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Phosphorus precipitation in septic systems induced by iron reduction: a process for phosphorus removal under anaerobic conditions

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ABSTRACT

Phosphorus in the effluents from decentralized septic tanks in the northeastern US imposes the threat of eutrophication on the sensitive receiving water bodies. Dissimilar to the popular nutrient-removal processes used in the wastewater-treatment plants, a lab-scale septic system retrofitted by iron amendment was developed in this study to stimulate phosphate precipitation in septic tanks. These results demonstrate that iron supplementation can effectively remove aqueous phosphorus in the septic system. In a stabilized anaerobic sequencing batch reactor (ASBR), more than 96% of the phosphorus was removed when iron was added at an Fe/P (molar ratio of Fe(III) addition to aqueous P) of 3. The iron demand for phosphorus precipitation in batch assays was considerably higher (an Fe/P ratio of 10 to achieve a phosphorus removal of 94.5%), indicating the presence of additional pathways for Fe(II) consumption, which was most likely due to the accumulation of extra Fe(II) consumers in the septic materials sampled. The removal of the soluble chemical oxygen demand in the ASBR was improved by 21–44% when the Fe/P ratio was increased from 1.5 to 3, suggesting that organic carbon was used as an electron donor for iron reduction; therefore, carbon mineralization was enhanced. Analysis of X-ray diffraction, electron microscopy, and energy dispersive X-ray spectroscopy show that vivianite was the main secondary mineral resulting from the iron reduction in the septic system.

Keywords: Septic system; Household sewage; Phosphorus removal; Iron amendment; Iron reduction; Vivianite

1. Introduction

Advances in understanding the eutrophication of water bodies suggest that controlling the phosphorus input is the primary key for reducing the problem [1–3]. In most cases, phosphorus is the limiting element, and a concentration as low as ~30 μg/L can stimulate algal growth in aquatic ecosystems [2]. In the rural country regions of the northeastern US, decentralized sewage is a possible phosphorus source for the local coastal and estuarine areas, which are particularly sensitive to nutrient input. Phosphorus in

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household sewage can result from, for instance, food and detergent [4–6]; its total concentration varies between 6–23 mg/L [7].

Approximately 25% of US households use onsite sewage disposal systems [8]. In septic tanks and the associated systems, phosphate mobility has been observed to be reduced due to sorption effect of the sediment and soil layers [9–11]. However, over a long period (decades), the P-retarding effect will eventually be exceeded because regulated setback distances of septic systems from lakeshores are often small (e.g. 15 m). Downgradient phosphate migration was identified in a number of mature septic system groundwater plumes [11–15]. More than 1 mg/L of phosphate-P could be present 20 m away from the infiltration bed [13]. On the other hand, researchers also noted that phosphate from septic effluent was still attenuated even in systems older than 10 years [14,15]. The P immobilization in the vadose zones of sediments is likely due to phosphate mineral precipitation (e.g. vivianite [$Fe_3(PO_4)_2{\cdot}8H_2O$], hydroxyapatite [$Ca_5(PO_4)_3(OH)$], strengite [$FePO_4{\cdot}2H_2O$], and variscite [$AlPO_4{\cdot}2H_2O$]), which are governed by redox levels [16,17].

In lake sediments, a substantial portion of P can be permanently immobilized in an Fe-bound form under strongly reducing conditions [18]. Iron geobiochemistry in sediment environments has been of great interest since the isolation of the first dissimilatory iron-reducing bacteria (DIRB) [19,20]. Biological iron reduction was assumed to have a large impact on sediment diagenesis and the exchange of nutrients and trace metals between sediments and the overlying water [21,22]. Phosphorus solubility and stability in sediments or soils can be influenced by iron reduction in two different ways: (a) the release of sorbed phosphate from the surface of iron minerals [e.g. Fe(III) oxyhydroxides] due to its reductive dissolution [23,24] and (b) the fixation of aqueous phosphate during secondary mineral formation (e.g. vivianite) [24–32]. Thermodynamic calculation indicated that vivianite precipitation is favorable in the anaerobic sediment layers as a permanent sink for phosphorus [18]. However, the actual presence of vivianite has rarely been positively confirmed in wastewater-treatment studies.

Biochemical precipitation may be a promising new strategy to artificially enhance phosphorus retention in anaerobic septic systems in which primary biological phosphorus removal processes via polyphosphate-accumulating bacteria are not possible. Recently, Robertson and coworkers studied the removal of sewage phosphorus in both a lab-scale column test and a full-scale filter (within a septic system) using granulated ferric oxyhydroxide media as the adsorbent [33,34]. They observed the formation of secondary mineral precipitates with high phosphorus contents, suggesting that the precipitation of Fe–P solids such as vivianite or strengite could have played a dominant role in the P attenuation. However, the P removal pathways and the product identification were not fully addressed.

The purpose of this study was to investigate the feasibility of phosphorus removal from septic wastewater via vivianite precipitation induced by biological iron reduction. Batch assays were conducted to investigate the variation in the aqueous phosphorus after iron supplementation in a household septic material; a bench-scale anaerobic sequencing batch reactor (ASBR) was subsequently employed to mimic simple septic tanks to study the liquid, biomass, and mineral phases in the system when it was amended by periodically dosing ferric oxyhydroxide slurry as an iron(III) material.

2. Materials and methods

2.1. External iron source and septic material

Amorphous ferric oxyhydroxide (A-FeOOH) was used as the external iron source in the experiments. It was prepared by neutralizing a 0.4 M solution of $FeCl_3$ to pH 7 with NaOH [23]. The obtained slurry was then washed thoroughly by deionized (DI) water to remove chloride. The iron concentration of the suspension was determined by 3 M HCl extraction [26]. A small amount of A-FeOOH was dried at room temperature and ground for structural characterization.

Twenty liters of septic material were sampled from a three-year-old residential septic tank (Dunstable, MA). The material was a homogenized mixture of accumulated sludge, scum, and the interlayer liquid.

Table 1
Characteristics of the septic wastewater from a three-year-old residential septic tank

Parameters	Septic wastewater
pH	6.52 ± 0.02
TCOD (mg/L)	24,000 ± 1,500
SCOD (mg/L)	850 ± 50
TSS (mg/L)	16,150 ± 150
VSS (mg/L)	13,825 ± 175
Aqueous P (mg/L)	28.75 ± 0.75
Aqueous Fe(II) (mg/L)	0.75 ± 0.00
Aqueous total Fe (mg/L)	0.5 ± 0.0
Extractable P (mg/L)	43.5 ± 4.5
Extractable Fe(II) (mg/L)	36.6 ± 0.0
Extractable total Fe (mg/L)	38.4 ± 0.0

The characteristics of the septic wastewater are shown in Table 1. The wastewater was stored at 4℃ and brought back to room temperature before use.

2.2. Batch assays

An A-FeOOH suspension was added into 117-ml glass serum vials containing 50 mL of septic wastewater at an Fe/P (molar ratio of Fe(III) addition to aqueous P in the wastewater) ratio of 1.5, the theoretical Fe/P in vivianite. The vials were then sealed with butyl rubber stoppers and put into a thermostat shaker at room temperature. The values of pH, TCOD, SCOD, aqueous P and Fe, 0.5 N HCl-extractable P, and Fe were tracked for 5 d. Iron-free vials were prepared as controls to observe the biological phosphorus uptake. In addition, Fe/P ratios of 1–10 (FeOOH dosage from 52 mg-Fe/L to 520 mg-Fe/L) were tested to evaluate the effect of the iron dosage on P removal from the septic wastewater. All assays were performed in triplicate.

2.3. Bench-scale ASBR

A bench-scale ASBR (New Brunswick Scientific Co. model Bioflo 110, Edison, NJ) with a 5-L working volume was used to simulate a conventional septic tank. The reactor was equipped with pH/ORP-monitoring and temperature-control systems. By using peristaltic pumps, a sequencing batch operation was performed as follows: feeding 20 min, reaction 23 h, settling 20 min, and withdrawing 20 min. For each cycle, 2.5 L of the treated wastewater was replaced by fresh synthetic household sewage after the periods of withdrawing (in the last cycle) and feeding. Agitation of 100 rpm was provided by a motor-driving blade. The temperature was maintained at 30 ± 0.2℃. Biogas was collected by Tedlar gas sampling bags (CEL Scientific Corp., Los Angeles, CA) and measured by a wet-tip gas meter (Wet Tip Gas Meter Co., Nashville, TN).

Synthetic household sewage was prepared with (per liter): 56 mg sucrose, 182 mg starch, 54 mg cellulose, 333 mg meat extract, 82 mg vegetable oil, 250 mg NaCl, 7 mg $MgCl_2{\cdot}6H_2O$, 4.5 mg $CaCl_2{\cdot}2H_2O$, 200 mg $NaHCO_3$, 85 mg commercial detergent, 16 mg K_2HPO_4, 1 ml trace solution, and 10 ml vitamin solution. The resulting COD was ~800 mg/L and P 28.5 mg/L. The trace solution contained (mg/L): H_3BO_3 (50), $ZnCl_2$ (50), $CuCl_2$ (30), $MnSO_4{\cdot}H_2O$ (500), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (50), $AlCl_3$ (50), $CoCl_2{\cdot}6H_2O$ (50), and $NiCl_2$ (50) [35]. All of the chemicals were either from Sigma-Aldrich Co., or Fisher Scientific, Inc. The ASBR was fed with the synthetic household sewage. An A-FeOOH slurry, after being fully stirred in the storage vial, was supplemented with 78 mg-Fe/L (an Fe/P of 1.5 as in vivianite) together with the synthetic sewage input during the startup period of the reactor; after two weeks of operation in a stable state, a higher iron level (156 mg-Fe/L, an Fe/P of 3.0) was used to study the dosage effect.

2.4. Analytical methods

The values of COD, pH, bicarbonate alkalinity (BA), PO_4-P, total suspended solids (TSS), and volatile suspended solids (VSS) were analyzed according to standard methods [36]. Aqueous parameters were measured by filtering water samples through 0.45 μm glass-fiber filter paper (Gelman A/E, Ann Arbor, MI). The Fe(II) and total Fe (FeT: Fe(II) + Fe(III)) concentrations were determined by reagent sets (Hach Co., Loveland, CO) based on the 1,10-phenanthroline colorimetric method [36]. Samples for the Fe(II) assay were acidified by hydrochloric acid and tested immediately to minimize their oxidation. HCl-extractable PO_4-P and HCl-extractable Fe species were obtained by treating suspensions in 0.5 N HCl overnight and were then measured as described above [26]. Volatile fatty acids (VFAs) were analyzed using a gas chromatograph (HP 6850 series, Wilmington, DE) with a flame ionization detector and a DB-WAXETR capillary column (30 m × 0.25 mm). CO_2 and CH_4 in the biogas produced were measured with a Shimadzu GC-8 equipped with a thermal conductivity detector and a Porapak N column. Helium was used as the carrier gas (100 mL/min) and the oven temperature was 40℃.

2.5. X-ray powder diffraction

Mineralogical characterization of the solid samples was carried out by X-ray powder diffraction on a Rigaku Ru300 with CuKα radiation (Japan). The diffractometer was operated at 50 kV and 300 mA. The sludge samples were collected from the ASBR after vigorous agitation (for a homogeneous state) by a 5-mL pipette and were washed twice by oxygen-free DI water, dried, and ground into a high-purity nitrogen atmosphere. The samples were then prepared into a finely pressed powder in a glass holder. The X-ray diffraction (XRD) patterns were collected over a 2θ range from 8° to 80° at a scan rate of $3^\circ\ \mathrm{min}^{-1}$.

2.6. Electron microscopy

The sludge samples were collected from the ASBR and fixed overnight in glass vials containing 2.5%

glutaraldehyde in 0.1 M sodium cacodylate (pH 7.4) at 4℃. The samples were washed twice in a 0.2 M cacodylate buffer solution (pH 7.4), post-fixed with 2% osmium tetroxide for 2 h at 4℃ and rinsed twice by DI water for 30 min. The samples were then dehydrated through a graded ethanol series and placed onto 100-mesh carbon-coated copper grids (SPI, West Chester, PA). TEM imaging was performed with a Philips EM400 TEM operated at 100 kV. The samples for SEM observation were coated by gold before being examined by a field-emission scanning electron microscope (FE-SEM) (JSM-7401F, JEOL, Japan). Qualitative energy dispersive X-ray spectroscopy (EDS) (EDAX Genesis V4.61 X-ray detector, USA) analyses were performed in SEM mode.

3. Results

3.1. Batch assays

3.1.1. Phosphorus removal by iron amendment

The A-FeOOH amendment was effective at removing PO_4-P from the septic wastewater. After a five-day incubation, 32% of the aqueous phosphorus was removed in the Fe-amended vials, compared to 2% in the Fe-free controls (Fig. 1(a)). During the first 16 h of reaction in the control samples, the PO_4-P concentration decreased by 30.1%; afterward, the P concentration recovered to almost the initial level (94% recovered) at the end of the tests. However, the A-FeOOH amendment improved the P removal throughout the test (e.g. increased by 18.1% in 16 h), and the P concentration remained relatively stable. For 0.5 N HCl-extractable P, there was no obvious difference detected between the Fe-amended samples and the controls. A decrease of ~6 mg/L was noticed in the initial period (16 h) in both groups, which is comparable with the aqueous phosphorus removal in the controls during the same period. This reveals that the initial decrease in aqueous P in the controls was due to biological uptake and that this portion of P was not 0.5 N HCl-extractable. The concentrations of the aqueous Fe series were negligible (<5 mg/L) during the entire test, which indicates that most of the iron was within solid phases, such as the precipitates and biomass (Fig. 1(b)). Extraction tests showed all of the FeOOH added was rapidly reduced to Fe(II) in the first hour after being added into the septic wastewater (Fig. 1(b)) because the extractable total Fe was approximately equivalent to the extractable Fe(II). During the initial 8 h of the batch assays, SCOD increased remarkably from 830 to ~2,300 mg/L in all of the samples, which may be caused by the dissolution of organic particles in the septic materials due to biological processes or the agitation effect during the incubation (Fig. 2). The SCOD value was 610 mg/L lower in the Fe-amended sample after five days, compared with the controls. However, such a change was not reflected in the TCOD concentration due to the high heterogeneity of the septic samples.

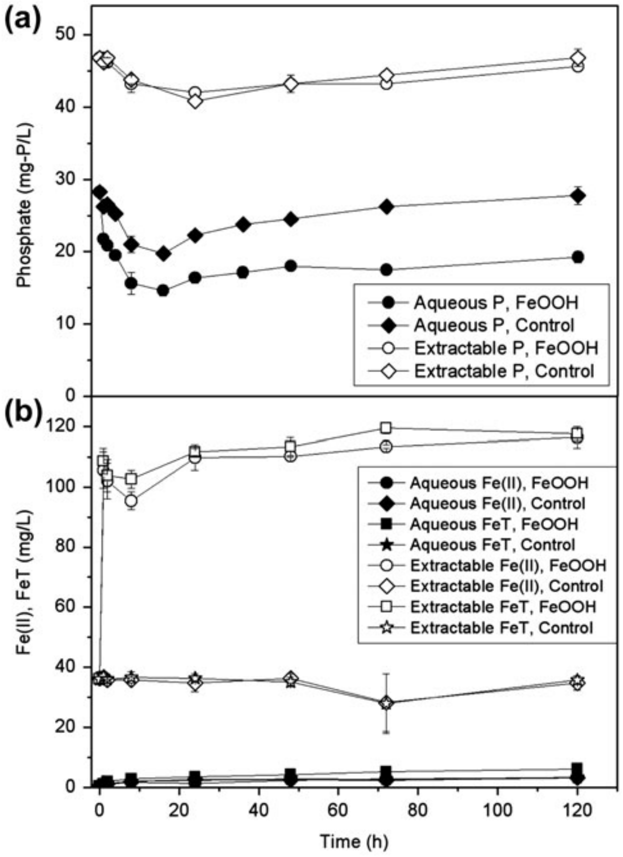


Fig. 1. Time series of the concentrations of aqueous and HCl-extractable PO_4-P (a) and Fe species (b) in the septic wastewater with and without FeOOH amendments. (Data from batch tests).

3.1.2. Effect of the iron dosage on phosphorus removal

Increase in the A-FeOOH supplementation effectively increased the PO_4-P removal from the septic wastewater (Fig. 3(a)). When the Fe/P was 10, 94.5% of the aqueous phosphorus was removed, whereas the removal efficiency was 8.69% at an Fe/P ratio of 1. Increases in the aqueous and extractable Fe(II) were also observed resulting from higher iron dosages (Fig. 3(b) and (c)). The iron reduction can be divided into two stages: a fast transformation in the first hour after FeOOH addition and a slow one over the

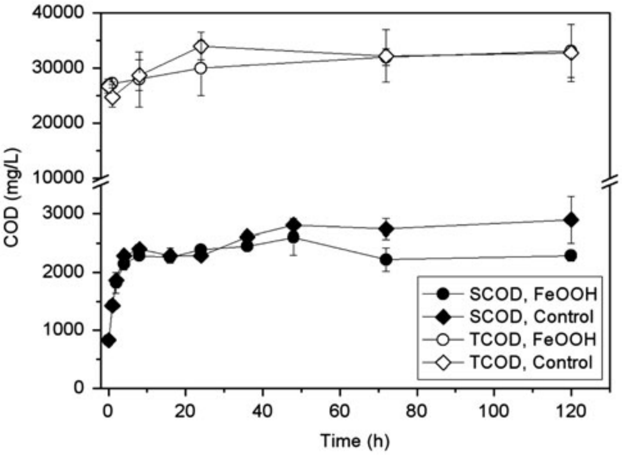


Fig. 2. Time series of the concentrations of SCOD and TCOD in the septic wastewater with and without FeOOH amendments. (Data from batch tests).

following days (Fig. 3(c)). In the experiments with Fe/P ratios from 0 to 5, the extractable Fe(II) approximated the extractable FeT and also the theoretical amount of iron in the system (the extractable FeT in the controls + the iron supplemented). When the Fe/P was 10, the extractable Fe(II) tested was 18.0 mg/L lower than the extractable FeT and the extractable FeT was 118.8 mg/L lower than the theoretical iron in the bottles (extractable Fe(II) = 405.0 mg/L, extractable FeT = 423.0 mg/L, and theoretical FeT = 541.8 mg/L). The results indicate that a portion of the A-FeOOH supplemented was not utilized at a Fe/P ratio of 10 because A-FeOOH is not completely extractable by 0.5 N HCl [26].

3.2. Continuous phosphorus removal in the ASBR

Ten days after the ASBR was started, the anaerobic system reached a stable state (Fig. 4). The PO_4-P removal efficiency increased gradually to ~45% (Fig. 4(a)) resulting from the iron reduction, as revealed by the aqueous Fe(II) tested (Fig. 4(b)). No difference was observed between the extractable Fe(II) and FeT during this period (before day 26) suggesting that all of the FeOOH supplemented was reduced (Fig. 4(c)). The pH, ORP, and BA values were approximately 6.20, −420 mV, and 250 mg/L as $CaCO_3$, respectively (Fig. 4(d–f)). The high TCOD of the effluent in the first several days was caused by the sludge washed out due to the poor settling ability and the selective pressure that SRB reactors generally have (Fig. 4(g)). The TCOD removal efficiency varied between 27 and 34% after the reactor became stabilized, whereas the SCOD removal was negligible.

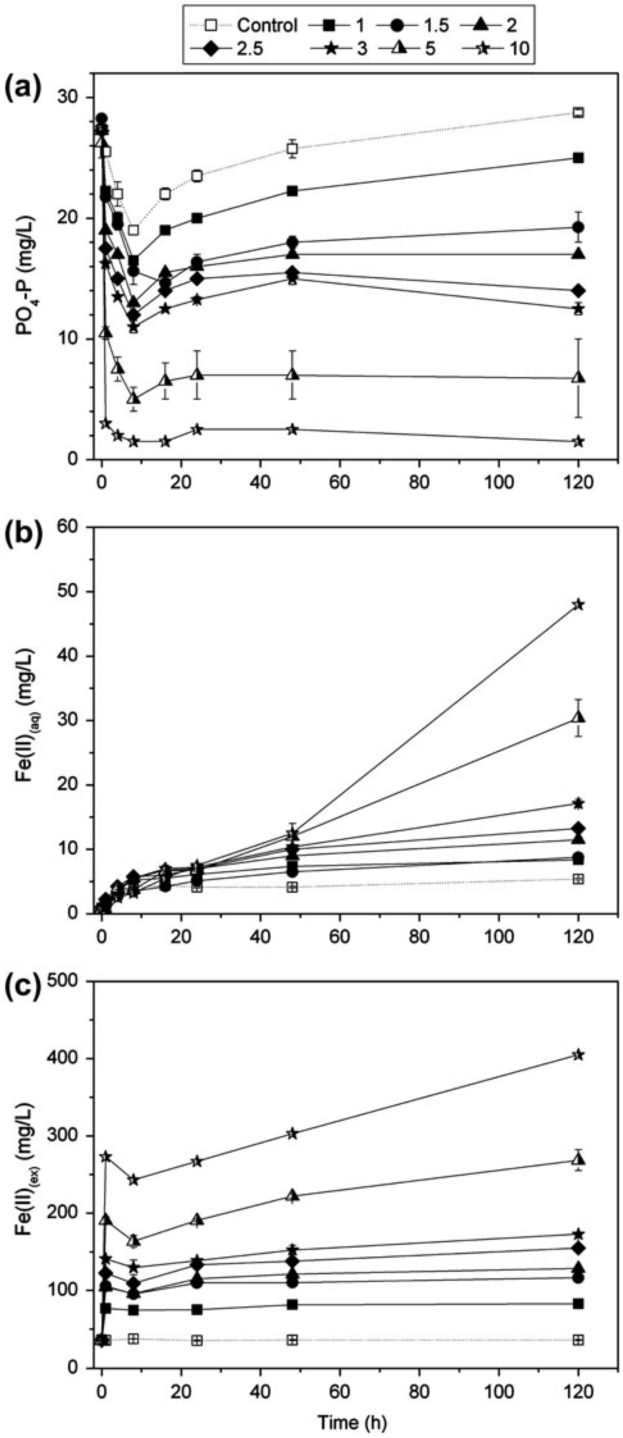


Fig. 3. Effect of FeOOH dosage on the concentrations of aqueous PO_4-P (a) aqueous Fe(II) (b) and HCl-extractable Fe(II) (c) in the septic wastewater. (Data from batch tests).

The increase in the Fe/P ratio to 3 after day 26 remarkably promoted phosphorus removal from the wastewater (Fig. 4(a), after the arrow). More than 96%

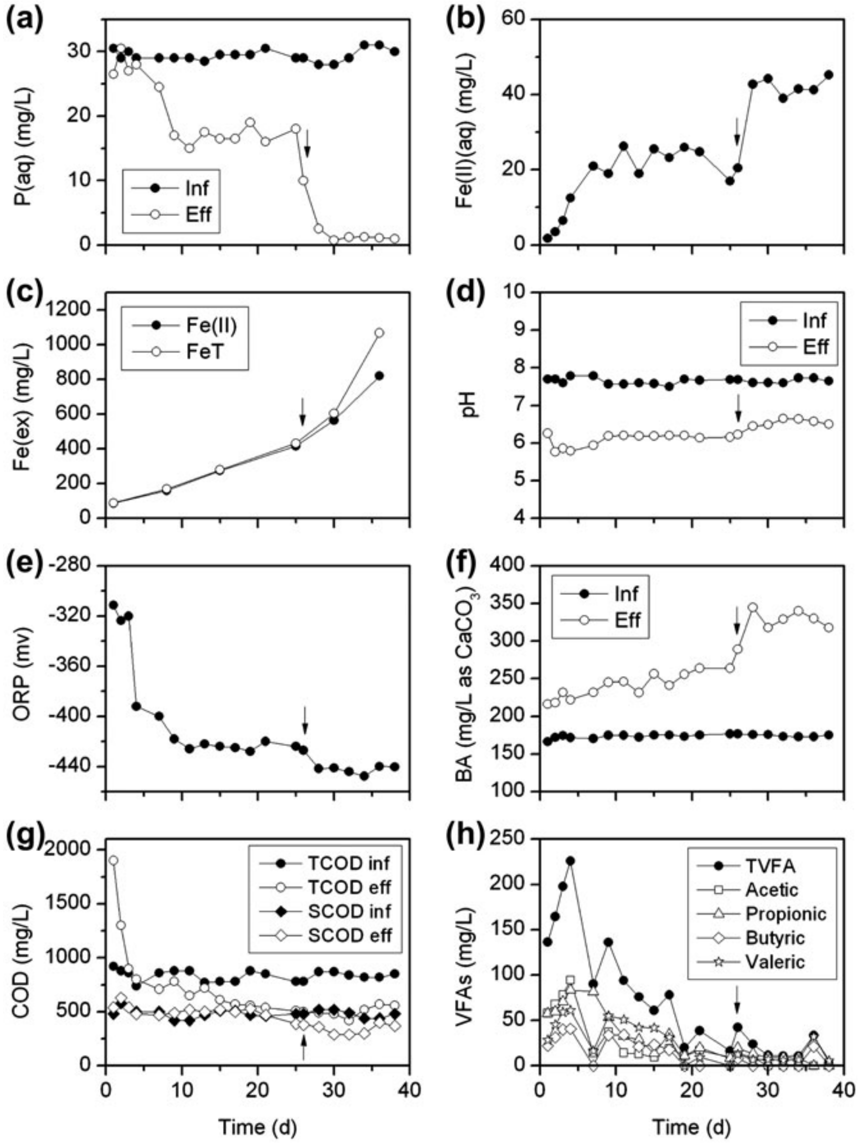


Fig. 4. Time series of aqueous PO_4-P (a) aqueous Fe(II) (b) HCl-extractable Fe species (c) pH (d), ORP (e) BA (f) CODs (g) and volatile fatty acids (h) in the ASBR fed with synthetic household sewage. The arrows indicate the increase in the A-FeOOH dosage (Fe/P ratio from 1.5 to 3). (Data from reactor tests).

of PO_4-P was removed when the reactor reached a new stable state. Aqueous Fe(II) increased to ~44 mg/L accordingly, due to the higher iron input. The concentration of extractable Fe was higher than that of extractable Fe(II), suggesting that part of the FeOOH added was not reduced; aqueous Fe(II) was at the same level as aqueous Fe over time (data not shown), indicating that the unreduced FeOOH remained in the solid phase. The pH, ORP, and BA values during this period were approximately 6.5, −440 mV, and 318–340 mg/L as $CaCO_3$, respectively. An enhancement of 21–44% in the SCOD removal was observed compared with that of the startup period.

VFAs accumulated up to 226 mg/L (as acetic acid) in the first several days and declined markedly when the iron reduction was activated (Fig. 4(h)). The biogas production was very low, and biogas could not be collected during the ASBR study. An analysis of the gas phase in the headspace of the ASBR showed methane production was decreasing and terminated within two weeks of operation (data not shown).

3.3. Results of XRD and TEM analysis

The synthesized FeOOH was an amorphous material as expected according to its XRD pattern (Fig. 5(a)). A TEM image clearly shows the difference between the amorphous FeOOH and a cubic crystal of the residual NaCl from the preparation of FeOOH (Fig. 6(a)). The mineral phase of the synthesized vivianite was demonstrated by comparing its XRD pattern with a reference pattern (Fig. 5(b)), and the TEM image of the vivianite is shown in Fig. 6(b). Quartz was the predominant mineral in the seed sludge of the ASBR (Fig. 5(c)). In the samples collected from the reactor in a stable state, vivianite was identified as a newly produced mineral phase (Fig. 5(d)). The TEM image of the precipitates exhibits the interaction among A-FeOOH, cells, and the vivianite produced (Fig. 6(c)). SEM observation reveals that there was a much greater amount of impurity in the seed sludge than in the samples from the stabilized ASBR (Fig. 7(a) and (b)). EDS analysis indicates that the minerals in the precipitates from the reactor were mainly vivianite, which is consistent with the results mentioned above. Therefore, the phosphorus removal in the reactor was mainly attributed to iron reduction and the subsequent vivianite precipitation.

4. Discussion

4.1. Iron reduction and phosphorus removal

In the non-Fe-amended septic controls, aqueous Fe series were negligible, yet a significant amount of 0.5 N HCl-extractable Fe(II) (~36 mg/L) was tested (Fig. 1(b)). The results indicate that all of the Fe existed as Fe(II) minerals in the sludge and that iron

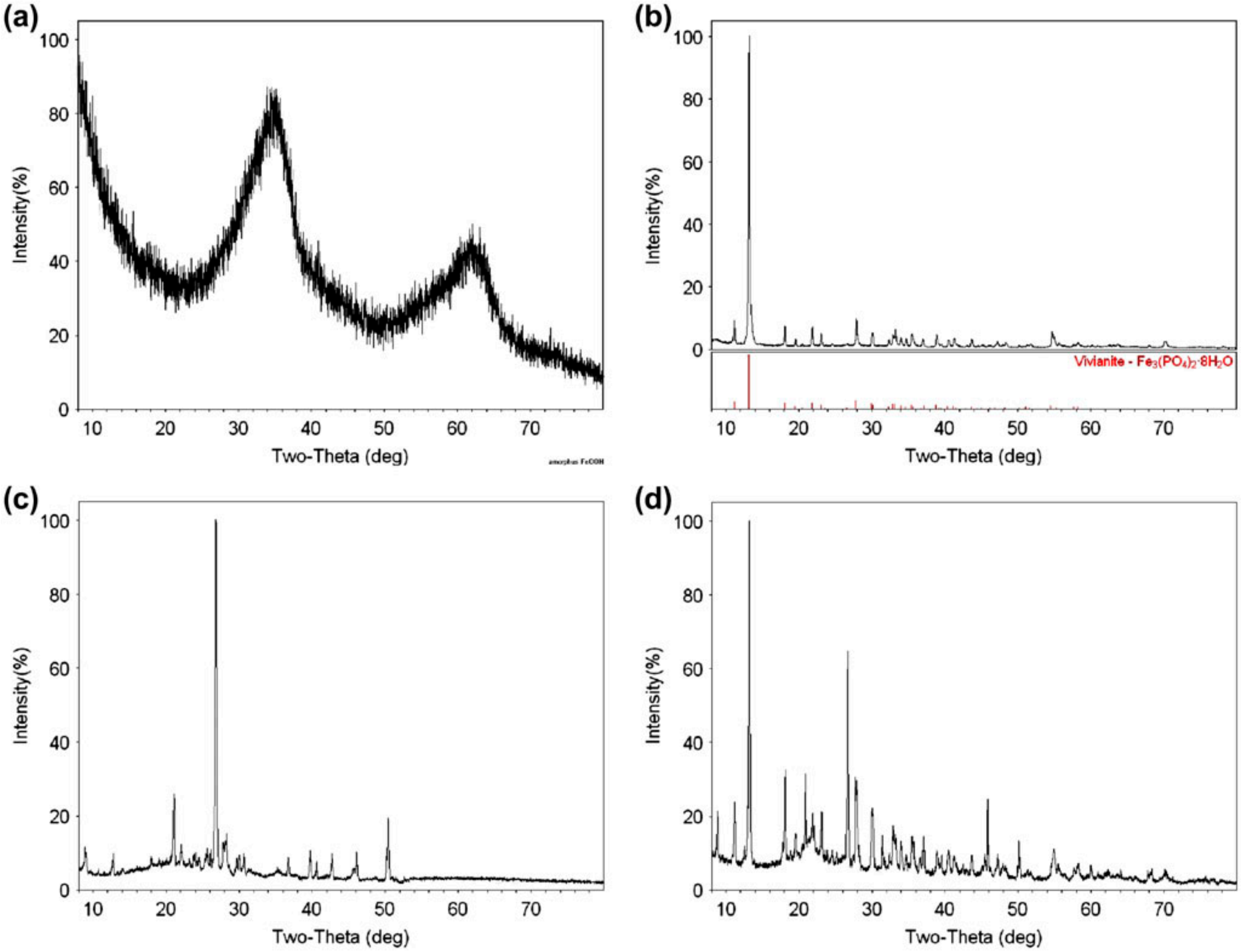


Fig. 5. X-ray diffractograms (XRD) of the synthesized A-FeOOH (a) the synthesized vivianite (b) the seed sludge for the ASBR start-up (c) and the precipitates from the continuously operated ASBR with FeOOH amendments (d).

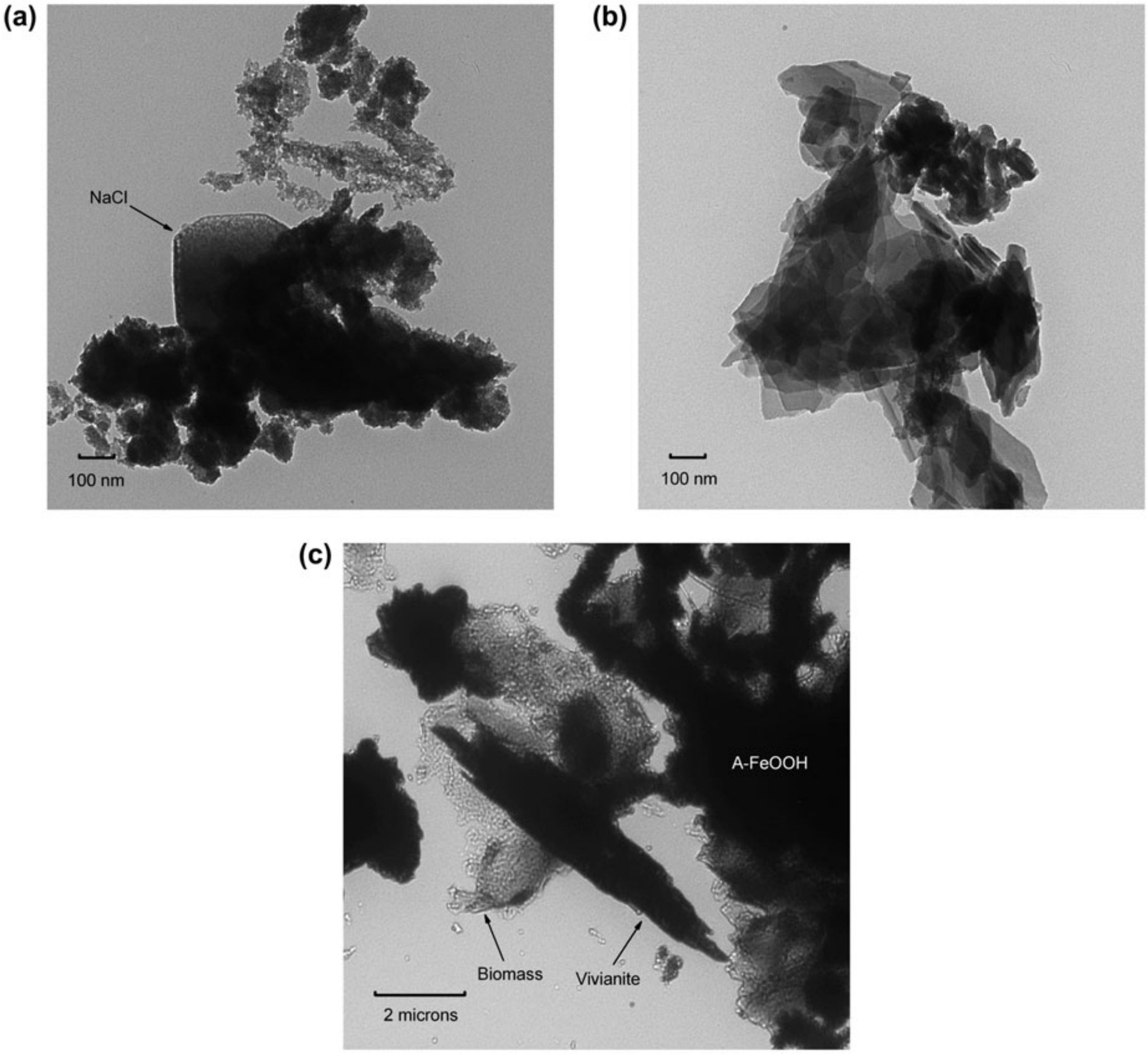
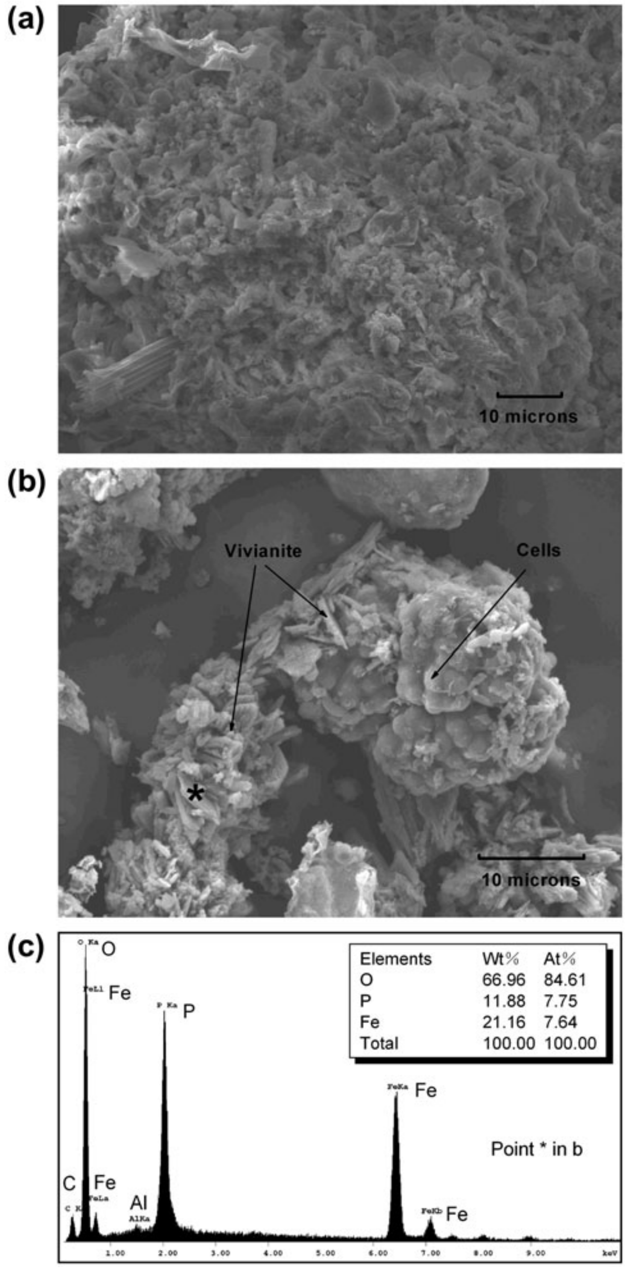


Fig. 6. Transmission electron micrograph of the synthesized A-FeOOH (a), the synthesized vivianite (b) and the precipitates from the continuously operated ASBR with FeOOH amendments (c).

reduction had obviously occurred naturally in the septic wastewater sampled. The concentration of extractable PO_4-P was higher than that of aqueous PO_4-P, suggesting that a certain amount of phosphorus was in the form of precipitates, possibly bound to Fe(II). The aqueous phosphorus removal achieved after the FeOOH amendment and enhanced by the higher iron dosage indicates that the removal was induced by iron reduction. Characterization of the solid samples from the ASBR suggests that the P removal was mainly via vivianite precipitation. Previous studies revealed that Fe(III) reduction in many natural sediment environments is generally biotic and involves DIRB [22,24,37]; however, the relatively fast iron reduction here can be partially attributed to chemical transformation by the reducing equivalents accumulated in septic samples (Fig. 1(b)).

The iron demand for complete PO_4-P precipitation in the batch assays was much higher than that in the reactor case indicating the presence of other Fe(II)-consuming pathways, such as the precipitation of magnetite [28,38], green rust [38], or siderite [26,32,39]. The accumulation of these Fe(II) consumers in the sampled septic wastewater can also explain the poor phosphorus removal in the initial period of the ASBR startup. For long-term, continuous operation, an Fe/P ratio of 3 was shown to be sufficient for phosphate precipitation under the conditions in this study, as revealed by



Elements	Wt%	At%
O	66.96	84.61
P	11.88	7.75
Fe	21.16	7.64
Total	100.00	100.00

Fig. 7. Scanning electron micrograph of the seed sludge for the ASBR start-up (a) and the precipitates from the continuously operated ASBR with FeOOH amendments (b) and EDS results of point * in b (c).

the high P removal efficiencies of >96% after day 26, even with a fraction of Fe(III) unreduced in the system (Fig. 4(c)).

A high level of aqueous Fe(II) was observed in the batch assays (48 mg/L) and the ASBR (44 mg/L) when a phosphorus removal of >90% was achieved, demonstrating that the vivianite precipitation was proceeding under Fe(II) supersaturation, which was also found in other studies [26]. Certainly, a specific amount of Fe(II) could be adsorbed by the biomass or precipitates, but it would not be responsible for the apparent supersaturation because that portion of the Fe(II) was not counted in the aqueous Fe(II) tested. A possible reason tends to be the formation of aqueous Fe(II) complexes that draw Fe(II) from the surface of iron oxide and promote its further reduction [32].

There are two different pathways expected for iron reduction in anaerobic environments: (a) chemical reduction mediated by reducing equivalents from other bioreactions or (b) biological reduction by enzymes from DIRB. Sulfate-reducing bacteria are often active participants in anaerobic systems, and the produced S^{2-} functions as an important reductant in the first case described above. However, the sulfate concentration in the feed wastewater of our study was insignificant and unlikely to contribute significantly to the iron reduction in the ASBR. In fact, the accumulation of Fe(II) before sulfate reduction in pore-water profiles suggested that Fe(III) can also outcompete sulfate reduction for electron donors, and oxidants in pelagic sediments were found to be consumed in the order of O_2 > manganese oxides ~ nitrate > iron oxides > sulfate, due to the decreasing energy production per mole of organic carbon oxidized [23,40].

4.2. Organic carbon degradation by iron amendment

SCOD removal by iron amendment was observed in the batch assays, compared to the activity of the controls (Fig. 2). The removed SCOD may have served as an electron donor for the iron reduction indirectly because most of the iron was reduced in the initial hours whereas the SCOD degradation was observed after a lag period. In the ASBR, no obvious SCOD removal was achieved at an Fe/P ratio of 1.5; however, it is reasonable to interpret the SCOD decline as being to some extent compensated by the dissolved organic carbon from the solid COD because a TCOD loss of 27–34% was obtained in the septic wastewater. This could be even higher because the effluent TCOD was partially from the washed-out sludge flocs. The conversion of COD from the solid phase was also demonstrated in the initial time of the batch assays when a large SCOD increase was noticed (Fig. 2). When the Fe/P ratio was increased to 3 in the reactor, the apparent SCOD removal was observed, indicating that carbon mineralization was enhanced and closely associated to the iron amendment (Fig. 4(g)).

Declines in the VFAs and the methane production in the ASBR revealed that fermentation products can be metabolized with concomitant iron reduction and the electron flow was diverted from methanogens to DIRB. The complete oxidation of organic matter coupled to dissimilatory Fe(III) reduction was previously reported [20]. The inhibition of methane production by iron addition can most likely be explained by: (a) Fe(III) reduction yields higher energy than when the electron equivalents proceed to methane and (b) the increased concentration of aqueous Fe(II) exerted toxicity on the sensitive methanogenic micro-organisms.

4.3. Mineral phases

The Fe(II) produced from iron reduction in an anaerobic environment can be re-immobilized as, for instance, siderite, vivianite, magnetite, and green rust [26]. The extent of iron reduction and the secondary mineralization are closely related and influenced by many factors, such as the form of the iron, the aqueous composition (e.g. phosphate, carbonate, and chelators), the pH, and the pe [29,31]. Magnetite was found to be a common metabolic product of a wide variety of iron-reducing bacteria especially at a low Fe(II)/Fe(III) ratio [41]. Its formation, nevertheless, can be inhibited in the presence of complexing ions, such as HCO_3^- or PO_4^{3-}, according to a thermodynamic calculation [26]. Magnetite will convert into siderite in a CO_2 atmosphere when the pe + pH value reaches ~2. The lower solubility product of vivianite (~10^{-36}) compared with those of other Fe-containing minerals suggests that vivianite is likely to be a more stable Fe(II) solid phase in some sedimentary environments when phosphate is present [28] and is of significance in controlling the phosphate concentration in water [17]. Our study demonstrates that vivianite can be the main mineral product in an Fe-amended septic system and that the strategy of phosphorus removal via iron-reduction-induced vivianite precipitation in septic tanks is promising.

Iron reduction in geochemical environments generally involves DIRB [31]. However, the extent of biotic and abiotic transformations and the corresponding conditions have not been clearly addressed. A better understanding of the mechanisms of this biochemical process would be crucial for efficiently utilizing iron materials for phosphorus precipitation in septic tanks. In addition, the microbial population dynamics resulting from iron amendments and the role of DIRB warrant further study.

5. Conclusions

The results from this study demonstrated that iron-reduction-induced phosphorus removal via vivianite precipitation can be achieved in septic systems.

- The theoretical Fe/P ratio of 1.5 in vivianite was insufficient for phosphorus precipitation from the wastewater indicating the existence of side pathways of iron utilization.
- In the ASBR in a stable state, more than 96% of phosphorus can be removed at the Fe/P ratio of 3, which was much lower than the iron demand in the batch assays (a Fe/P ratio of 10 for 94.5% P removal).
- SCOD removal was enhanced by 21–44% when the iron dosage was increased from an Fe/P ratio 1.5 to 3 in the ASBR and would have been used as an electron donor in the iron reduction.
- Vivianite was the primary mineral product in the precipitates from the reactor, which was consistent with the iron-induced phosphorus removal.

Acknowledgments

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