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## Integrating nano-scale zero valent iron (nZVI) in phosphorus removal from aqueous solution through porous media: packed-column experiment

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**Abstract:** This study investigates phosphorus removal from water through nZVI/river-sand packed columns. In order to evaluate their maximum phosphorus adsorption capacity, batch tests were first conducted for a synthesized nZVI (5:3.5 g / FeCl<sub>3</sub>: NaBH<sub>4</sub>) and river-sand. Aqueous solution of 25 mg/l phosphorus concentration was introduced to three-Plexiglas packed-columns (65 cm length, 10 cm inner diameter and PV=1.53 L) with different layers configuration. Solid precipitates of nZVI were characterized using TEM, XRD, BET and LD analyzers. Break-through curves showed that maximum phosphorus removal efficiency was recorded as 98.8% in Column 2 with two layers of nZVI/river-sand after only 17 hours, whereas Column 3 as a control column showed a rapid saturation (fully saturated by day 9). Dissolved oxygen values were clearly decreased in the first and second columns due to oxygen consumption by nZVI oxidation, unlike Column 3 in which the values were almost close to the influent value. River-sand showed relatively high adsorption capacity of phosphorus as a porous medium.

**Keywords:** Phosphorus removal; nano-scale zero valent iron (nZVI); packed-column experiment, in-situ remediation, nZVI characterization

### 1. INTRODUCTION

Phosphorus as one of the major nutrient is considered to be an essential element for all forms of life. However; in terms of water quality, excessive concentration of phosphorus can speed up eutrophication in water bodies. When it reaches surface water bodies, phosphorus tends to be the limiting nutrient leading to a rapid growth of algal bloom [1]. Consequently, it causes a plummet in the dissolved oxygen levels as a result, which consequently may affect the aquatic life harmfully and damage an existing ecosystem [2]. Dissolved phosphorus can be found in water on two forms, polyphosphate, orthophosphate and organic phosphate [3]. High phosphorus concentrations in groundwater can migrate from stream banks and adjacent land through aquifers into surface water bodies, therefore, it may affect both of surface and groundwater qualities [4]. Hence, phosphorus removal from water plays a significant role in decreasing such impact on the aquatic environment and the drinking water quality as well.

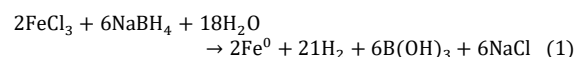
Currently, there has been much concern about minimizing the influence of such elevated phosphorus concentration on water quality and aquatic systems. Hence, different methods have been extensively applied for phosphorus removal from water such as chemical precipitation, co precipitation and adsorption on sorbents surface [5]. In the interest of high removal efficiency and reasonable cost, adsorption is considered to be one of the most efficient mechanisms in phosphorus removal from aqueous solutions [6]. As one of the most efficient and non-toxic adsorbents, zero valent iron (ZVI) has been widely used for water remediation of various pollutants [7]. The nano-scale of such iron particles increases the specific surface area, furthermore the core-shell structure with iron hydroxide shell enhances the reactivity towards most of the soluble contaminants in water [6].

Despite of the widespread investigation of nZVI efficiency in phosphorus removal through batch experiments, few studies concerned with the removal of phosphorus in porous media. Wen et al., [6] reported a maximum adsorption capacity of (245.65 mg-P/g-nZVI) to reach phosphate removal efficiency of 99% within 5 min from the start of the experiment. In a recent study, ZVI packed columns were used to check the impact of column's pre-conditioning on phosphate removal from aqueous solution with initial concentration of 20 mg/l [8]. The maximum phosphorus adsorption capacity reported in the former study was 152 mg-P/g-Fe [8]. The aim of this study is to investigate the efficiency of nZVI in phosphorus removal from water as well as determination of its maximum phosphorus adsorption capacity on nZVI surface. We demonstrate packed columns filled with nZVI supported on river-sand as pilot unit of an in-situ remediation method.

### 2. MATERIALS and METHODS

#### 2.1 Synthesis of nZVI

Chemical reduction method of Ferric chloride by sodium borohydride following reaction (Eq.1), was used to synthesize nZVI [9].



Ferric chloride hexahydrate solution was prepared by dissolving 5 g of FeCl<sub>3</sub>.H<sub>2</sub>O (99.0%, Junsei Chemical Co., Japan) in 125 mL of deoxygenated deionized (DI) water. Moreover, 3.5 g of Sodium borohydride (NaBH<sub>4</sub>, 98.0%, Sigma-Aldrich Inc., USA) were dissolved in 125 mL of (DI) water and pumped dropwise into a 500 mL four-neck flask kept in water bath with stirring (at 25 ± 0.5° C and 250 rpm) containing the former ferric

chloride solution using a roller pump at a rate of 20 mL/min. In order to reduce the oxidation of nZVI, anaerobic environment was provided through a continuous nitrogen gas purging during the synthesis. With regard of ensuring a complete reaction, the aging time of the mixture inside the four-neck flask was 20 min. The black iron precipitates were collected by vacuum filtration and then washed three times with DI water and anhydrous ethanol. The synthesized nZVI was kept refrigerated in a sealed container at 5° C in case it was not used immediately in batch tests.

## 2.2 Batch experiments

Batch experiments were performed to investigate the mechanism and kinetics of phosphorus adsorption on nZVI. All batch experiments were conducted in 300 mL conical flasks sealed with screw caps at room temperature ( $25 \pm 2^\circ$ ), and mixed with a standard magnetic stirrer (SRS316AA; 50 mL to 3L, 120V, 60Hz, ADVANTEC MFS, Inc., Japan) at 300 rpm. Phosphate solutions were prepared by adding several convenient amounts of potassium dihydrogen orthophosphate ( $\text{KH}_2\text{PO}_4$ , 99.5%, Kanto Chemical Co., Japan) to 250 mL of DI water. Nitrogen gas was purged into all solutions for 15 min prior starting the experiment, to preserve the anaerobic conditions for the reaction. Sodium hydroxide (NaOH, 97%, Wako Co., Japan) and hydrochloric acid (HCl, 35–37%, Wako Co., Japan) were used carefully to maintain the neutral pH conditions ( $7 \pm 0.5$ ) of all solutions. In order to determine the equilibrium phosphorus adsorption capacity of nZVI, a set of batch experiments were performed using different adsorbate concentrations (5, 10, 25, 50 and 100 mg/L) and fixed dosage of adsorbent (mass ratio of 1:1). 2 mL samples were withdrawn and filtered by 0.45  $\mu\text{m}$  membrane at specific time intervals

(5, 10, 15, 30, 60, 90, 120, 150 and 180 min) for phosphorus analysis. Adsorption capacity was calculated using the following (Eq.2):

$$q_t = \frac{V(C_o - C_t)}{m} \quad (2)$$

Where  $q_t$  (mg/g) is the adsorption capacity at time (t),  $C_o$  and  $C_t$  (mg/L) are phosphorus concentrations at initial time and at time (t) respectively,  $m$  (g) is the adsorbent mass, and  $V$  (liters) is the volume of the solution. Batch experiments were also conducted to estimate the approximate phosphorus adsorption capacity of river-sand as a porous medium material used in the column experiment.

## 2.3 nZVI characterization

The iron particles were analyzed using several equipment in order to determine their physical characteristics. The surface morphology was investigated using a transmission electron microscopy (TEM, JEM- 2100F, JEOL Co., Japan). Specific surface area (SSA) of the obtained nZVI was measured by (Micromeritics 3Flex, USA) using Brunauer–Emmett–Teller (BET- $\text{N}_2$ ) adsorption method at 77 K. Laser diffraction (LD) analyzer (SALD- 2300, Shimadzu Co., Japan ) was used to determine particle size of the synthesized nZVI after 30 min sonication. In order to distinguish the mineral composition of nZVI particles, X-ray diffraction (XRD) was performed using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) on TTR Rigaku diffractometer conducting at 40 kV and 40 mA, with scanning angle ( $2\theta$ ) ranged from  $3^\circ$  to  $90^\circ$  and scanning speed of  $2^\circ \text{ min}^{-1}$ .

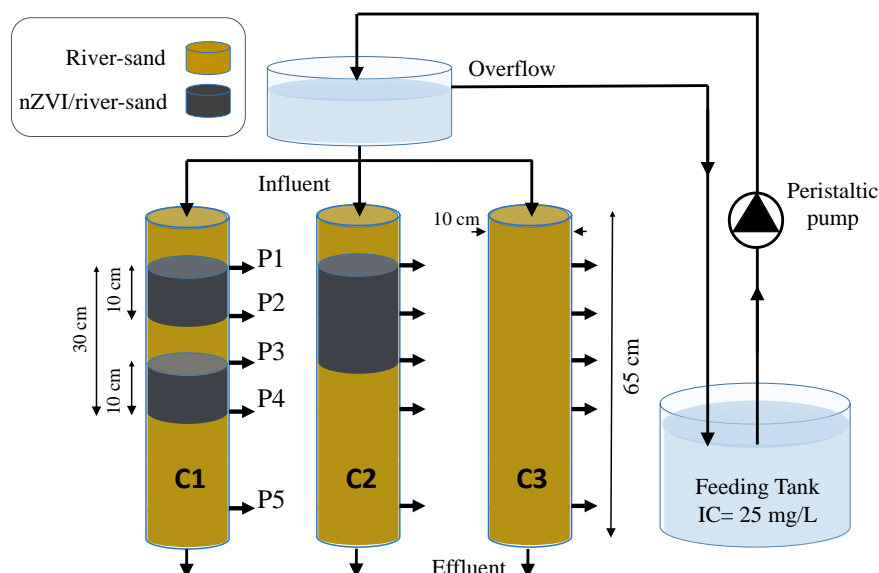


Fig. 1. Schematic of packed-columns.

Table 1. Column experimental conditions

Property	Parameter	Value
Column	Pore volume	1.53 L
	Porosity	30 %
	Bulk density	1.189 g/cm <sup>3</sup>
	Pore water velocity	0.38 m/h
	Flow rate	15 mL/min
Phosphorus solution	Concentration	25 mg/L
	pH	7 ± 0.5

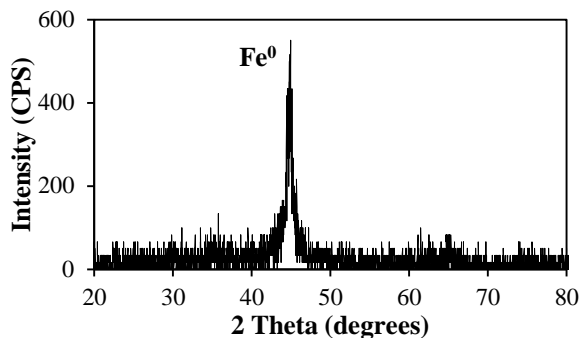


Fig. 2. X-ray diffraction (XRD) pattern of nZVI

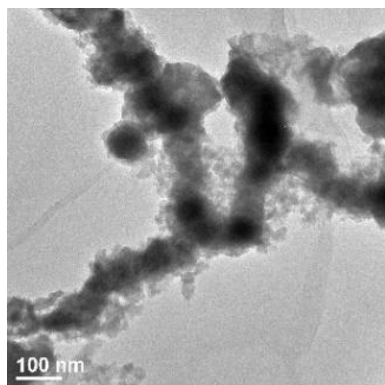


Fig. 3. TEM image of nZVI (100 nm resolution)

#### 2.4 Lab-scale packed columns

Column experiments were conducted on three packed-Plexiglas columns with length of 65 cm and inner diameter of 10 cm. Fig.1 indicates the configuration and dimensions of the three columns. Aqueous solution with phosphorus concentration of 25 mg/l was pumped downward into the columns from a 700 L tank using a system of peristaltic pump, tubes, distributor tank and an overflow collector to control the hydraulic heads along the experiment. The first layer at the top (10 cm long) was filled with river-sand only in order to maintain a uniform flow of the influent. First and second columns (C1, C2) were packed with river-sand (Kobaya, Miyazaki, Japan) as a major porous media, interspersed with different configuration of a homogenous nZVI/ river-sand mixture (1% [Fe/Sand] mass ratio, 20 g of nZVI); distributed as two separated layers (10 cm long each) and one combined layer (20 cm long) in C2 and C1 respectively. The third column (C3) was filled with river-sand only in order to act as a control column. Synthetic influent water with phosphorus concentration of 25 mg/L was prepared by dissolving KH<sub>2</sub>PO<sub>4</sub> (99.5%, Kanto Chemical Co., Japan) in water. The pH values were adjusted to be fixed at 7 ± 0.5 to simulate the natural groundwater. Septum caps along the columns allowed for

collecting water samples before and after the reactive layers along the columns. Effluent samples from the three columns were collected for residual phosphorus analysis, moreover samples from the feeding tank were regularly analyzed to ensure the initial phosphorus concentration during the experiment. Difference in water heads in each column were measured throughout the experiment using peizometric tubes, in order to calculate the accurate pore water velocity. Operational conditions of the column experiment is shown in Table.1.

#### 2.5 Analysis

Phosphorus and iron concentrations of all samples from batch and column experiments were filtered by 0.45 µm membrane to be analyzed for phosphorus and iron concentrations using UV-Vis spectrophotometer (DR 3900, Hach Co., USA). Moreover, pH and dissolved oxygen values were measured by (LAQUA act, Portable pH meter D-72, HORIBA Scientific Co., Japan) and (HQ30D Portable Multi Meter pH, Conductivity, TDS, Salinity, Dissolved Oxygen (DO), Hach Co., USA).

### 3. RESULTS and DISCUSSION

#### 3.1 Characteristics of precipitates

Fig.2 shows the XRD patterns of synthesized iron within the range of 3° to 90° (2θ), a major peak appeared at 2θ of 44.8 corresponding to intensity of 516 cps confirming the presence of (α-Fe) crystalline phase. Such high intensity peak ensures the periodic arrangement of particles; therefore we may imply that it is well defined in terms of crystallinity. Specific surface area of nZVI obtained from BET analysis was approximately 58.23 m<sup>2</sup>/g, which is coherent with an earlier study (61 m<sup>2</sup>/g) [2], and higher than other stated values [10], [11].

TEM image of iron particles is shown in Fig.3 depicting their aggregated necklace-structure [2]. Several images were taken and average particle size was evaluated with an approximate value of 42 nm. Particle size of nZVI that determined from LD analyzer showed a close value to the former size with a median particle diameter of around 44 nm. Size distribution results indicates that around 70 % (volume) of the particles have diameter less than 55 nm.

#### 3.2 Batch tests and adsorption isotherms

Equilibrium batch experiment results with varying adsorbate concentration plotted in Fig.4 (a) depict phosphorus removal efficiency more than 98 % for the low initial concentrations (5, 10 and 25 mg/L), and reduced gradually by the increase of the initial concentration. River-sand showed a relatively high phosphorus removal efficiency by around 85% for initial concentration of 5 mg-P/L, and decreased by the increase of the initial concentration as it is shown in Fig.4 (b). In order to determine the best isotherm model to describe the adsorption results, linear forms of Langmuir and Freundlich isotherms were plotted as it is displayed in Fig.5. Results in Table.2 show the calculated parameters of both isotherms including equilibrium phosphorus

Table 2. Adsorption isotherm models equations and corresponding calculated parameters

Model	Equation	Linear form	Adsorption parameters	
			Parameter	Value
Langmuir	$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L C_e}$	$q_{max}$ (mg-P/g-nZVI)	53.19
			$K_L$ (L/mg)	0.994
			$R^2$	0.995
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	$K_f$ (L/g)	3.572
			$n$	2.047
			$R^2$	0.965

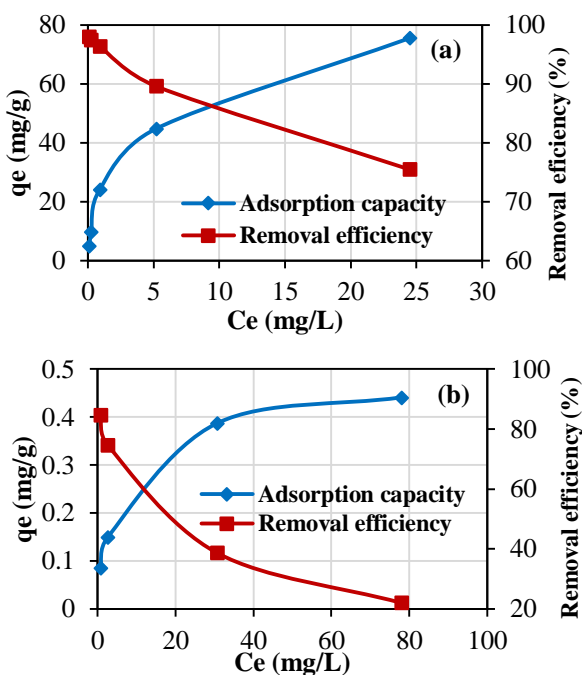


Fig. 4. Phosphorus adsorption capacity and removal efficiency (a) nZVI, (b) river-sand

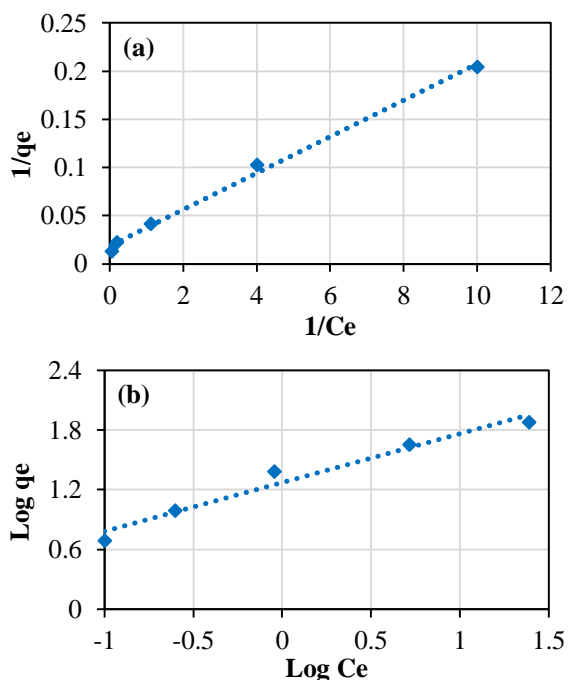


Fig. 5. Adsorption isotherms (a) Langmuir, (b) Freundlich

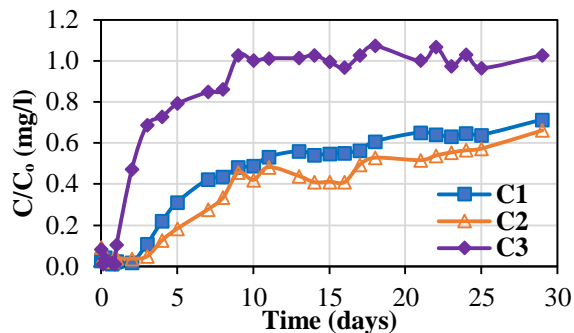


Fig. 6. Break-through curves of phosphorus in the three columns

adsorption capacity  $q_e$  of 53.19 mg/g, such value is higher than a previous reported data [2]. Moreover, calculated regression values ( $R^2$ ) indicate that Langmuir isotherm is more fitted to the present adsorption data.

### 3.3 Phosphorus removal in column experiment

Breakthrough curves (BTCs) of phosphorus were plotted using the ratio of  $C/C_0$  as a function of time (where  $C$  and  $C_0$  represent effluent and inlet phosphorus concentration respectively). Results in Fig.6 shows a slight higher efficiency of phosphorus removal in C2 (with two separated layers of nZVI/river-sand) compared to C1 (with one combined layer of nZVI/river-sand), whereas river-sand in C3 showed rapid saturation as the ratio of  $C/C_0$  increased dramatically to reach unity and become fully saturated by the 9<sup>th</sup> day from the start of the experiment.

During the first two days of the experiment, phosphorus adsorption reached the highest capacity in C1 and C2. Subsequently, it was followed by a dramatic increase in phosphorus concentration starting from day 3. Therefore, phosphorus removal efficiency in the two columns dropped consequently over the next following 26 days from the maximum (97.8% and 98.9%) to 29% and 34% for C1 and C2 respectively. With regard to determining the total adsorption capacity in the three columns, Cumulative phosphorus amount that trapped in each column was calculated. The highest cumulative phosphorus amount (456 mg-P/L) was trapped in C2; comparing to C1 (413 mg-P/L), after 29 days from the beginning of the experiment without reaching full saturation condition. On the contrary, C3 (river-sand) showed the lowest trapping capacity of phosphorus (184 mg-P/L).



The average percentage of phosphorus removal along 29 days of experiment was calculated where C2 with two

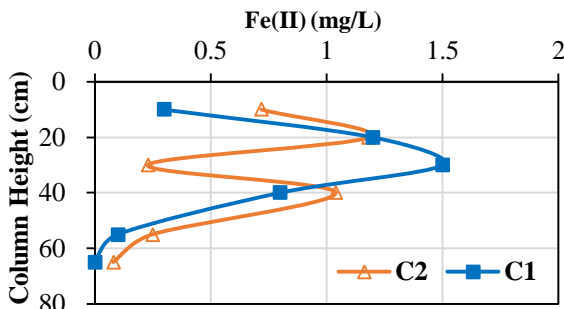


Fig. 7. Ferrous Iron ( $Fe^{2+}$ ) concentration along the two columns (7 days from the start of the experiment)

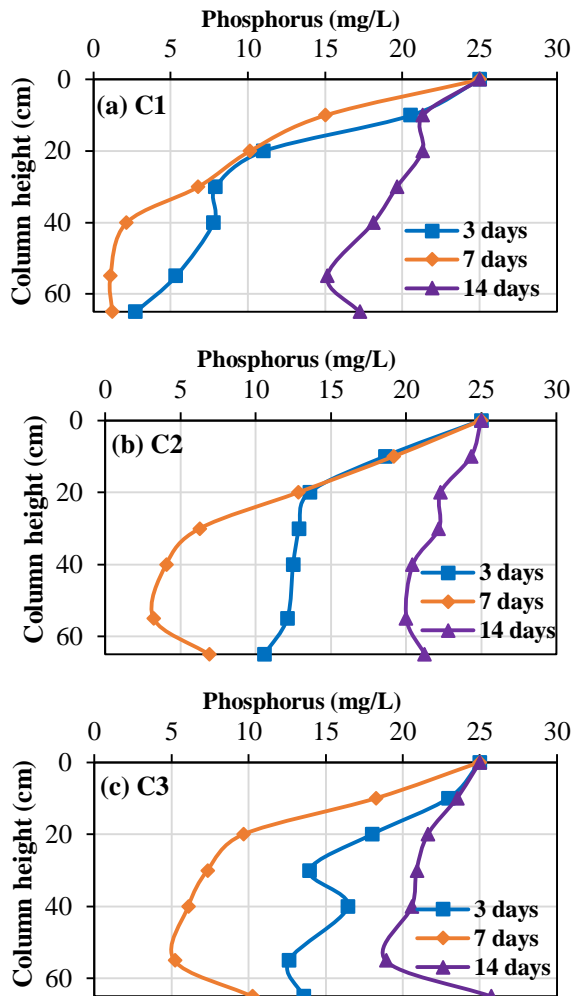


Fig. 8. Phosphorus profiles of the three columns

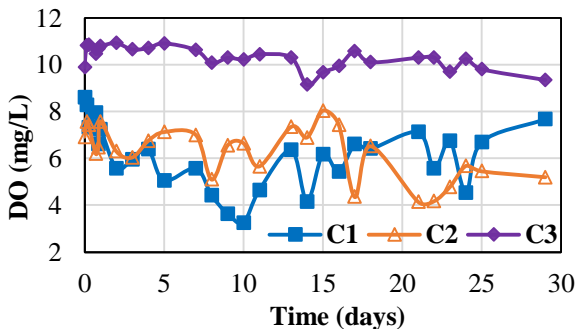


Fig. 9. Dissolved oxygen values of effluent in the three columns

layers of nZVI/river-sand showed the highest average removal efficiency of 68 % among the three columns. Comparing to the value of C1 with 62 % removal efficiency, this slight increase is related to the enhancement of phosphorus co-precipitation on the released iron oxidized forms with in the river-sand layer in C2. Fig.7 depicts that ferrous iron concentration reached the highest values just after the 1<sup>st</sup> reactive layer, and subsequently reduced due to phosphorus co-precipitation with in the sand layer.

### 3.4 Measurements along columns

Measurements of effluent pH in the three columns showed a slight decrease during the 1<sup>st</sup> day to reach 6.6, 6.7 and 6.4 for C1, C2 and C3 respectively. This reduction at the beginning is due to the forming of iron oxidized outer layer; the lower the pH value, the faster the iron surface corrosion [8]. Subsequently, it started increasing to fluctuate around the influent pH value for the rest of the experiment days. The oxidation process of  $Fe^0$  in the presence of water results yield  $OH^-$  ions which increases pH value again to reach more than 8 at some points along the experiment.

Plotted data in Fig.8 shows phosphorus concentration values along the three columns. The highest reactivity of nZVI corresponding to the best phosphorus adsorption was determined after 7 days (adsorption of about 88% of initial phosphorus amount). Thenceforth, it was decreased by the 14<sup>th</sup> day, this may be referred to the full occupation of the active sites on the oxidized iron particles [8]. Dissolved oxygen (DO) values were clearly decreased in C1 and C2 as it was consumed by nZVI oxidation process unlike C3, in which the values fluctuated around the inlet value of 10.7 mg/L as it is shown in Fig.9.

### 4. CONCLUSION

Synthesized nano-scale zero valent iron (nZVI) was integrated in phosphorus removal experiments from aqueous solution, in which it showed a promising performance as a reactive material in the in-situ remediation methods. The relatively high specific surface area (58.23  $m^2/g$ ) and the proper size (44 nm) of the iron particles enhanced the adsorption capacity to reach 53.19 mg-P/g-nZVI, which is considered superior to some preceding reports performed under the same neutral conditions. Configuration of two 10 cm layers of nZVI/river-sand showed a slight better performance in phosphorus adsorption than one combined 20 cm layer. River-sand showed relatively high adsorption capacity of phosphorus as a porous medium. The majority of cumulative trapped amount of phosphorus was retained by the first layer of nZVI/river-sand in both of C1 and C2. Second column with 2 layers of nZVI/river-sand showed the highest average removal efficiency of 68 % along the 29 days of the experiment. The main target of this study is the full scale application of such in-situ remediation technique, therefore a primary testing of a pilot system is essential.

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