application except for modifying reactive material. In this section, the mechanisms and challenging to treat phosphorus by iron particles are explained. A new method which can achieve efficient removal on phosphorus and low cost are proposed.

The mechanisms of phosphorus removal by ZVI have not been completely revealed yet. According to Wen et al. [20], it is assumed that the main mechanism is adsorption. However, more investigation is needed for understanding the complete mechanisms of phosphorus removal by NZVI.

Besides, there has been a serious problem in adsorption, which is referred to as clogging. The mechanism and influence of clogging are presented in Figure 3.1. The paths of water are interrupted by clogging of generated products on the surface. This problem hinders the contact with phosphorus and NZVI, which leads the decline of phosphorus removal.

Based on above mechanisms and challenging, this study proposed multi-layer of PRBs walls as a new method for solving the problem. This new design divides reactive materials, and support material which has high permeability is inserted between reactive materials as shown Figure 3.2. The inserted support material enables uniform distribution and persistent contact between NZVI and phosphorus, which enables to keep sufficient adsorption.

To sum up, the objective is exploring the optimum design for PRBs application by conducting column experiment under various configurations. First, the effect of modifying reactive material on phosphorus removal was investigated. Second, the effectiveness of multi-layer was investigated as high efficient and inexpensive method. The effect of support material, pore water velocity through the column and various state of NZVI were also examined.

Fig. 3.1 Decline of adsorption capacity by clogging.

Sufficient adsorption by re-distribution
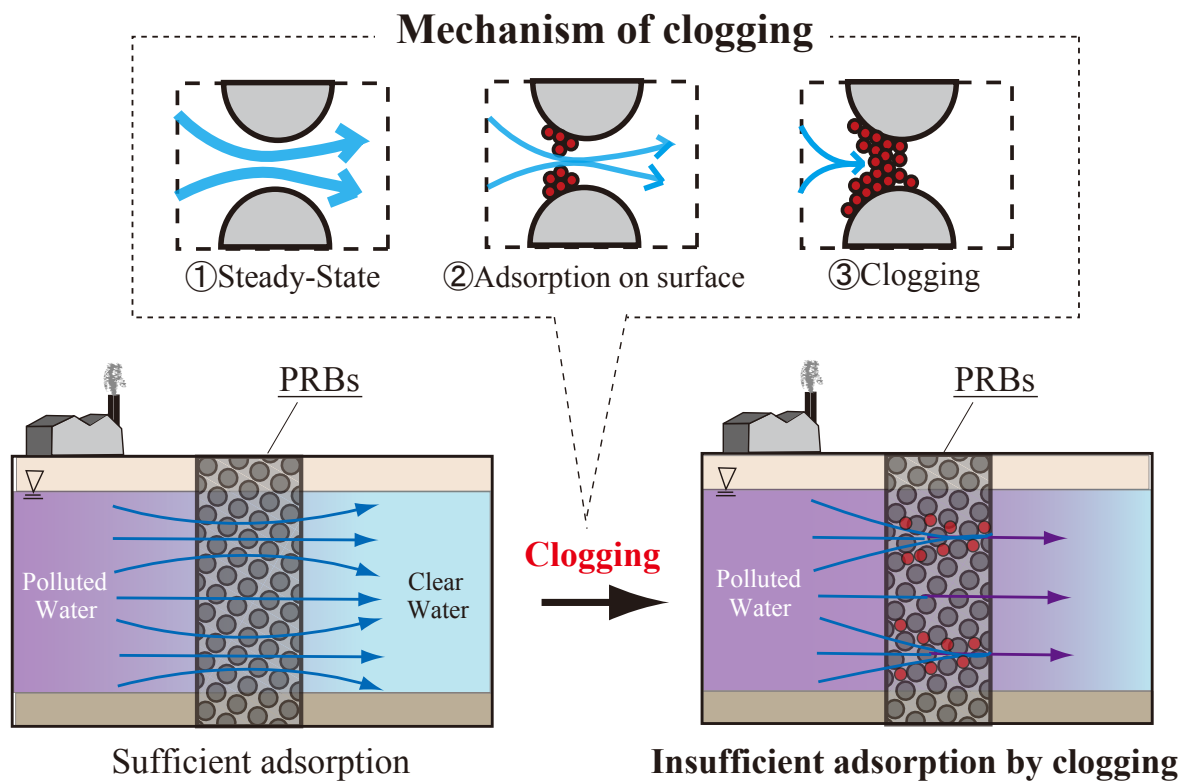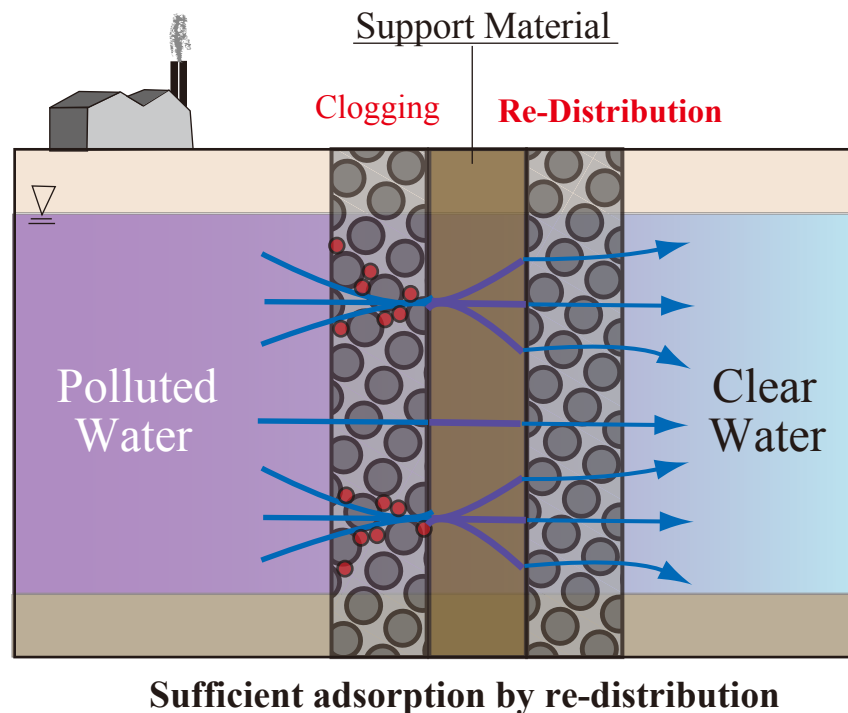
Fig. 3.2 Proposed Multi-Layer system in PRBs.

3.2 Column configuration

Based on the above objectives and hypothesis, each column configuration was determined as shown Figure 3.3 and Table 3.1. The flowchart of this experiment is presented in Figure 3.4. Only river sand was filled in Column 1 as control column. The river sand was chosen as support material due to its high draining performance and low cost. In Column 2 to Column 7, the removal efficiency in different reactive material and layout was examined. The reactive material was mixed with support material in mixture state to improve porosity. The standard sand was filled instead of river sand as support material in Column 8. The efficiency of different flow rate was examined in Column 9. The best combination of reactive material design was used in Column 8 and Column 9. Finally, the interference of other ions was examined with simulated groundwater in Column 10. Key parameters of PRBs design were investigated as follows:

First, the efficiency of Bimetallic-NZVI in porous media was examined with flow rate, support material and state of reactive material fixed. Next, the efficiency of multi-layer design on phosphorus removal was examined. Finally, further experiments were conducted with flow rate, support material and state of reactive material changed.
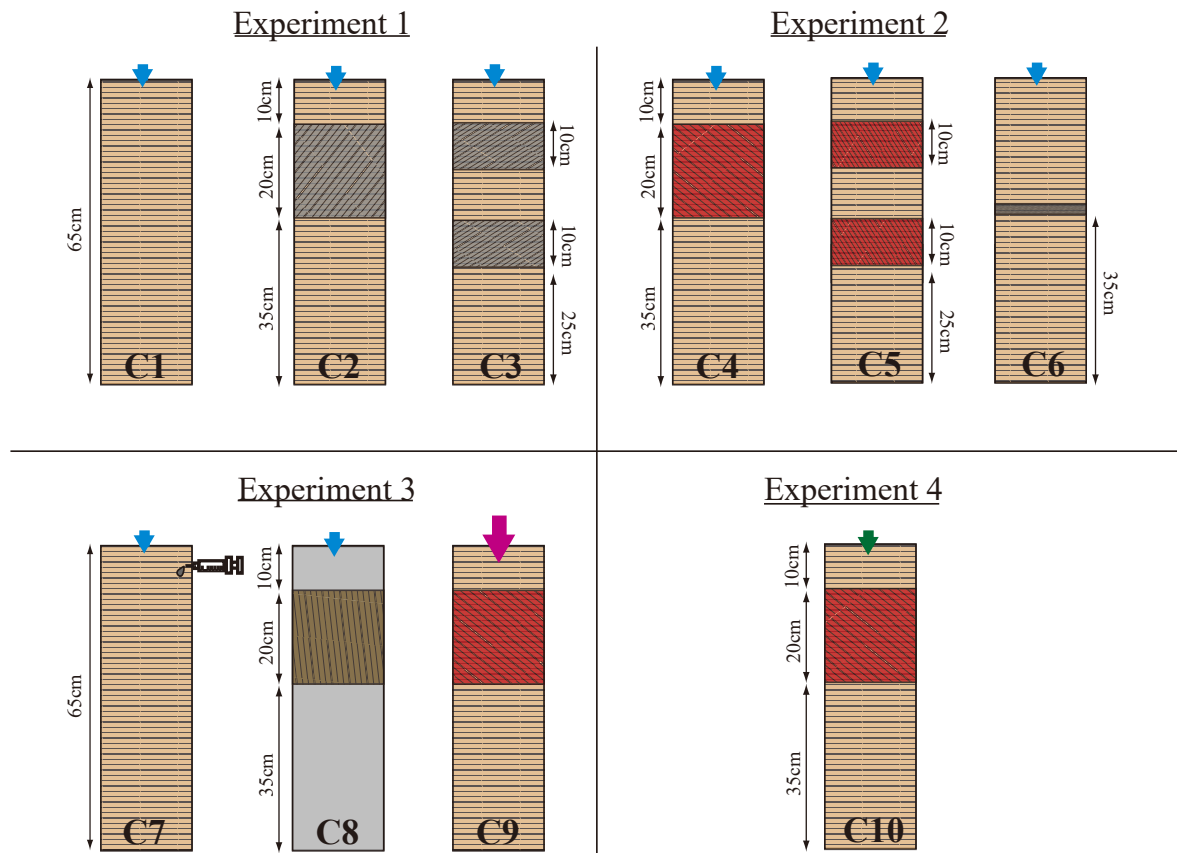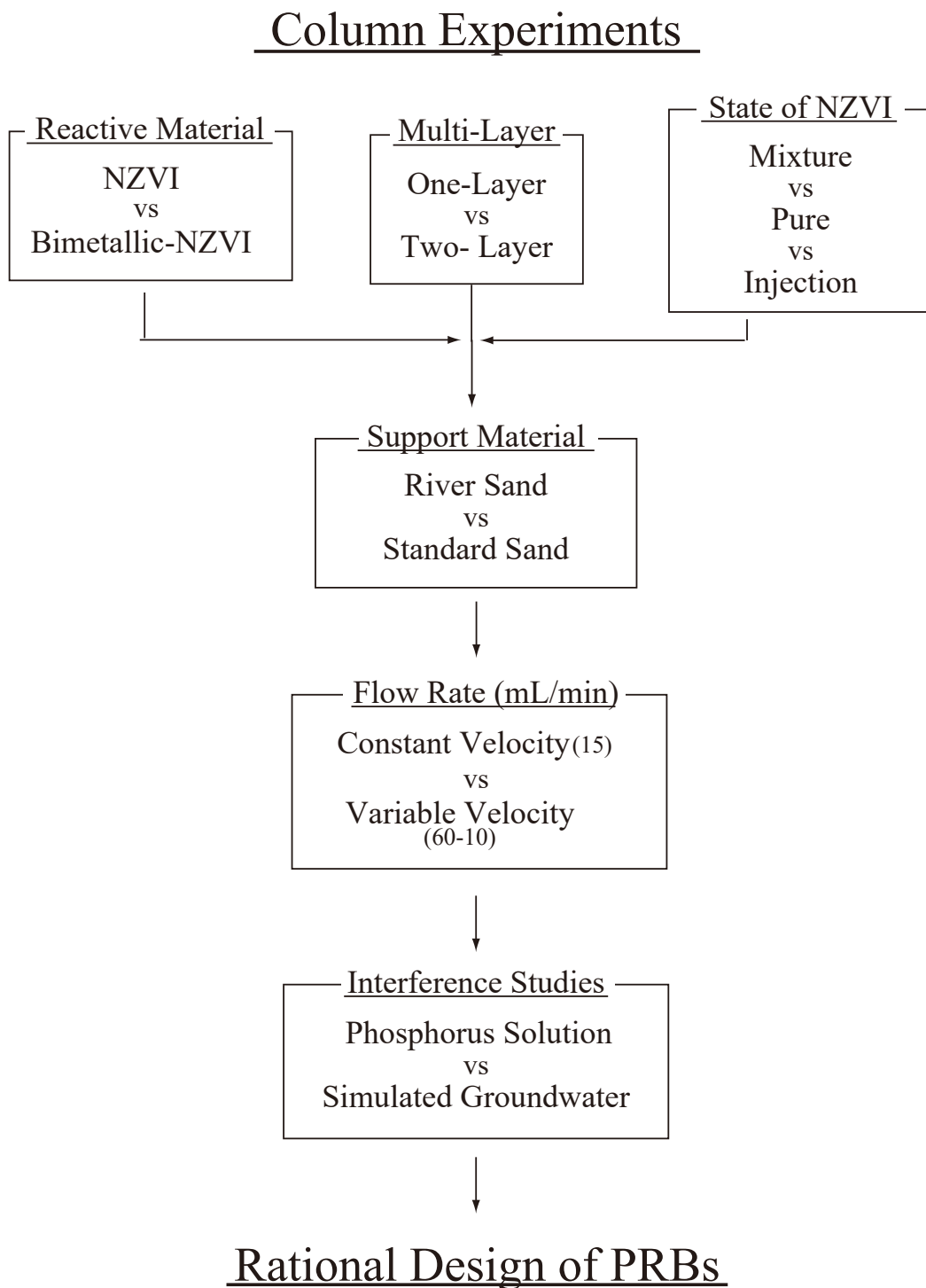
Fig. 3.3 Schematic overview of the column configuration.

Table 3.1 Experimental design in present work.

No.	Layers	Reactive Material	Dosage (g)	State	Support Material	Flow Rate (mL/min)	Solution	Days
C1					Rivr Sand	15	Phosphorus	30
C2	1	Fe	20	Mixture	River Sand	15	Phosphorus	30
C3	2	Fe	20	Mixture	River Sand	15	Phosphorus	30
C4	1	Fe/Cu	10	Mixture	River Sand	15	Phosphorus	30
C5	2	Fe/Cu	10	Mixture	River Sand	15	Phosphorus	14
C6	1	Fe	10	Pure	River Sand	15	Phosphorus	14
C7		Fe	10	Injection	River Sand	15	Phosphorus	14
C8	1	Fe/Cu	10	Mixture	Standard Sand	15	Phosphorus	14
C9	1	Fe/Cu	10	Mixture	River Sand	$60-10$	Phosphorus	14
C10	1	Fe/Cu	10	Mixture	River Sand	15	Simulated GW[1]	14

1 GW: Ground Water

Column Experiments

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┌─ Reactive Material ─┐   ┌─ Multi-Layer ─┐   ┌─ State of NZVI ─┐
│        NZVI         │   │   One-Layer   │   │    Mixture      │
│         vs          │   │      vs       │   │      vs         │
│  Bimetallic-NZVI    │   │   Two- Layer  │   │     Pure        │
└─────────────────────┘   └───────────────┘   │      vs         │
                                              │   Injection     │
                                              └─────────────────┘
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┌─ Support Material ─┐
│   River Sand   │
│   vs   │
│   Standard Sand   │
└────────────────────┘

┌─ Flow Rate (mL/min) ─┐
│ Constant Velocity(15)│
│   vs   │
│   Variable Velocity │
│   (60-10)   │
└──────────────────────┘

┌─ Interference Studies ─┐
│   Phosphorus Solution │
│   vs   │
│ Simulated Groundwater │
└────────────────────────┘

Rational Design of PRBs

Fig. 3.4 Framework of the experiments and factors investigated on phosphorus removal in the column.

3.3   Experimental methods

This experiment was conducted using the column system mentioned in Chapter 2. Three columns were used at a time. The first experiment (C1–C3) was conducted using 20 g reactive material in each column and kept for a month. The subsequent experiments (C4–C10) were conducted using 10g reactive material in each column and kept for two weeks due to save of costs and time. Phosphorus solution (P: 25 mg/L) was used in Column 1 to Column 9. The variation of flow rate is presented in Table 3.2. The components of simulated groundwater used in Column 10 were shown in Table 3.3.

Table 3.2 Flow rate in Column 7.

Time (hr)	Flow rate (mL/min)
0–12	60
12–24	40
24–36	30
36–48	15
48–	10

Table 3.3 Chemical compositions of simulated groundwater used in Column 10.

Parameter	Ca_2^+	Cl^-	Na^+	SO_4^{2-}	HCO_3^-	Mg_2^+	P
Concentration (mg/L)	31.36	79.0	131.0	203.0	89.58	8.07	25.0

3.4   Experimental results

First, this section provides comparison methods of the results in each experiment. Next, the comparison results in the different configuration columns are presented. The comparison on phosphorus removal were conducted through all the experiments. The removal efficiency with time was compared by two methods due to the difference in the dosage of reactive material. In case of the same dosage, phosphorus removal rate was adopted. Removal rate (r) was calculated as follow:

$$r = \frac{C_0 - C_t}{C_0} 100 \tag{3.1}$$

where C_0 and C_t represent the initial and effluent phosphorus concentration (mg/L), respectively. In case of the different dosage, phosphorus adsorption capacity (q) was used for comparison. Phosphorus adsorption capacity was calculated as follow:

$$q = \frac{C_0 - C_t}{M} V \tag{3.2}$$

where M and V represent the dosage of the reactive material (g) and the inflow (L), respectively.

The measurement results in the respective conditions are described below, in the order of phosphorus removal, pH, ORP and DO values. The results of the control column (C1) are also shown in all graphs.

3.4.1 Effect of modifying reactive material

Figure 3.5 shows the comparison of phosphorus adsorption capacity when the different reactive materials were used in one-layer. Figure 3.6 presents the results in case of two-layer design. Column 1 contains only river sand as a control column. The results indicated that the both reactive materials were effective on phosphorus removal in porous media. The control column (C1) indicated the state of having no effect on removing phosphorus after 10 days, while the columns used NZVI (C2&C3) and Bimetallic-NZVI (C4&C5) kept effectiveness over 14 days. Compared to the columns used NZVI (C2&C3), positive effects were found in that used Bimetallic-NZVI (C4&C5). These results indicated that copper addition of NZVI resulted in doubling the effect on removing phosphorus in 14 days in this experiment. In summary, Bimetallic-NZVI was more effective than NZVI in porous media for a long period as with the batch experiment results.

The results of pH when used the different reactive materials in one-layer design and two-layer design are indicated in Figure 3.7 and Figure 3.8, respectively. pH values were slightly increasing in all columns (C1–C5) involving the control column though there were slight fluctuation. The temporal changes of pH showed a similar tendency in all columns through the experiments. The columns used NZVI (C2&C3) presented higher values than the control column (C1), while that used Bimetallic-NZVI (C4&C5) indicated lower values.

Figure 3.9 provides the measured values of ORP when the different reactive materials were used in one-layer. Figure 3.10 presents the results in case of two-layer design. The graphs showed that there has been a slight decrease in the values of ORP of all columns (C1–C5). In comparison with the control column, ORP values of the columns used NZVI (C2&C3) showed low values. On the contrary, that used Bimetallic-NZVI (C4&C5) showed high values than the control (C1).

The results of DO when used the different reactive materials in one-layer design and two-layer design are appeared in Figure 3.11 and Figure 3.12, respectively. There were no significant changes of DO among all columns (C1–C5) during the experiments though there were slight fluctuation. Compared with the control column (C1), both of the columns used NZVI (C2&C3) and Bimetallic-NZVI (C4&C5) showed lower DO values. No significant differences were found in the use of the different reactive materials.
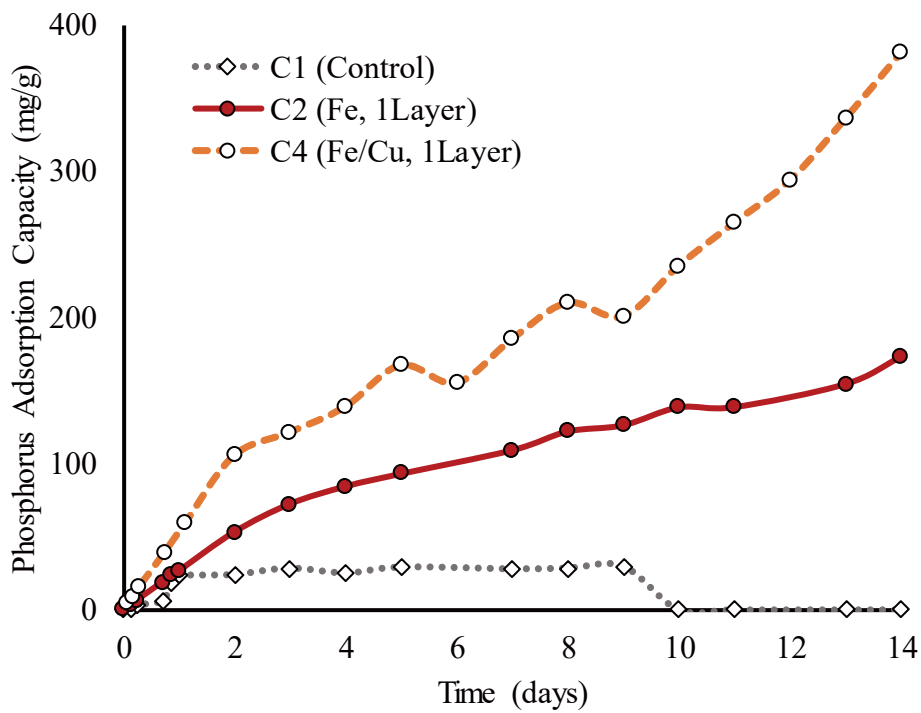
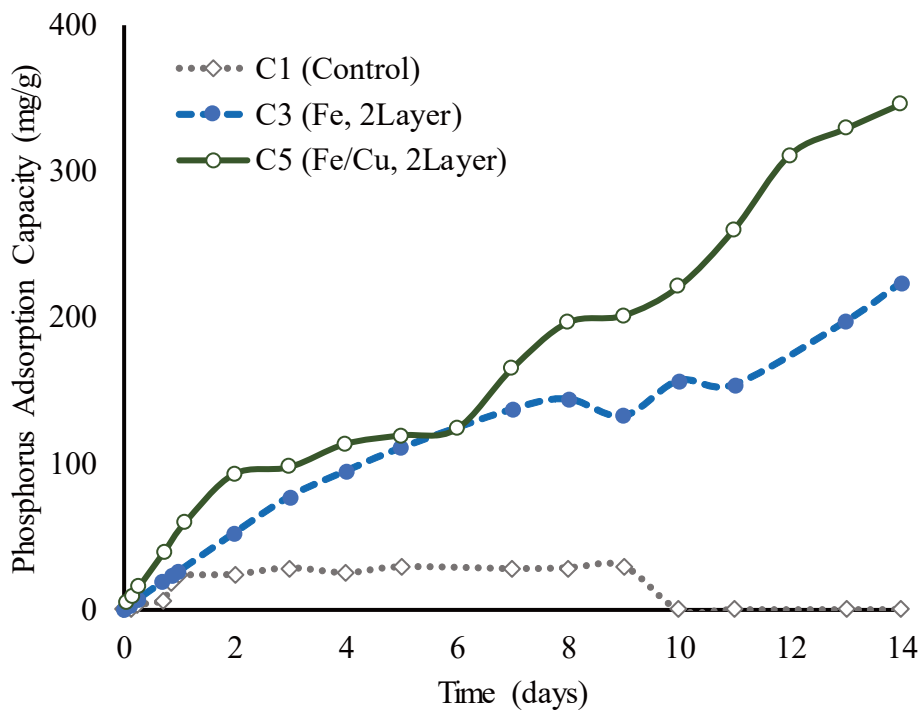**Fig. 3.5** Effect of modifying reactive material on phsphorus removal in one-layer design.

Fig. 3.6 Effect of modifying reactive material on phsphorus removal in two-layer design.
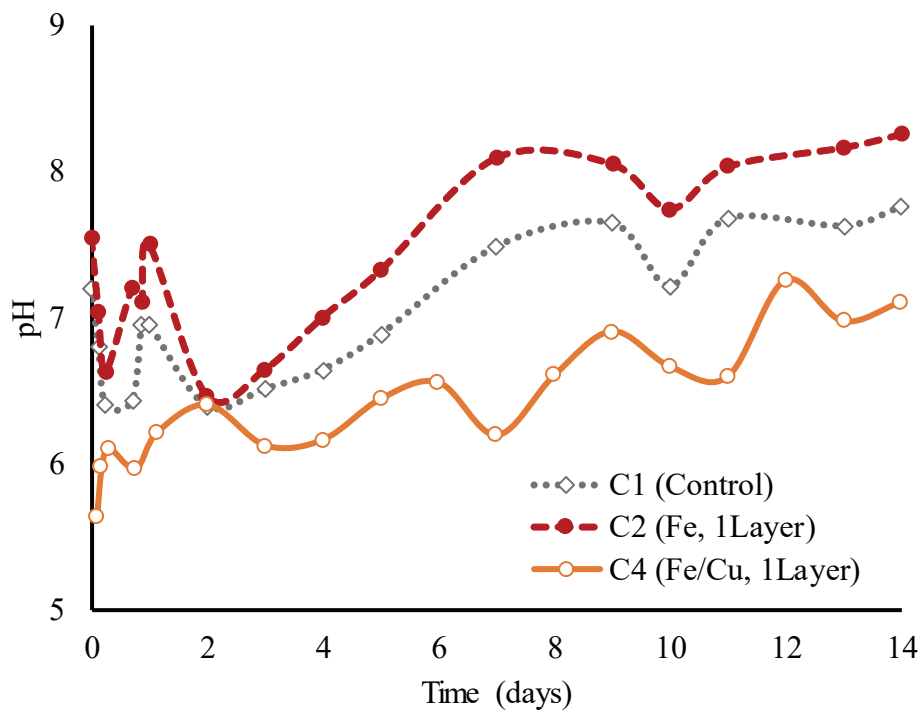
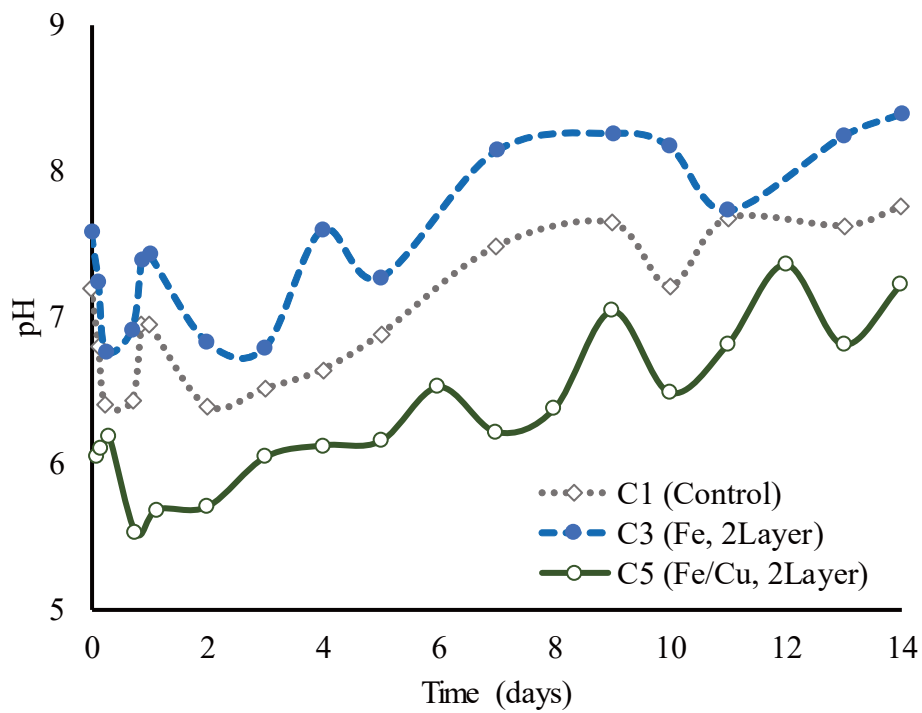**Fig. 3.7** Effect of modifying reactive material on pH changes in one-layer design.

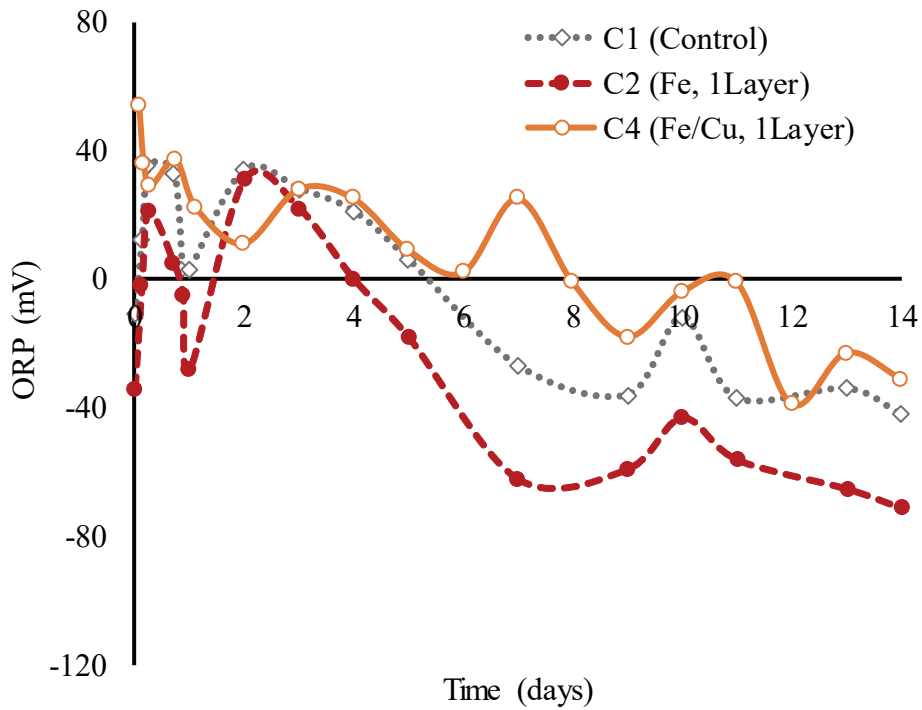**Fig. 3.8** Effect of modifying reactive material on pH changes in two-layer design.

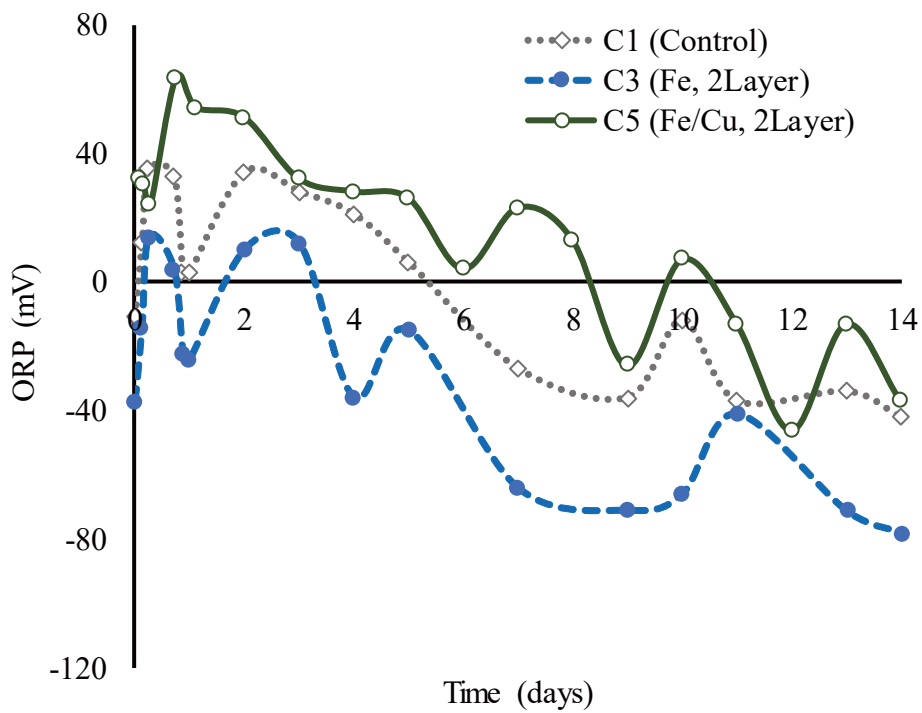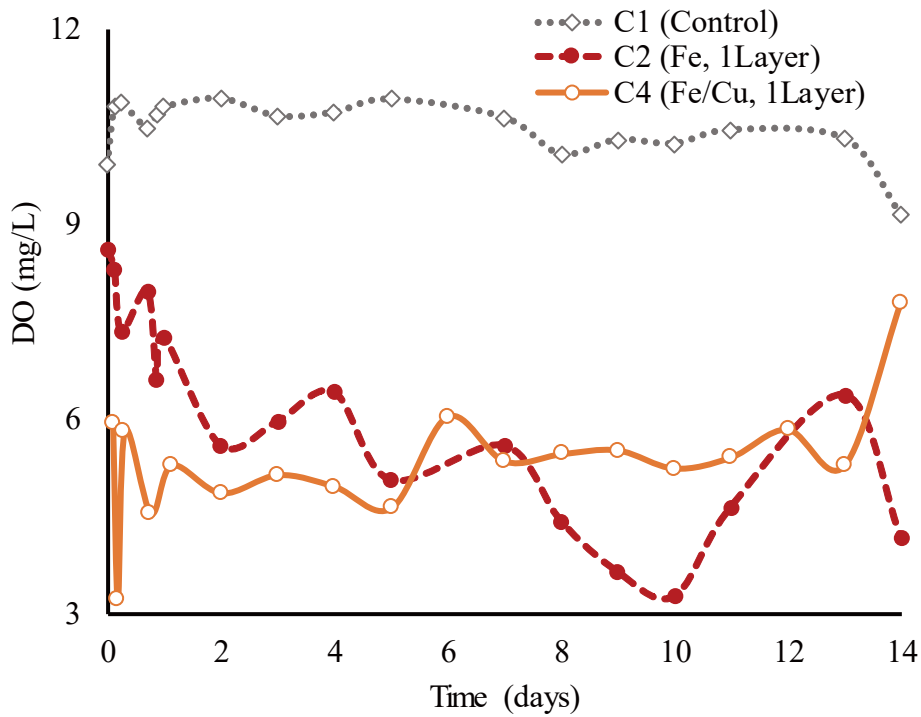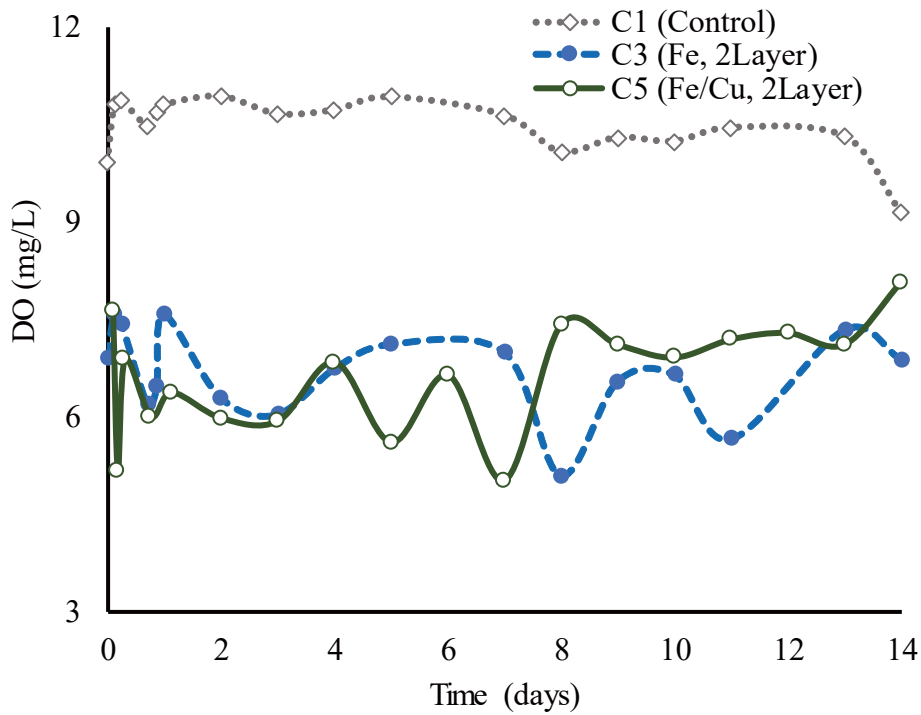**Fig. 3.9** Effect of modifying reactive material on ORP changes in one-layer design.

Fig. 3.10 Effect of modifying reactive material on ORP changes in two-layer design.

Fig. 3.11 Effect of modifying reactive material on DO changes in one-layer design.

Fig. 3.12 Effect of modifying reactive material on DO changes in two-layer design.

3.4.2 Effect of multi-layer

Figure 3.13 presents the comparison of phosphorus adsorption capacity between the one-layer design and two-layer design when the same reactive materials were used. Figure 3.14 illustrates the results when used Bimetallic-NZVI as reactive material. In case of using NZVI as reactive material, no significant difference were observed until two days. In comparison with the column designed in one-layer (C2), that designed in two-layer (C3) indicated slightly high efficiency in 14 days as expected. However, in case of using Bimetallic-NZVI as reactive material, there were slightly positive effects in one-layer design column (C4) until nine days against all expectations. Subsequently, no significant differences were observed after nine days. Overall, multi-layer design did not affect removing phosphorus greatly.

The results of pH in the different layer design columns when used NZVI as reactive material are indicated in Figure 3.15. The results when used Bimetallic-NZVI are shown in Figure 3.16. In case of using NZVI (C2&C3), no particular propensities were observed according number of layers. Interestingly, significant low values were obtained in the two-layer design column used Bimetallic-NZVI (C5) until three days.

Figure 3.17 provides the results of ORP values in the different layer design column when used NZVI. Figure 3.18 shows the results when used Bimetallic-NZVI. In case of using NZVI as reactive material, two-layer design column (C3) which was more effective on phosphorus removal showed slightly low ORP values over 14 days. Likewise, there were slightly low figures in one-layer design column (C4) until nine days in case of using Bimetallic-NZVI. Overall, these results indicated that there was correlation between phosphorus adsorption capacity and ORP values.

The measured results of DO in one-layer and two-layer design when used NZVI are appeared in Figure 3.19. The results when used Bimetallic-NZVI are illustrated in Figure 3.20. Two-layer design columns (C3&C5) showed high DO values in both results. The correlation between phosphorus adsorption capacity and DO values was not found in this experiments.
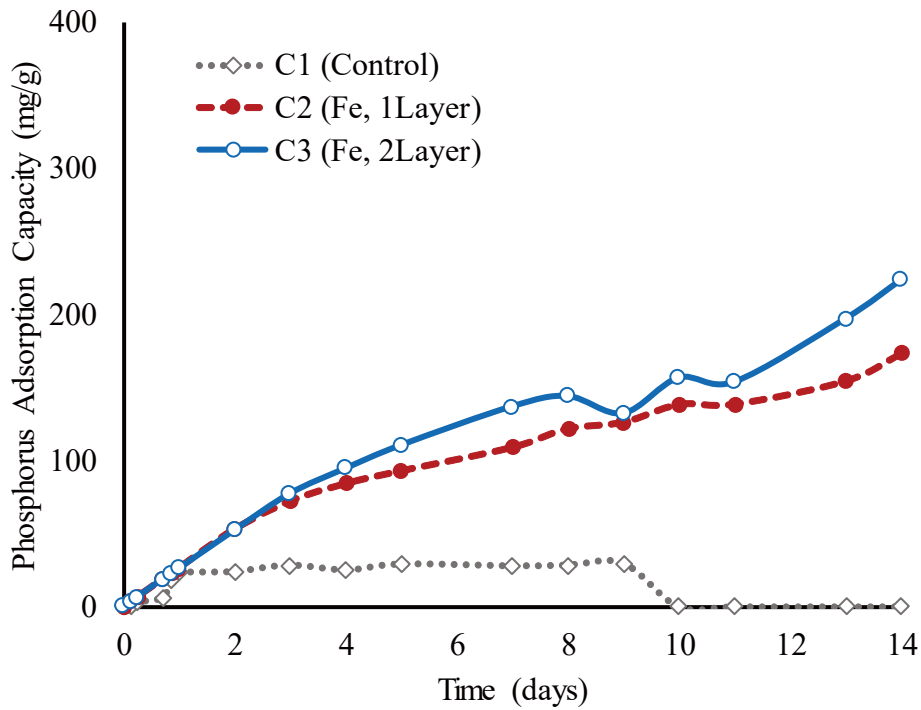
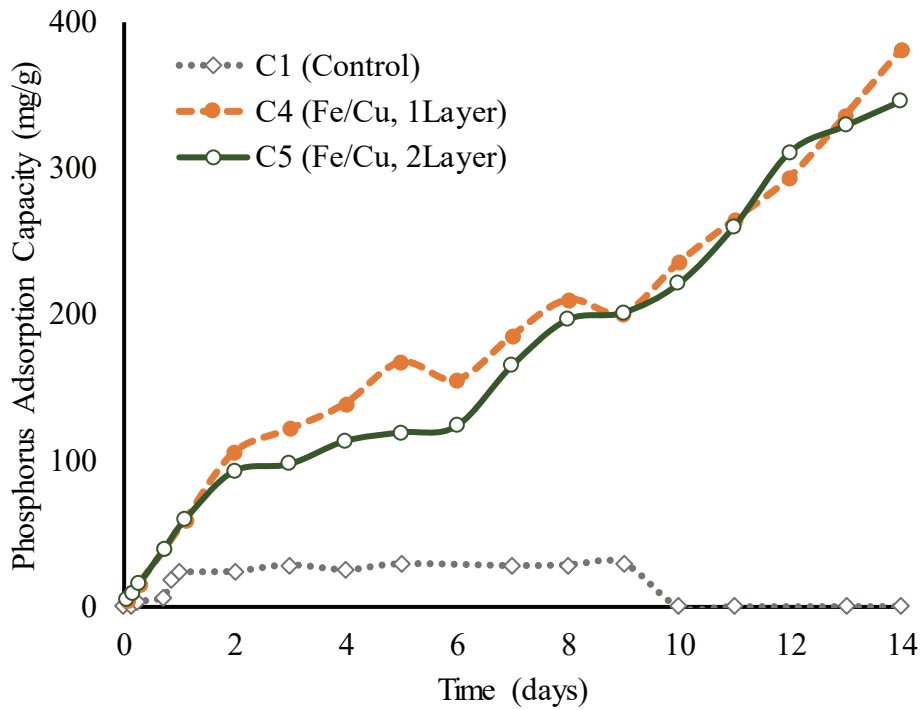**Fig. 3.13** Effect of multi-layer on phsphorus removal used NZVI.

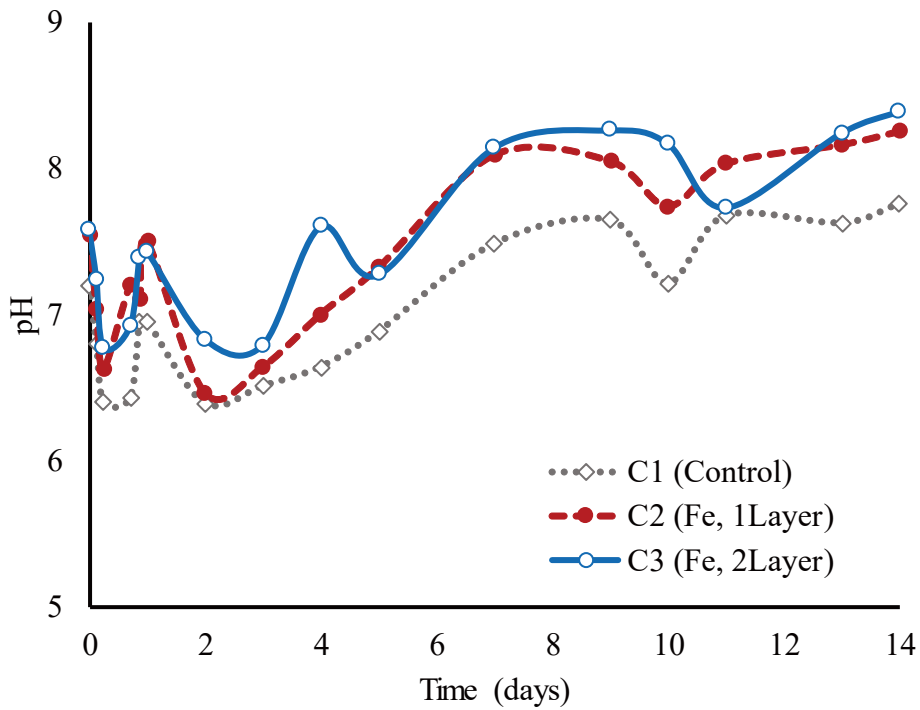**Fig. 3.14** Effect of multi-layer on phsphorus removal used Bimetallic-NZVI.

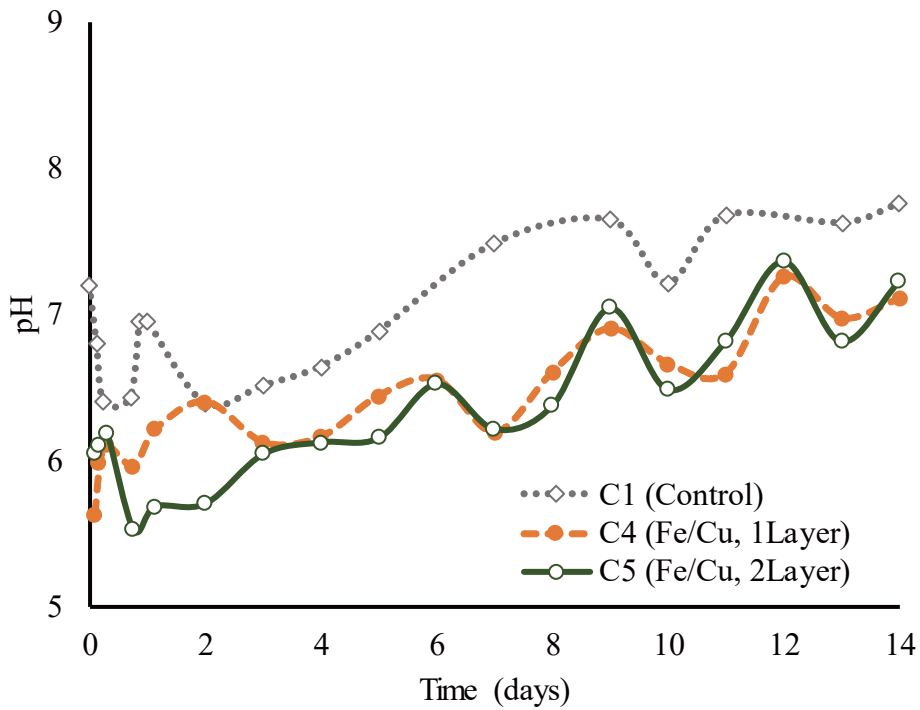**Fig. 3.15** Effect of multi-layer on pH changes used NZVI.

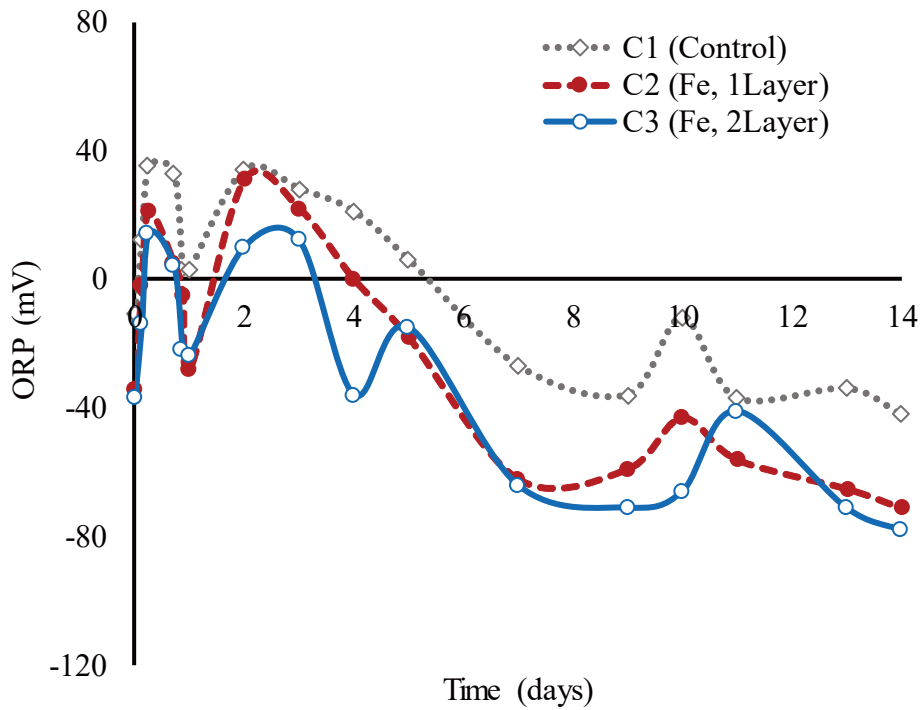**Fig. 3.16** Effect of multi-layer on pH changes used Bimetallic-NZVI.

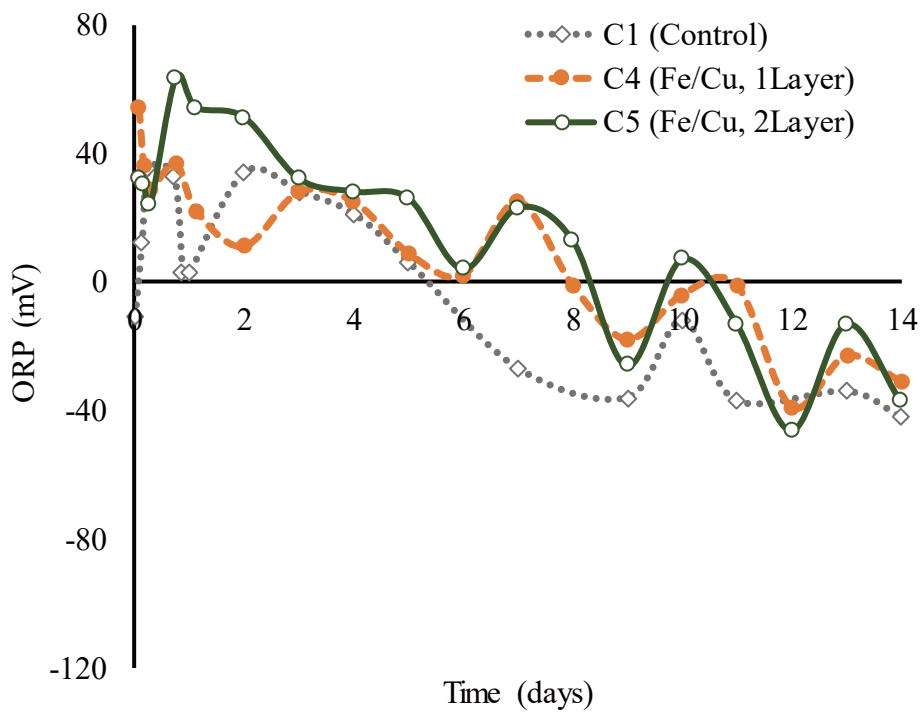**Fig. 3.17** Effect of multi-layer on ORP changes used NZVI.

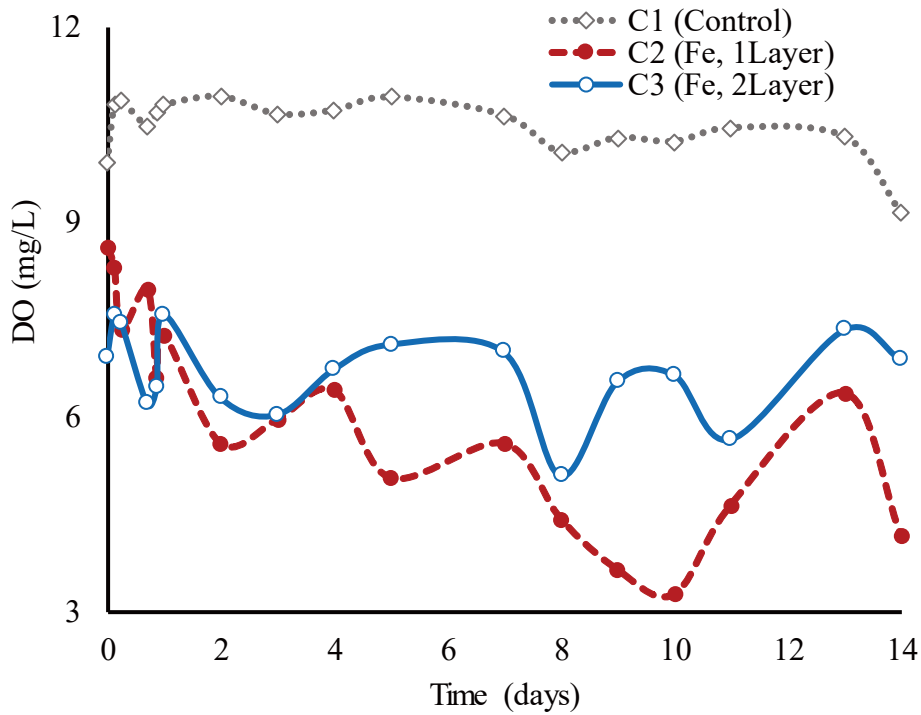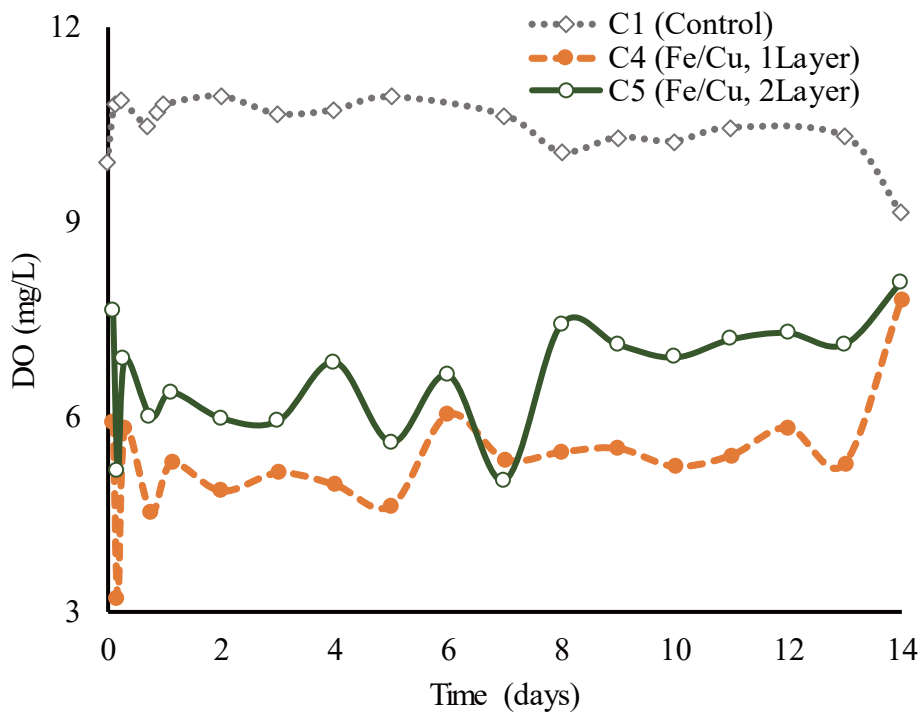**Fig. 3.18** Effect of multi-layer on ORP changes used Bimetallic-NZVI.

Fig. 3.19 Effect of multi-layer on DO changes used NZVI.

Fig. 3.20 Effect of multi-layer on DO changes used Bimatallic-NZVI.

3.4.3   Effect of reactive material state

Figure 3.21 shows the comparison on phosphorus adsorption capacity among the columns used different NZVI status as reactive material. The efficiency in the column which used the mixture of NZVI/sand as reactive material (C2) was the lowest over 14 days. Until two days, the column which contained only NZVI (C6) was more effective. However, the column injected NZVI directly (C7) resulted in the best performance after three days. Overall, the status of reactive material did not greatly affect removing phosphorus in these experiments.

The results of pH in the columns used different NZVI state are indicated in Figure 3.22. In comparison to the control column (C1), the column used NZVI/sand (C2) showed slightly high values. It was not indicated obvious difference between the values in the control column and injected column (C7). Interestingly, significant low values were observed in the column packing pure NZVI (C6).

Figure 3.23 provides the results of ORP values in the columns used different reactive material state. There were clear trends of decreasing during the experiments in all columns. Compared with the control column (C1), the column with NZVI mixture (C2) and the injected column (C7) showed low values. By contrast, the column used only NZVI (C6) showed obvious high ORP values over 14 days.

The measured DO results in the columns with different status of NZVI as reactive material are appeared in Figure 3.24. In comparison with the control column (C1), we can see that all columns resulted in lower values. No significant differences were found among three columns.
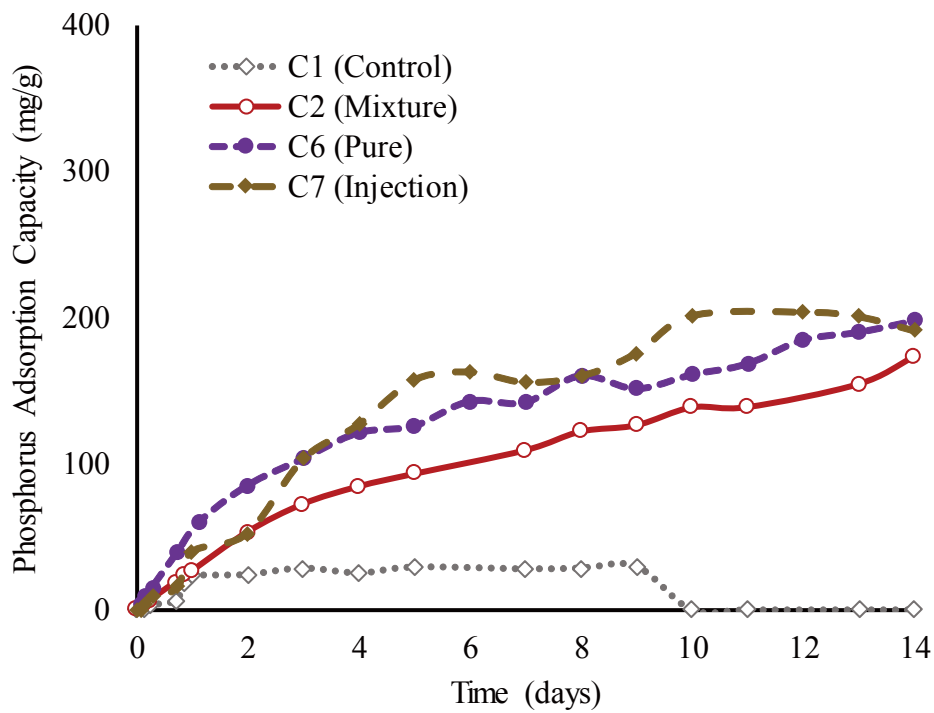
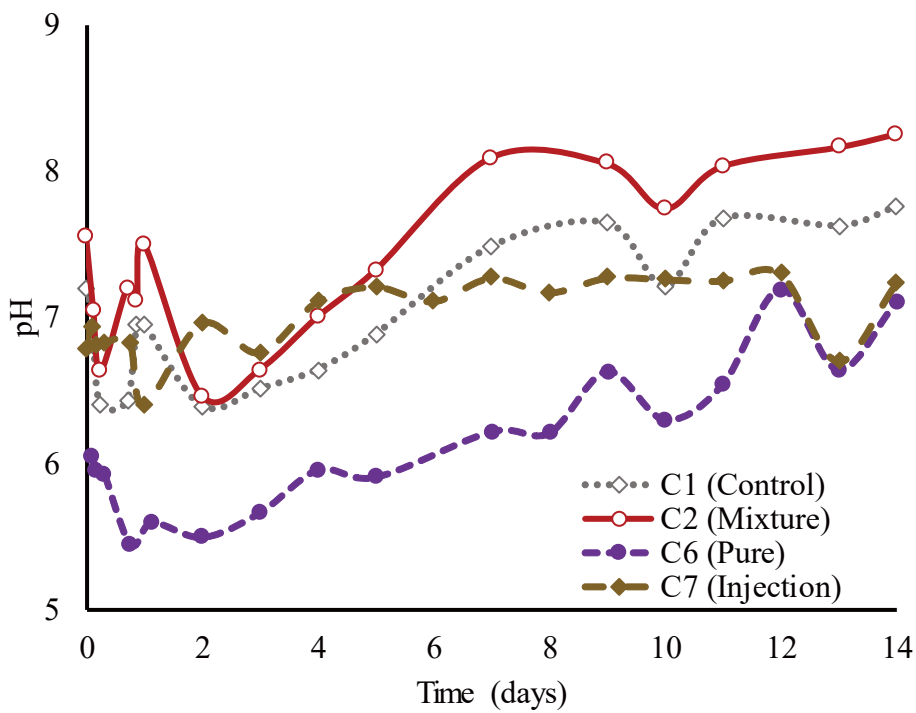**Fig. 3.21** Effect of reactive material state on phsphorus removal.

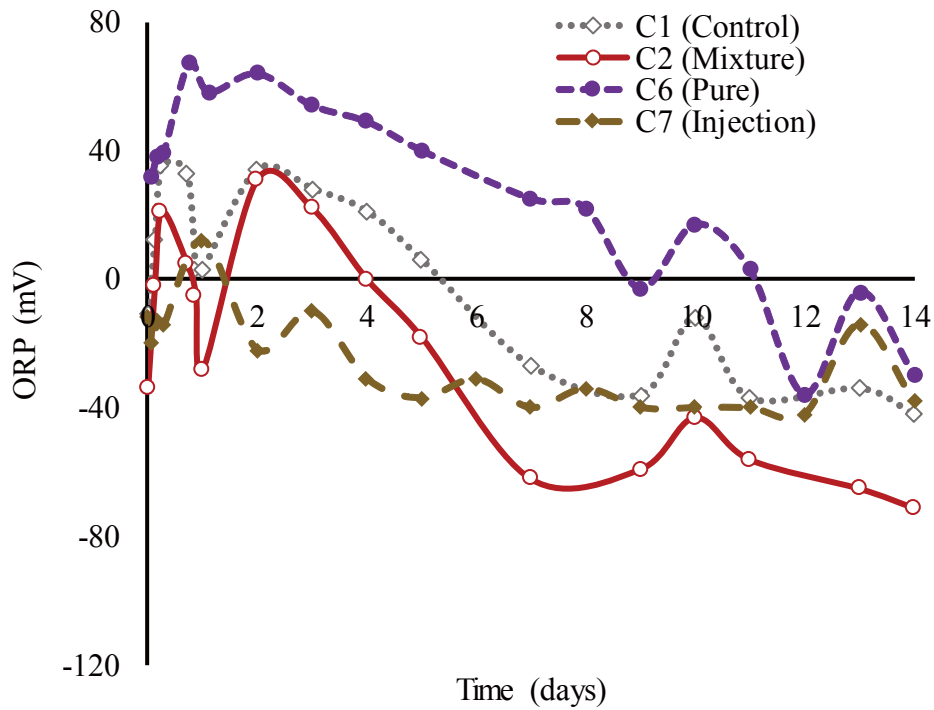**Fig. 3.22** Effect of reactive material state on pH changes.

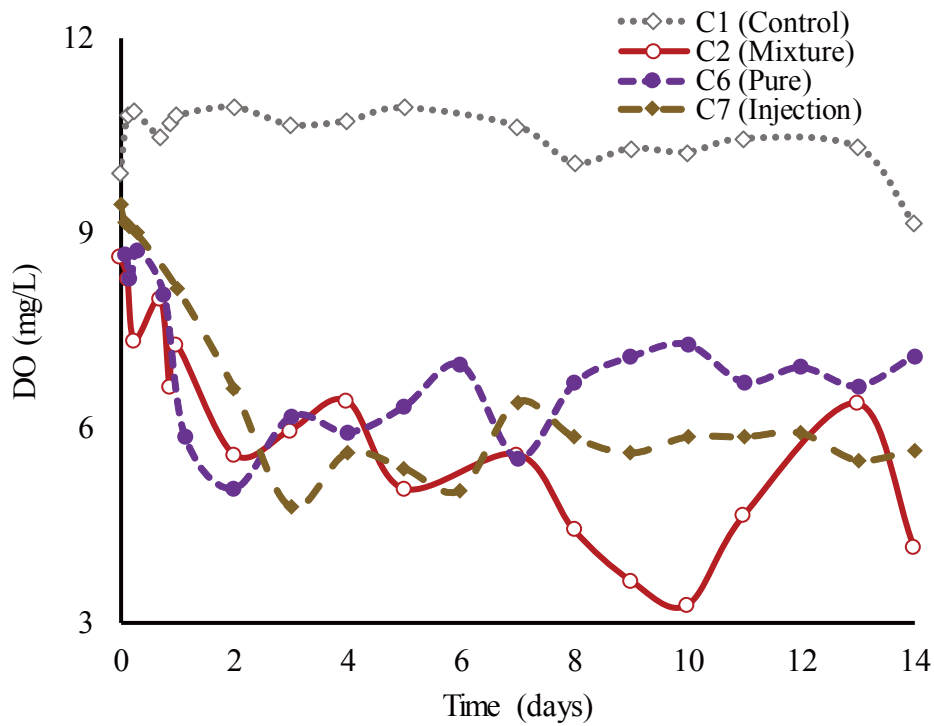**Fig. 3.23** Effect of reactive material state on ORP changes.

Fig. 3.24 Effect of reactive material state on DO changes.

3.4.4 Effect of support material

Figure 3.25 shows phosphorus removal rate in the columns used different support materials. In all columns, almost completely phosphorus removal was observed at the start of the experiments. Removal rate began to decline after two days in the column with river sand (C4) though it dropped after one day in the control column (C1) and the column with standard sand (C8). The results indicated that using river sand as support material resulted in more than doubling the effect on removal phosphorus in 14 days. Overall, it seems to be natural to conclude that river sand is better as support material than standard sand.

The obtained pH values in the columns with different support materials are indicated in Figure 3.26. In case of using standard sand as support material (C8), pH values increased sharply after the start of the experiments. Subsequently, it remained constant around seven and did not trend of increasing gradually. In case of using river sand (C4), pH showed low values around 5.5 at first. Subsequently, it begun to increase gradually and reached around seven in 14 days. There were the same tendencies of increasing gradually in the columns used river sand (C1&C4).

Figure 3.27 provides the results of ORP values as a function time in the columns with different support materials. In case of using standard sand as support material (C8), ORP values showed lower and decreased sharply, Subsequently, it remained around −40 and never indicated plus values. By contrast, ORP values showed a tendency of decreasing in case of using river sand (C1&C4). It reached around −40 in 14 days, while it indicated around 40 at the first of experiment.

The results of DO in the columns used different support materials are appeared in Figure 3.28. In comparison with the control column (C1), we can see that all columns resulted in lower values. The value in the column used river sand (C4) remained around five over 13 days. By contrast, that in the column used standard sand (C8) increased slightly through the experiment.
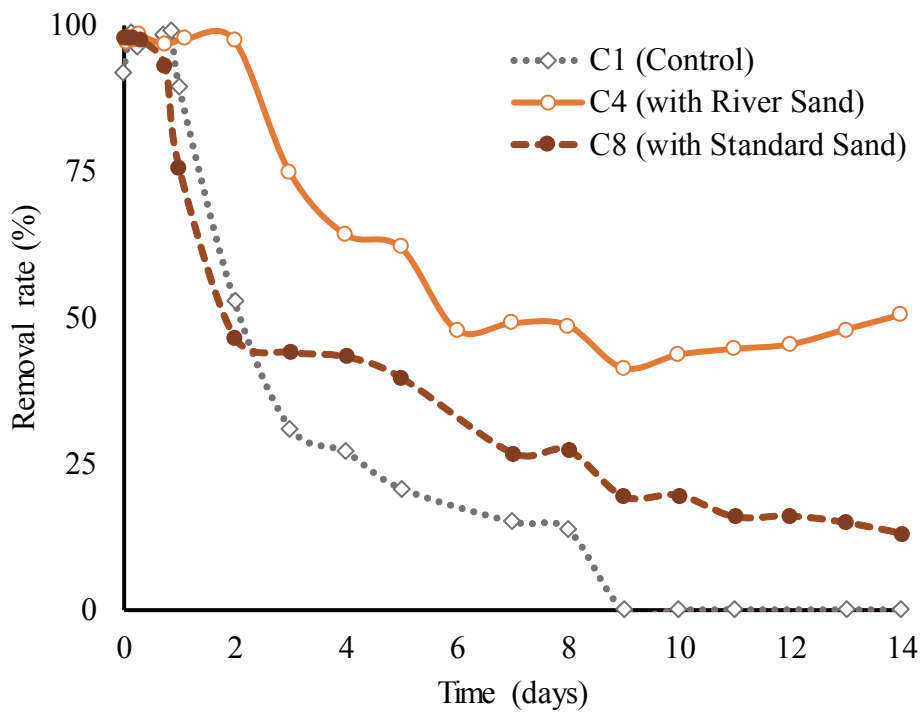
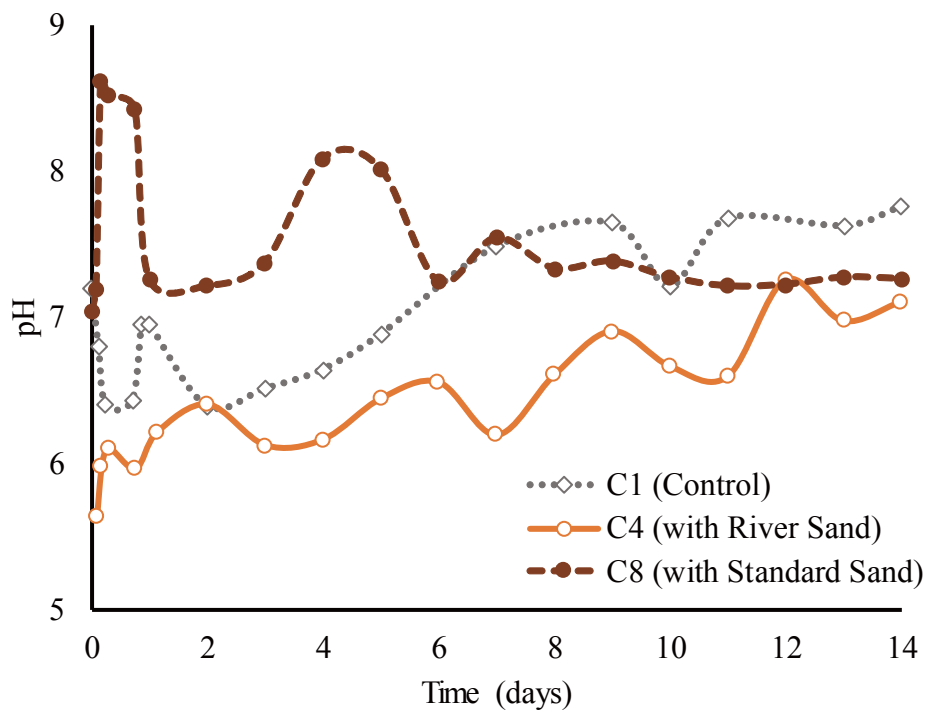**Fig. 3.25** Effect of support material on phsphorus removal.

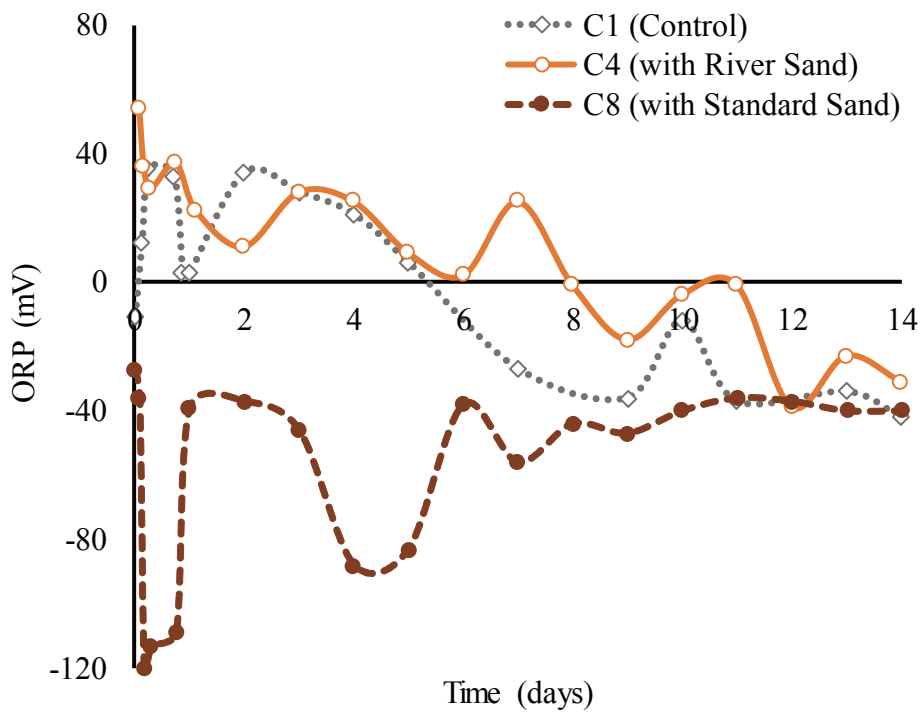**Fig. 3.26** Effect of support material on pH changes.

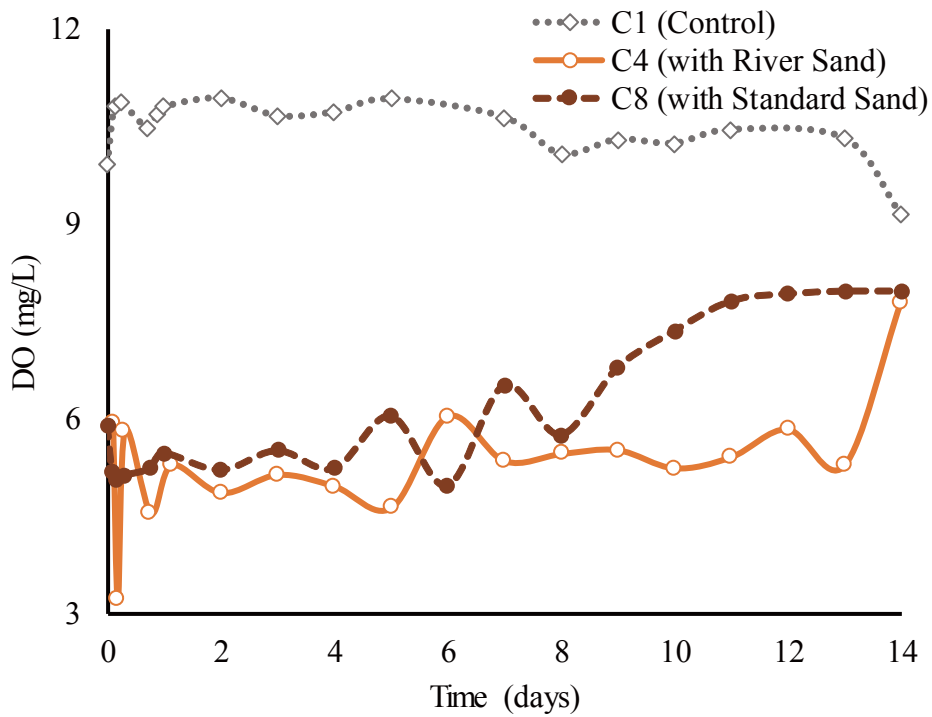**Fig. 3.27** Effect of support material on ORP changes.

Fig. 3.28 Effect of support material on DO changes.

3.4.5 Effect of flow rate

Figure 3.29 shows phosphorus removal rate under different flow rates. The flow rate in the columns with constant value (C1&C4) were 15 mL/min. The variable flow rate (C9) were decreased each 12 hour. Compared with the column at constant flow rate (C4), the removal efficiency was significantly low in Column 9 when the flow rate was high. After 48 hours, it improved dramatically as the flow rate changed 10 mL/min. After four days, the removal rate in Column 9 exceeded that in Column 4 and reached around 50% in 14 days. Overall, it seems to be natural to conclude that low flow rate has a positive effect on phosphorus removal.

The results of pH values in the columns under different flow rates are indicated in Figure 3.30. In case of the constant flow rate (C4), pH value showed around 5.5 at first. Subsequently, it increased gradually and reached around 7.0 at the end of the experiment. By contrast, pH values in the column under unfixed flow rate (C9) showed around 6.0 at first. Subsequently, it increased quickly after 24 hours and reached around 7.5 at the end. The values in Column 9 were higher than that in Column 4 through the experiment.

Figure 3.31 provides the results of ORP values as a function time in the columns under different flow rates. The value was around 60 at the first of the experiment in Column 4. Subsequently, it decreased gradually and reached around -30 in 14 days. The sharply changes were shown after 24 hours in Column 9 as with the results of phosphorus removal and pH values. The ORP values in Column 9 were lower than that in Column 4 even after changing flow rate to 10 mL/min.

The results of DO under different flow rates are appeared in Figure 3.32. In comparison with the control column (C1), we can see that all columns resulted in lower values. No significant differences were found among three columns. There were sharply increasing on 14 day due to some error.
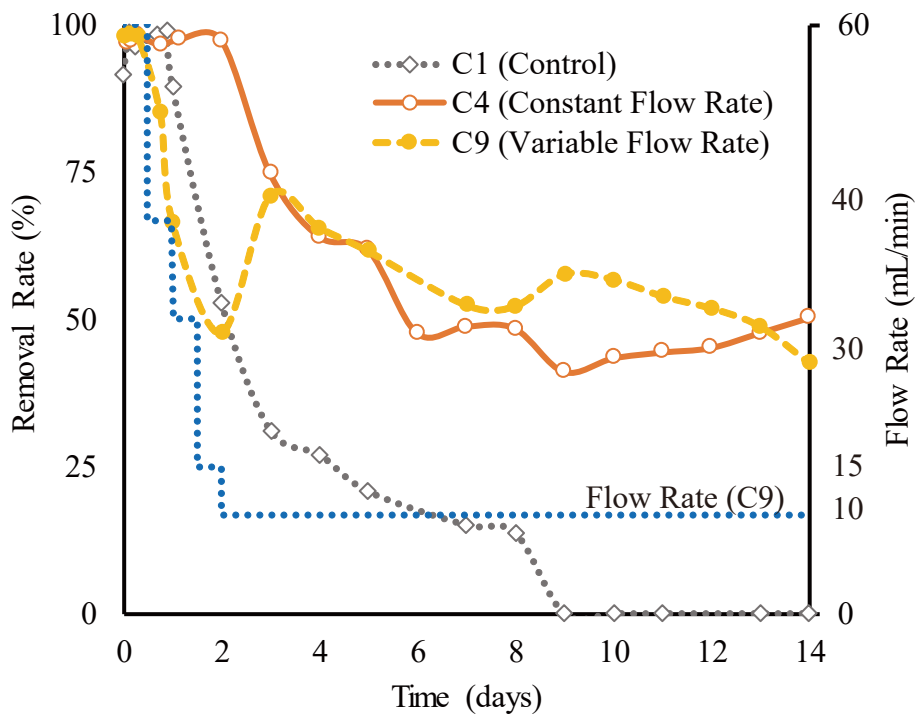
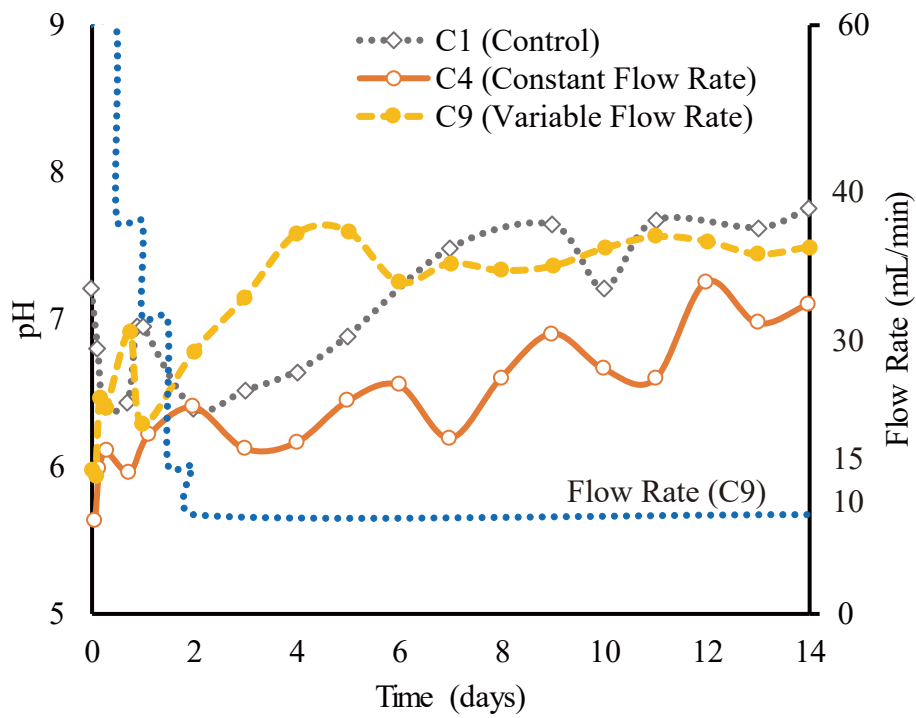**Fig. 3.29** Effect of flow rate on phsphorus removal.

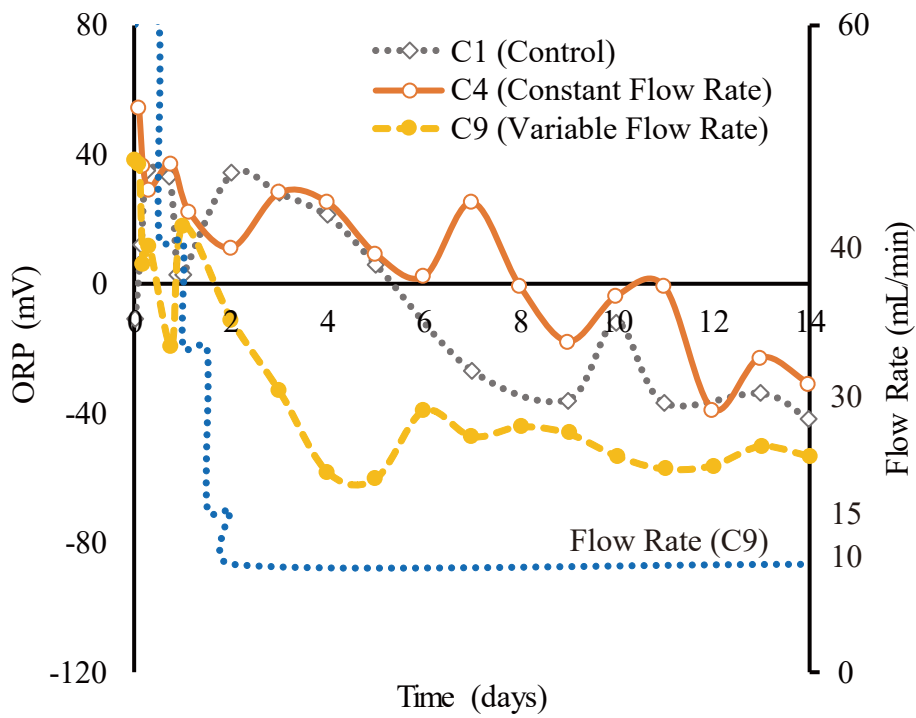**Fig. 3.30** Effect of flow rate on pH changes.

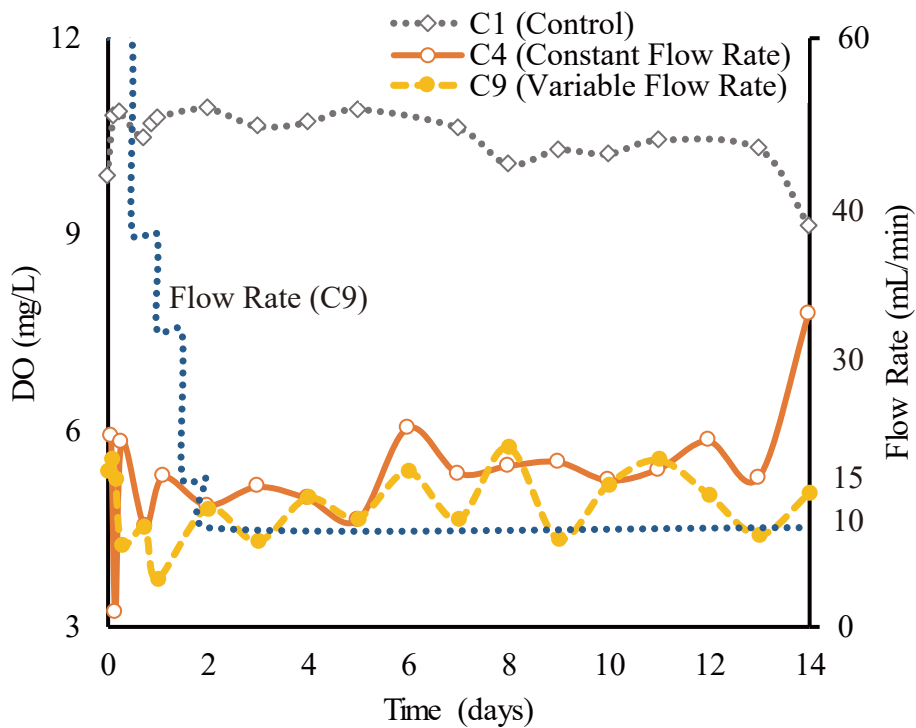**Fig. 3.31** Effect of flow rate on ORP changes.

Fig. 3.32 Effect of flow rate on DO changes.

3.4.6 Interference studies

Figure 3.33 shows phosphorus removal rate when the different solutions were injected into the columns. In all columns, almost completely phosphorus removal was observed after the start of the experiments. The removal rate kept around 100% in four days in the column with simulated groundwater (C10) though it dropped after two days in the column with phosphorus solution. However, high efficiency was observed in Column 4 after 10 days compared to Column 10. It reached around 50% in both columns in 14 days.

The results of pH values in the columns with different solutions are indicated Figure 3.34. The values of pH in Column 10 were higher than that in Column 4 through the experiment. The results did not show the correlation between phosphorus removal and pH values.

Figure 3.35 provides the results of ORP in the columns used phosphorus solution and simulated groundwater with phosphorus. In case of using synthesized groundwater (C10), the values showed around -80 at the first sample. Subsequently, it increased sharply and reached around 0. It begun to decline and indicated around -80 in 14 days. The values in Column 10 were lower than that in Column 4 through the experiment. The results did not show the correlation between phosphorus removal and ORP.

The results of DO in the columns used different solutions are appeared in Figure 3.36. Compared to the values in Column 4, that in Column 10 were higher at first. Subsequently, it decreased to five days. Interestingly, the values begun to increase to around eight days.
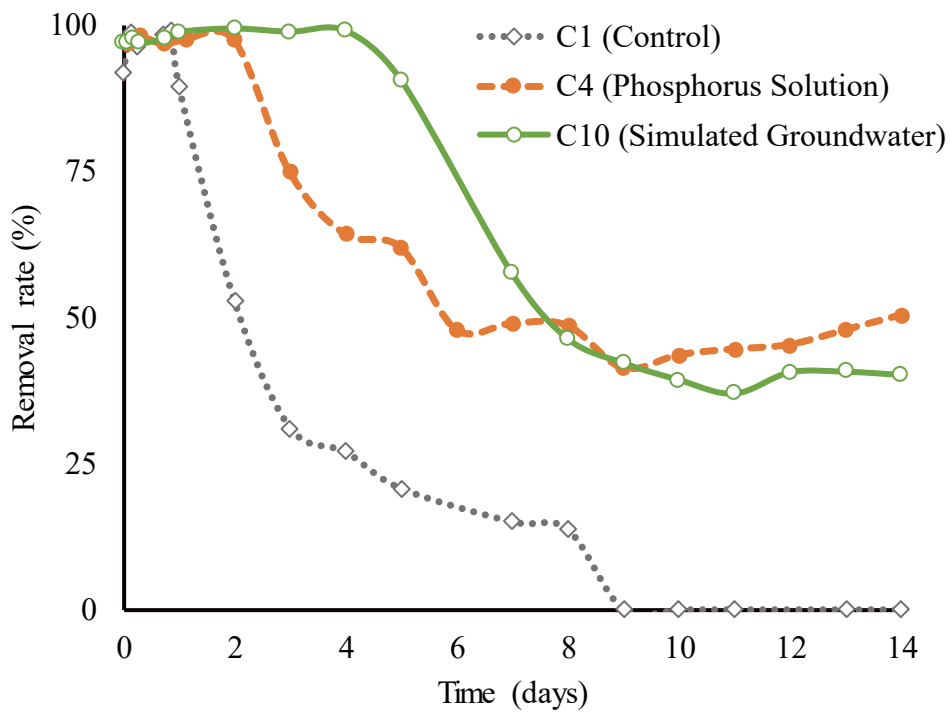
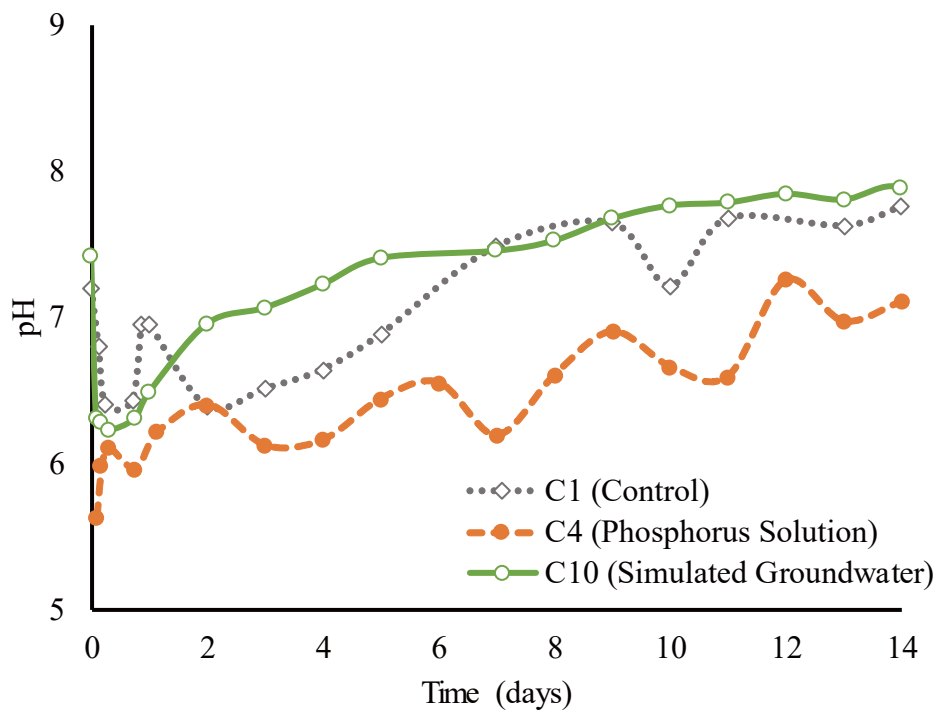**Fig. 3.33** Effect of other ions on phsphorus removal.

Fig. 3.34 Effect of other ions on pH changes.
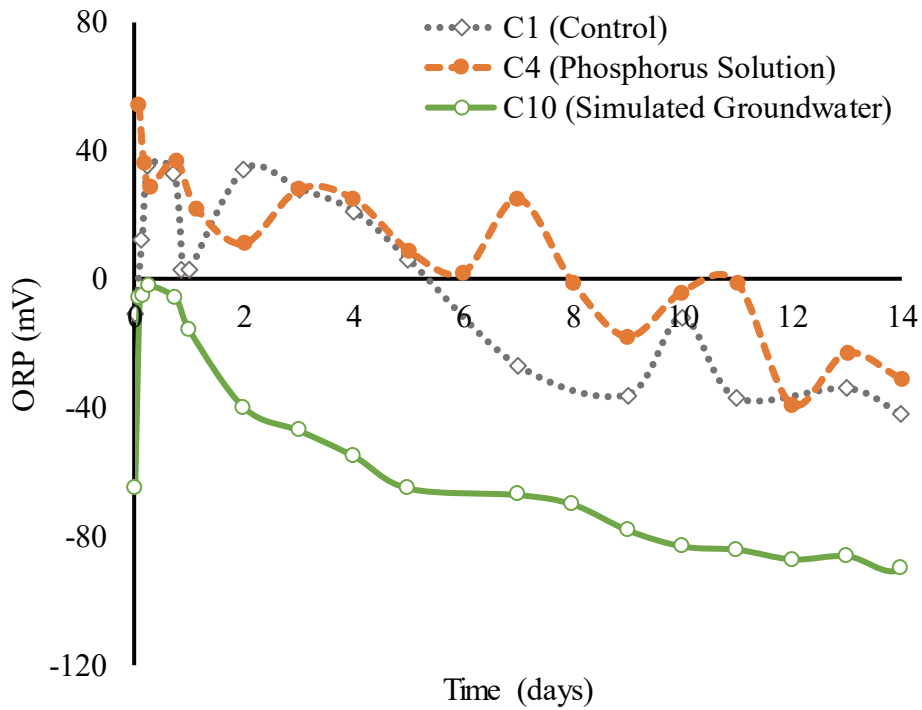
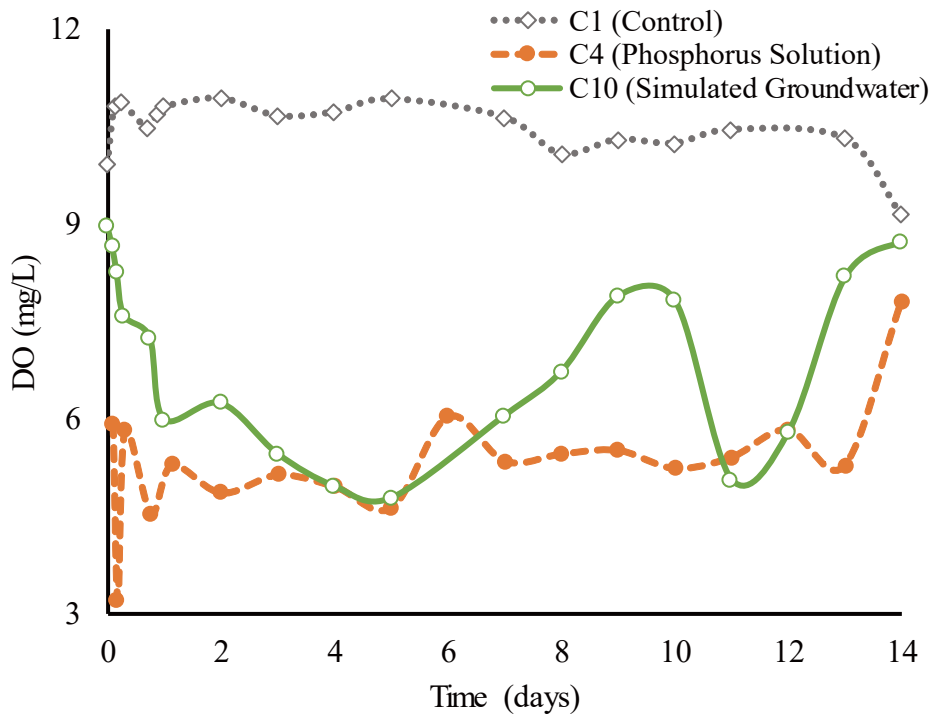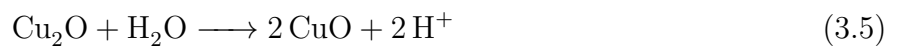**Fig. 3.35** Effect of other ions on ORP changes.

Fig. 3.36 Effect of other ions on DO changes.

3.5 Discussion

A significant efficiency of Bimetallic-NZVI on phosphorus removal in porous media for a long term was found as expected. Phosphorus adsorption capacity of Bimetallic-NZVI (335 mg/g) have doubled than that of NZVI (173 mg/g) in 14 days as with our previous batch study. In our previous study, it was hypothesized that the corrosion on the surface caused by copper enhances phosphorus adsorption. Additionally, it seems possible that this result is due to pH values. Many researchers have reported that low pH enhances phosphorus adsorption [21, 22]. In this experiment, the addition of copper increases H^+ ions as following reaction.

$$Cu^{2+} + 2\,e^- \longrightarrow Cu \tag{3.3}$$

$$2\,Cu + H_2O \longrightarrow Cu_2O + 2\,H^+ \tag{3.4}$$

$$Cu_2O + H_2O \longrightarrow 2\,CuO + 2\,H^+ \tag{3.5}$$

Discharged H^+ ions decrease pH values, which enhances more adsorption. It is suggested that the use of Bimetallic-NZVI as reactive material is effective on phosphorus removal in PRBs application.

The design of multi-layer improved phosphorus removal in case of using NZVI as reactive material. It is presumed that inserted river sand between reactive materials decreased clogging and increased contact time with phosphorus and iron particles. On the contrary, no significant differences were found between one-layer and two-layer design on phosphorus removal in case of using Bimetallic-NZVI as reactive material. A possible explanation for this result may be the low pH values caused by copper. It can be presumed that some reactions occurred between inserted river sand and phosphorus under low pH conditions, which changed phosphorus forms. The changed phosphorus might not have been easily removed by iron particles. There is a possibility that the second layer did not remove sufficiently due to the formation change of phosphorus. The reaction between soil and phosphorus is known as "Phosphorus Fixation", and it easily occurs under low pH conditions and hardly occurs at pH values above 6.0. In this study, removal rate was low with pH values lower than 6.0 in Column 5. After that duration, the phosphorus adsorption capacity increased as the values of pH increase. Overall, these results indicate that multi-layer design of PRBs has a possibility to be useful, however, pH values and support material are critical on phosphorus removal.

No significant differences were found among the state of reactive material. It is suggested that the mixture with support material (NZVI/sand) is suitable due to its high porosity in long term application. The use of standard sand as support material has resulted in the low removal efficiency of phosphorus. There is a possibility that the increase of pH has caused the removal efficiency to decrease sharply. This result suggests that support material is very important to design PRBs on phosphorus removal. The results with different flow rate showed the importance of water velocity in porous media on phosphorus removal. The phosphorus removal with high flow rate was significantly lower value in spite of the same con

guration. This result indicates that a contact time between phosphorus and reactive material is very critical. There were no significant differences between using phosphorus solution and simulated groundwater on phosphorus removal over 14 days. However, it is possible that other ions make pH values increase, which may induce low efficiency on phosphorus removal for a long period in PRBs.

Chapter 4

Conclusion

In this study, the aim was to investigate a rational design on removing phosphorus by NZVI for PRBs application through the laboratory-scale column experiment. The first major finding was that Bimetallic-NZVI (Fe/Cu) performed effective on phosphorus removal in porous media for a long term as with our previous batch experiment. The result of this study indicated that the adoption of Bimetallic-NZVI as reactive material may improve the performance of PRBs. The second major finding was that multi-layer design of PRBs had a possibility to be contribution on phosphorus removal, however, pH values and the characteristics of support material were key parameters. This study also signified that the contact time between phosphorus and NZVI may affect phosphorus removal efficiency.

A further study should be conducted to reveal an optimum design of PRBs application. One of the limitations of this study is that we were not able to collect enough number of samples for a statistical analysis. This is an important issue for future work. It is hoped that the outcome of the present study would be of some worth to the practical application of NZVI.

Acknowledgement

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