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Simultaneous removal of nitrate, phosphate, and fluoride using a ZVI-packed bed electrolytic cell

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ABSTRACT

The present study aims to treat wastewater containing anionic contaminants such as nitrate, phosphate, and fluoride generated by the etching process of the semiconductor industry. The ZVI-packed bed electrolytic cell was developed to treat the contaminants using reduction, adsorption, and precipitation by electrochemical reactions. The 1 L reactor was operated with a voltage of 600 V, a flow rate of 30 mL/min (HRT: 12 min, EBCT: 33 min), and a packing ratio of 2:1 (v/v, silica sand to ZVI). Synthetic wastewater consisting of 30 mg/L as N, 10–50 mg/L as PO_4^{3-}, and 5–30 mg/L F^- was used for the experiment. Different combinations of anionic contaminants were tested in the experimental setup. Results indicated that nitrate, phosphate, and fluoride were removed at greater than 90%. When the reactor was operated without nitrate to act as a support electrolyte, phosphate, and fluoride removal efficiencies dropped drastically. Ammonia was produced during nitrate reduction, which led to iron oxidation. The FESEM and EDX analyses were performed to further investigate the electrochemical behavior in the ZVI-packed bed electrolytic cell.

Keywords: Nitrate reduction; Electrolytic cell; Zero-valent iron; Electrocoagulation

1. Introduction

Increasing nitrate concentrations in groundwater is a considerable environmental problem. Excessive application of fertilizers in agriculture causes the infiltration of large quantities of nitrate into underground and surface water [1]. The United States Environmental Protection Agency recommends less than 10 mg/L as N for nitrates in potable water [2]. Conventional nitrate purification processes including flocculation, sedimentation, and filtration appear to show no measurable effects [1,3]. Thus, physical and chemical methods such as reverse osmosis, chemical denitrification, and electrodialysis have been developed to eliminate nitrate from water [4]. However, these processes have various limitations due to complicated operation systems and cost problems.

To overcome these problems, electrochemical technologies using a ZVI-packed bed cell have been tested by the authors for the removal of nitrate [5].

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Electrochemical methods through the nitrate reaction have several advantages: no requirement of chemicals before or after the treatment, production of less sludge, small area demand, and low-investment cost [6].

Meanwhile, nitrate, phosphate, and fluoride are components of semiconductor industry wastewater generated from the etching process. Several physicochemical and biological processes have been investigated for the removal of dissolved nutrients in wastewaters.

To a certain extent, fluoride in drinking water at less than 0.5 mg/L is useful for bone and teeth development. However, continuous intake of fluoride in excess causes skeletal and dental deformities. Thus, the WHO standard permits fluoride at only 1.5 mg/L as a safe limit [7]. Conventional methods for fluoride removal are chemical precipitation based on adding lime, alum, and rare earth elements; ion exchange; adsorption; reverse osmosis, and nanofiltration. Among those, adsorption is being considered as the most appropriate way to remove fluoride. However, there are some disadvantages, such as sludge generation, continuous chemical injection, and decreased wastewater reusability due to residual salts [8,9]. Granular-activated alumina, bone char, zeolite, and calcite as alternative adsorbents are also difficult to use due to low adsorption capacity, pH conditions, and lack of mechanical strength [10].

On the other hand, phosphate directly impacts eutrophication in inland and coastal waters, and its international wastewater standard maximum limits range from 0.1–2 mg/L P [11]. As the most well-known methods for phosphate removal, adsorption methods are promising since they allow simple and economical operations resulting in less sludge production and fewer disposal problems. In phosphate treatment in wastewater, the removal method to precipitate phosphate involves the application of dissolved cations, such as Al^{3+}, Ca^{2+}, Fe^{3+}, and Fe^{2+} [12].

The present work aimed to study the electrochemical reduction of nitrate and adsorption of phosphate and fluoride simultaneously to improve the efficiency of wastewater treatment processes from synthetic wastewater using a ZVI-packed bed electrolytic cell as a novel electrolytic system. Phosphate and fluoride are easily combined with Fe ions and oxides. Effects of interaction between the anions and characteristics of electrolysis were investigated using multiple experiments to determine better operation parameters such as concentration. Reaction products and removal mechanisms were also discussed.

2. Materials and methods

2.1. Chemicals and materials

Sodium nitrate ($NaNO_3$, >99%, guaranteed reagent, Junsei), sodium phosphate dibasic (Na_2HPO_4, >99%, Reagent Plus, Sigma–Aldrich), and sodium fluoride (NaF, 99.8%, ACS Reagent, J.T. Baker), were used to make synthetic wastewater contaminated with nitrate, phosphate, and fluoride. A peristaltic pump (Easy-load® II, Cole-Parmer Instrument Co.) and tubing (4.8 mm inner diameter, 96410-25, Masterflex®) were used to feed the solution uniformly. The sphere type of ZVI (Fe > 98.4%, 0.6 mm diameter, Sanga Co.) and silica sand (<0.3 mm diameter, Joomoonjin silica sand Co.), were used as packing materials (780 g of silica sand and 1,340 g of ZVI were used for each experiment). A direct current power supply (XG600-2.8, Sorensen) was used to apply a potential of 600 V to the reactor and to measure the electric current consumption. Adequate safety precautions were taken with respect to the power supply. Platinum clad niobium netting was used as an anode placed at the bottom of the reactor to avoid a sacrificial anode, and stainless steel netting was used as a cathode at the top of the reactor (an electrode gap of 200 mm).

2.2. Experimental set-up and procedure

The ZVI-packed bed electrolytic cell was constructed as previously described [5]. The ZVI-packed bed electrolytic cell was developed to treat contaminants using electrochemical reduction, adsorption, and precipitation by electrocoagulation. The reactor was operated with 600 V, a flow rate of 30 mL/min (HRT 12 min, EBCT 33 min) and a packing ratio of 2:1 (v/v, silica sand to ZVI). Silica sand and ZVI were mixed by a ball mill over 1 h for uniform distribution. The synthetic wastewater was made with nitrate (initial concentration was always fixed at 30 mg/L as N), phosphate, and fluoride. All aqueous solutions were prepared using deionized water, and the experiment was conducted at room temperature.

2.3. Analytical methods

Nitrate, nitrite, ammonia, and phosphate were measured by an HACH (DR-2800) spectrophotometer [13]. Fluoride was measured by a fluoride electrode (Orion 9609BNWP, Thermo Scientific, USA). To observe, the morphological surface characteristics, a field-emission scanning electron microscope (SU70, Hitachi) was used at 15 kV of acceleration voltage, and energy dispersive X-ray analysis was conducted in the Center for Materials Analysis at Seoul National University.

3. Results and discussion

3.1. Effect of phosphate concentration

Fig. 1 shows the nitrate (a), ammonia (b), nitrite (c), and phosphate (d) concentrations in effluents with different phosphate concentrations (0, 10, 30, and 50 mg/L as PO_4^{-3}). The maximum nitrate removal efficiency was 94% at 60 min (Fig. 1(a)) without phosphate. Nitrate removal decreased with higher phosphate concentration, and nitrite, as an intermediate of nitrate reduction, increased. At 24 h, nitrate removal efficiencies were 90, 82, 66, and 57% at phosphate concentrations of 0, 10, 30, and 50 mg/L, respectively. Phosphate removal kinetics was very fast in the first stage. However, phosphate removal efficiencies decreased in proportion to the concentration. Removals of 96, 77, 70% phosphate were observed at phosphate concentration of 10, 30, and 50 mg/L at 24 h, respectively.

Decreased nitrate removal in higher phosphate conditions is due to the blockage of reactive sites on the surface of iron by specific adsorption of the inner-sphere complex forming ligands with phosphate and iron [14]. However, the results of phosphate 30 mg/L without nitrate, which are not presented in the figures, indicated a phosphate removal efficiency of approximately 30%. In this case, nitrate seems to act as a support electrolyte. Thus, nitrate in wastewater increased the current and promoted corrosion of iron that generates a significant synergy effect for electrocoagulation of phosphate. This indicates that iron corrosion seems to be an important step for efficient reduction of nitrate and electrocoagulation of phosphate. In addition, coagulation between phosphate

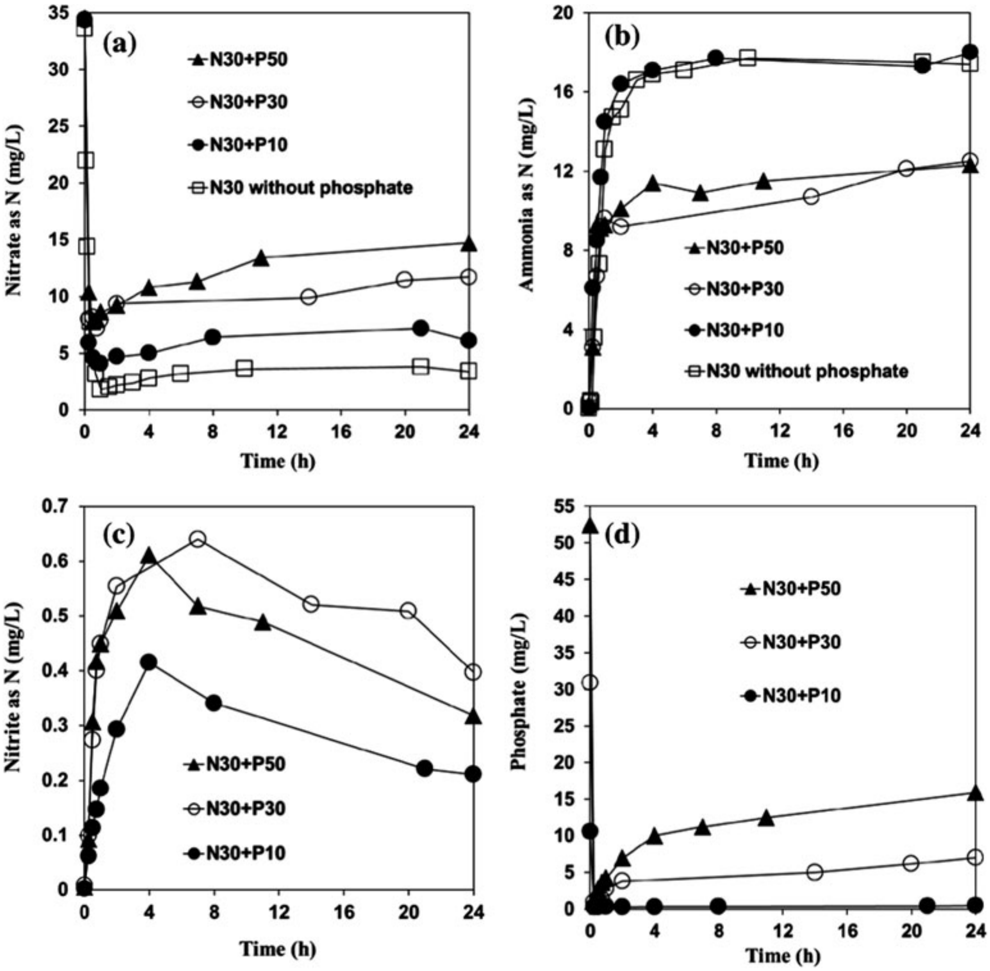

Fig. 1. Nitrate (a), ammonia (b), nitrite (c), and phosphate (d) concentrations in effluent with phosphate concentrations of 0, 10, 30 and 50 mg/L as PO_4^{-3} and nitrate 30 mg/L as N.

and iron is known to take place easily in neutral pH conditions [15]. Thus, most of the phosphate seems to precipitate on the bottom of the reactor at acidic zones, and to the middle of the reactor at alkaline zones. In all cases, the effluent temperature, electric current, and pH in effluent were around 40˚C, 0.1 A and 10.8–11.2, respectively.

3.2. Effect of fluoride concentration

Fig. 2 shows nitrate (a), ammonia (b), nitrite (c), and fluoride (d) at different fluoride concentrations (0, 5, 10, and 30 mg/L F^-). The maximum removal efficiency of 98% was observed for nitrate with fluoride at 30 mg/L at 30 min (Fig. 2(a)). In contrast to the previous results, the removal efficiency of nitrate and ammonia concentrations in effluent increased with higher fluoride concentration, and nitrite lower than 0.1 mg/L was observed in all cases. Even small quantities of fluoride in wastewater can lead to increased temperature, current, and pH in effluent to about 50˚C, 0.15 A and maximum 11.6, respectively. The reason seems to be that fluoride promotes the decomposition of the oxide film on the ZVI surface [16], so that nitrate or other anions have more opportunity to react with the ZVI. As a result, lower nitrate and nitrite and higher pH and ammonia, which are known as end products of nitrate reduction, were observed compared with conditions with no fluoride added. Neutral pH conditions are appropriate to precipitate fluoride, similar with phosphate [17], and electromigration helps the deposition of fluoride at the bottom to middle of the reactor near the anode. In case of fluoride at 5 mg/L without nitrate (not presented in figures), fluoride removal efficiency was around 20% for similar reasons to the case of phosphate, indicating delays in iron corrosion.

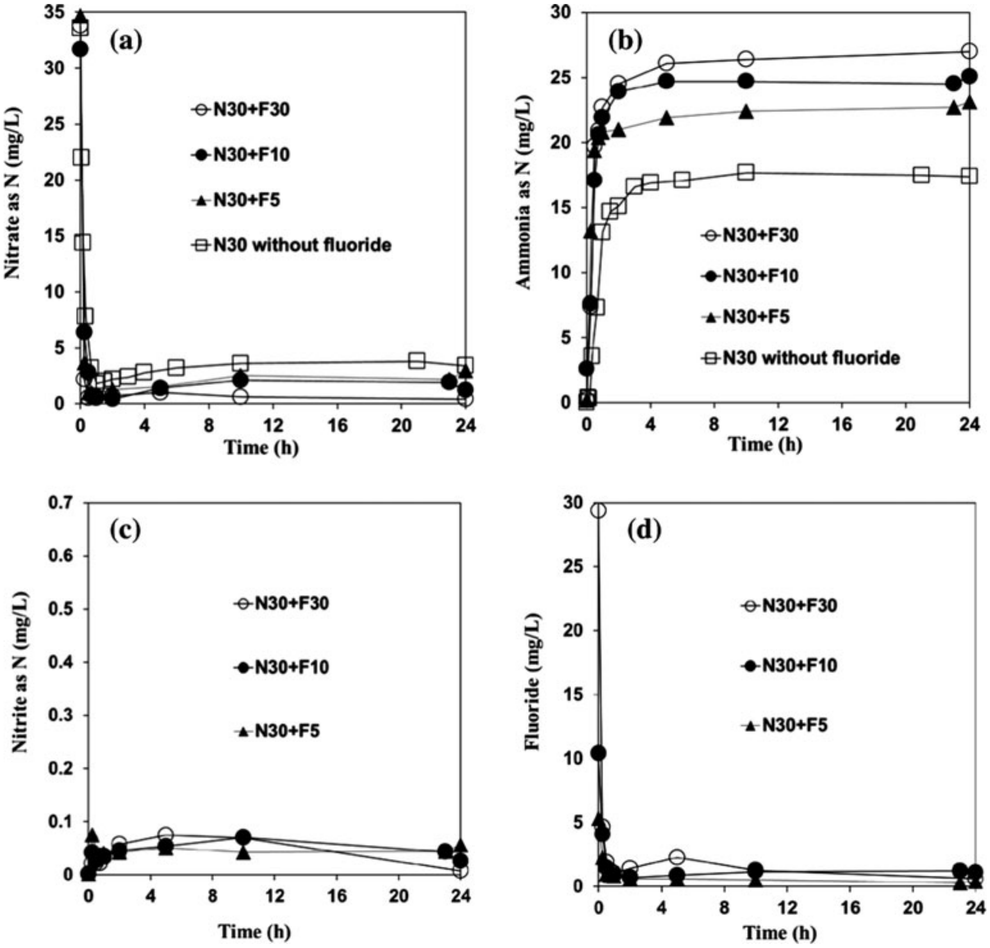

Fig. 2. Nitrate (a), ammonia (b), nitrite (c), and fluoride (d) concentrations in effluent with fluoride concentrations of 5, 10, and 30 mg/L F^- and nitrate 30 mg/L as N.

3.3. Effect of different mixing conditions of phosphate and fluoride

A mixed feed of nitrate, phosphate, and fluoride was carried out to observe the mutual relationship in the ZVI-packed bed electrolytic cell. Fig. 3 shows nitrate (a), ammonia (b), nitrite (c), phosphate (d), and fluoride (e) at different concentrations of nitrate 30 mg/L, phosphate (0 and 30 mg/L) and fluoride (0 and 5 mg/L). The control experiment including all three anions (nitrate 30 mg/L as N, phosphate 30 mg/L and fluoride 5 mg/L) was also performed without electricity. As previous results showed, adding phosphate inhibited nitrate removal, whereas adding fluoride promoted nitrate removal. Also, there was very little removal of nitrate without electricity. Ammonia, which was generated by nitrate reduction, showed higher concentrations, when fluoride was added and it showed lower concentrations when phosphate was added. If fluoride exists in wastewater, the phosphate removal efficiency increases due to synergistic effects of electrocoagulation with ZVI. Meanwhile, the fluoride removal efficiency was almost the same regardless of the presence of phosphate. In all experiments, the effluent temperature and electric current were maintained around 40–50℃ and 0.1 A. However, further operation could not proceed due to sharply increasing temperature to 100℃ and current to 0.5 A, when all were mixed together (nitrate 30 mg/L, phosphate 30 mg/L, and fluoride 5 mg/L). Higher electrolyte conditions led to higher current flow.

In the control experiment without electricity, nitrate, nitrite, ammonia, and fluoride concentrations did not change, and phosphate was only removed at about 40–50% in the early stage. However, removal efficiency decreased over time. It seems that phosphate was adsorbed on the surface of oxidized ZVI in contact with water.

3.4. Analysis of used ZVI particles

Fig. 4 shows the FESEM of the used ZVI that were sampled after completion of the experiments of nitrate 30 mg/L adding phosphate 50 mg/L (a) and nitrate

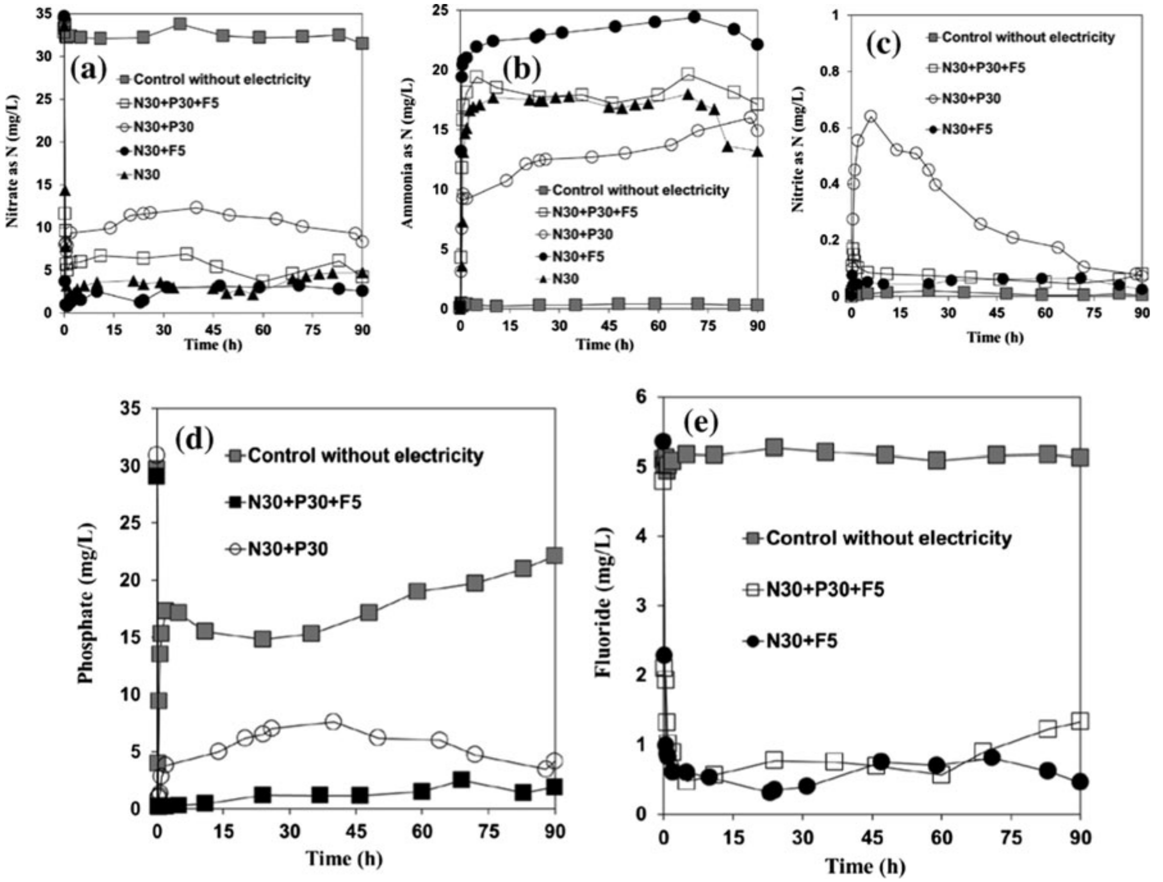

Fig. 3. Nitrate (a), ammonia (b), nitrite (c), phosphate (d), and fluoride (e) concentrations in effluent with different mixing conditions of nitrate 30 mg/L as N, phosphate 30 mg/L as PO_4^{-3}, and fluoride 5 mg/L F^-.

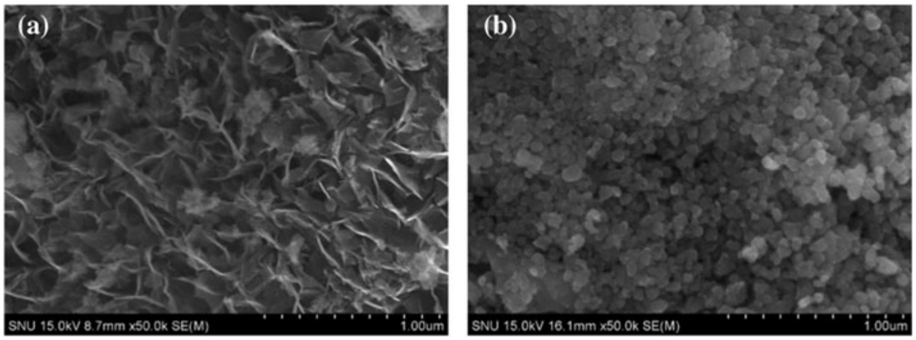

Fig. 4. The FESEM micrograph of the iron surface with magnification of 50×: plate shapes (a) with phosphate 50 mg/L as PO_4^{-3} and spherical shapes (b) with fluoride 10 mg/L F^- adding nitrate 30 mg/L as N.

30 mg/L adding fluoride 10 mg/L (b). The FESEM analysis observed iron oxides with plate shapes (Fig. 4(a)) and spherical shapes (Fig. 4(b)). Iron phosphate hydrate, magnetite, and iron hydrogen phosphate are electrocoagulation products [18]. According to the EDX results in this study, hematite (Fe_2O_3) and magnetite (Fe_3O_4) were major corrosion products, and various metallic hydroxide and oxide flocks, such as iron phosphate hydroxide and oxide and iron fluoride oxide were observed. Sodium and silicate complexes were also detected at trace amounts.

3.5. Removal mechanisms of anionic substances

When anions pass through the anode in the bottom of the reactor, transportation of anions to the cathode could be retarded due to electrical migration and then nitrate could be reduced. An acidic environment near the anode due to generated hydrogen ions with electrolysis of water can accelerate the corrosion of iron, whereupon reduction of nitrate and electrocoagulation of anions would be promoted. At that time, nitrate acts as a support electrolyte. Thus, coagulation of phosphate and fluoride seems to increase due to acceleration of iron oxidation. As the operation progresses, the upper part of the reactor gradually becomes alkaline with reactions of iron oxidation and nitrate reduction. Under these alkaline pH conditions, anions are removed by adsorption onto the iron oxide and hydroxide. The ferrous ion generated by corrosion of ZVI can take many forms of iron oxide and others, such as iron phosphate hydroxides and iron fluoride passage through the cathode.

4. Conclusions

Greater than 90% removal efficiencies for nitrate, phosphate, and fluoride were achieved using a ZVI-packed bed electrolytic cell. As a result, removal efficiency was better than when nitrate presented with phosphate and fluoride. Because nitrate acts as a support electrolyte, since the oxidation of ZVI was promoted by the enhancing effect, the removal efficiency of anionic contaminants by the adsorption onto the oxidized region of ZVI surface was increased further. The nitrate removal efficiency decreased with higher phosphate concentration, but it increased with higher fluoride concentration. Plate like and spherical shaped crystals of iron hydroxide and oxide complexes were found on the ZVI surfaces after the experiments.

Acknowledgments

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