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The role of clay minerals in the reduction of nitrate in groundwater by zero-valent iron

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ABSTRACT

Bench-scale batch experiments were performed to investigate the feasibility of using different types of clay minerals (bentonite, fuller's earth, and biotite) with zero-valent iron for their potential utility in enhancing nitrate reduction and ammonium control. Kinetics experiments performed with deionized water (DW) and groundwater (GW) revealed nitrate reduction by Fe(0) proceeded at significantly faster rate in GW than in DW, and such a difference was attributed to the formation of green rust in GW. The amendment of the minerals at the dose of 25 g L⁻¹ in Fe(0) reaction in GW resulted in approximately 41%, 43%, and 33% more removal of nitrate in 64 h reaction for bentonite, fuller's earth, and biotite, respectively, compared to Fe(0) alone reaction. The presumed role of the minerals in the rate enhancement was to provide sites for the formation of surface bound green rust. Bentonite and fuller's earth also effectively removed ammonium produced from nitrate reduction by adsorption, with the removal efficiencies significantly increased with the increase in mineral dose above 5:1 Fe(0) to mineral mass ratio. Such a removal of ammonium was not observed for biotite, presumably due to its lack of swelling property. Equilibrium adsorption experiments indicated bentonite and fuller's earth had maximum ammonium adsorption capacity of 5.6 and 2.1 mg g⁻¹, respectively.

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1. Introduction

Nitrate is one of the most commonly found contaminants in surface- and groundwater worldwide. There are several potential sources of nitrate, including animal wastes, septic tanks, municipal wastewater treatment systems and decaying plant debris, but nitrogen-enriched fertilizers for farming accounts for the majority of nitrate entering into the environment (Suthar et al., 2009). When present in excess in aquatic systems, nitrate poses two important environmental problems: eutrophication of surface waters and contamination of groundwater. High levels of nitrate have been associated with serious health issues, including methemoglobinemia (blue baby syndrome in babies), miscarriages and non-Hodgkin's lymphoma (Little et al., 2001). Nitrate has regulatory health limits of 10 mg N L⁻¹ in US Environmental Protection Agency and 25 mg N L⁻¹ in European Union.

Numerous research efforts have gone to find better technologies to treat nitrate. Biological denitrification, reverse osmosis, and ion-exchange are among the most commonly used processes. Chemical reduction has been extensively tested as an alternative to the conventional methods. Number of studies have demonstrated the effectiveness of zero-valent iron for the reduction of nitrate (Cheng

et al., 1997; Huang et al., 1998; Alowitz and Scherer, 2002; Westerhoff and James, 2003; Huang and Zhang, 2004). But, the major concern associated with iron mediated nitrate treatment is generation of ammonium as an end product (Huang et al., 1998; Westerhoff and James, 2003; Huang and Zhang, 2004), and this could undermine the benefits of Fe(0) treatment since there is a great possibility of accumulation of ammonia. Besides, the iron corrosion products (e.g. lepidocrocite, goethite, akaganeite, maghemite, siderite) have been deemed to cause passivation of Fe(0) (Gu et al., 1999; Farrell et al., 2000; Huang et al., 2003; Huang and Zhang, 2005), although some iron oxides (magnetite and green rusts (Fe(II)/Fe(III) oxyhydroxyl salts)) are redox-active and could serve as a secondary reducing agent for contaminants.

The successful treatment of nitrate by Fe(0)-based systems depends on how long the surface reactivity Fe(0) can be retained and how well ammonium production can be minimized. The potential utility of silica minerals for reducing surface passivation of Fe(0) has been demonstrated in a previous study in which the rate enhancing effect of the minerals was attributed to the scavenging of the reaction precipitates (Oh et al., 2007). In this regard, the use of other clay minerals in combination with Fe(0), especially those with high adsorption capacity for cations, can be beneficial for reducing iron passivation. Recently, Li et al. (2010) reported that the use of pillared bentonite in combination with Fe(0) substantially enhanced nitrate removal and suggested ferrous iron

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scavenging by bentonite as one of the reasons for the enhanced removal. Besides, another anticipated role of clay minerals in Fe(0)-based nitrate treatment is that they could serve as an adsorbent for ammonium because of the negative charge on the surface at near neutral and alkaline conditions.

In this study, the feasibility of using different types of clay minerals (bentonite, fuller's earth, and biotite) in conjunction with Fe(0) for their potential utility in enhancing nitrate reduction and ammonium control was investigated. Bentonite is an aluminium phyllosilicate, generally consisting mostly of calcium montmorillonite. Fuller's earth is referred to as a calcium montmorillonite treated with sulfuric acid for surface activation. Montmorillonite minerals are well known for their expandability that renders high adsorption capacities for cations within the interlayer structure. For example, high sorption capacity of fuller's earth for ammonium has been demonstrated (Rožić et al., 2000). In contrast to montmorillonite minerals, biotite is a non-expandable phyllosilicate mineral within mica group with relatively low cation exchange capacity (CEC) values. The amendment of these minerals in Fe(0) system is expected to have different effects in terms of nitrate reduction and ammonium removal since they possess different mineralogical properties, as well as chemical characteristics.

2. Materials and methods

2.1. Chemicals and materials

Iron powder (96%, particle size 125–150 μm) and nitrate standard solution (1000 mg L^{-1}) were purchased from Fisher Scientific, USA. Biotite (Wards Scientific, Canada), bentonite and fuller's earth (Donghae Chemical Co., South Korea) were used without pre-treatment. Mineralogical composition as specified by the manufacturers, BET surface areas determined from N_2 physisorption using an ASAP 2020 surface analyzer (Micromeritics, USA), and CEC values determined using ammonium acetate method (Vazquez et al., 2008) are given in Table SM-1 in Supplementary materials (SM). The groundwater (GW) sample was collected from Hongseung, South Korea, transported to the laboratory in a pre-cleaned plastic container, and kept refrigerated until use. The concentrations of major cations and anions are as follows; Ca^{2+} 78, Mg^{2+} 18, Na^+ 17, K^+ 4, HCO_3^- 116, Cl^- 57, SO_4^{2-} 19, and NO_3^- 156 mg L^{-1} . Synthetic nitrate solution (DW) was prepared in deionized water (18 $\text{M}\Omega\text{ cm}$, Purelab, Elga, UK).

2.2. Experimental methods

Laboratory-scale batch experiments were conducted using 25 mL high density polyethylene vials (Fisher Scientific, USA) under anaerobic condition (5% H_2 , 95% N_2 , Coy Laboratory, USA). The vials were initially filled with 20 mL GW or DW samples, followed by the addition of 0.5 g of Fe(0) and 0.5 g of individual minerals. The reactions were allowed to occur at room temperature ($23 \pm 2^\circ\text{C}$) in a water bath shaker at 150 rpm (Lab. Companion, USA). At each sampling occasion, the reactors were sacrificed to collect supernatant for filtration with 0.45 μm filter (Whatman, USA), and the filtrates were analyzed for nitrate and ammonium. In separate batch tests, the effect of mineral doses was examined by varying the amount of minerals from 0.01 to 0.5 g, while keeping the amount of Fe(0) constant (0.5 g) for 64 h reaction time. Samples for batch experiments were prepared in duplicate and the average values are reported.

Adsorption isotherm experiments were performed to assess the adsorption capacities of bentonite, fuller's earth and biotite for ammonium. Ten milliliter of ammonium solution of varying initial concentrations in 25 mL vials were shaken with 0.1 g adsorbent for

24 h in the shaker table ($23 \pm 2^\circ\text{C}$). Solutions were prepared with deionized water and no pH adjustment was made during the reaction. After reaction, samples were filtered using 0.45 μm PVDF filter and analyzed for ammonium.

Concentrations of nitrate and other anions in GW (SO_4^{2-} , Cl^-) were determined using ion chromatograph (Dionex CX-120, USA) equipped with a Dionex AS-14 analytical column. The mobile phase consisted of 1 mM NaHCO_3 and 3.5 mM Na_2CO_3 with a flow rate of 1.32 mL min^{-1} . Ammonium concentration was measured using Nessler's method with UV/Vis spectrophotometer (DR4000/HACH, USA). The pH of solution was measured using a pH meter (Horiba, Ltd. Kyoto, Japan). The concentration of cations in GW samples was measured using an inductively coupled plasma-optical emission spectrometer (Ultima 2C, Horiba-Yuvon, France). After reactions, the suspension of the reacted materials was transferred to the anaerobic chamber to prevent further oxidation, dried and prepared for X-ray diffraction (XRD) analysis. Mineralogical compositions in the reacted materials were measured using X-ray diffractometer (X-Pert MPD, Philips, Netherlands) with Cu $\text{K}\alpha$ radiation at 40 kV and 30 mA. The diffraction data were obtained between 3° and 75° with a $0.02^\circ 2\theta$ step and 0.5 s per step. The resulting peaks and intensities of each mineral were compared with the powder diffraction files published by the International Centre for Diffraction Data.

3. Results and discussion

3.1. Reduction of nitrate in DW and GW by Fe(0)

The reduction of nitrate by Fe(0) in DW and GW is shown in Fig. 1. Nitrate in both waters decreased rapidly during first 12 h, followed by much slower decrease afterwards. Nitrate concentrations were leveled off at 1.6 and 1.1 mM in 38 h after initiation of reaction, corresponding to 28% and 56% nitrate removal in DW and GW, respectively. The initial decrease within first 12 h accounted for approximately 60% and 85% of the total decrease in DW and GW, respectively. Such a reaction behavior as characterized by initial removal of nitrate and rapid inactivation of Fe(0) was typical for unbuffered Fe(0) reactions (Huang et al., 1998). Inactivation of Fe(0) was attributed to the development of corrosion and reaction precipitates on iron surface, of which formation is expedited at elevated pH (Gu et al., 1999; Puls et al., 1999;

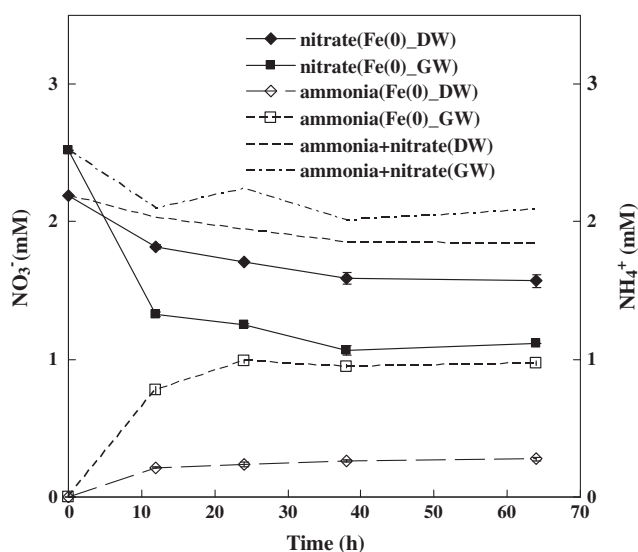
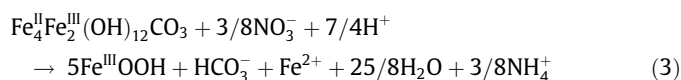
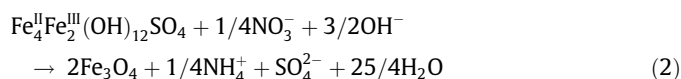
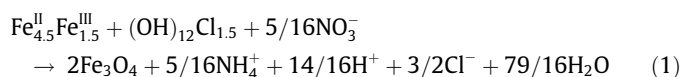


Fig. 1. Nitrate reduction by Fe(0) in DW and GW (Fe(0) dose: 25 g L^{-1}).

Phillips et al., 2000). Other probable causes of surface inactivation may include pH increase that leads to iron corrosion prevention, and loss of surface bound ferrous iron due to oxidation.

The solution pH of DW and GW increased from 7.0 and 7.2 to 9.9 and 9.8 during first 12 h, respectively, and remained relatively constant until the end of reaction, with the pH values being 0.1–0.3 unit lower than those of DW throughout the reaction (Fig. SM-1). Although the effect of lower pH cannot be ruled out in the enhancement of nitrate removal observed in GW, such small differences in pH values appear to be too small to yield the observed difference in nitrate removal. The increase of pH in GW reaction suggests the buffering capacity imparted by HCO_3^- was consumed during initial phase of reaction and that its buffering effect was not sufficient to maintain the pH at lower values. In other words, hydroxide ions generated from iron oxidation in the initial phase of reaction effectively cancelled out the buffering effect of HCO_3^- and further led to speciation to carbonate that possibly underwent precipitation reaction with cations at elevated pH condition. The analysis of the GW solution during the reaction indicated more than 95% of the initial HCO_3^- disappeared within the first 12 h, and those of calcium and magnesium steadily decreased over the course of reaction (Fig. SM-2). This suggests at least some portion of carbonate was removed as reaction precipitates including CaCO_3 , MgCO_3 and FeCO_3 . These minerals were suggested to form in $\text{Fe}(0)$ reactions under groundwater conditions and, when formed, they could inhibit the redox reaction by physically blocking the reactive sites on $\text{Fe}(0)$ surface (D'andrea et al., 2005; Lo et al., 2006).

Given the little effect of solution pH, the increase of reaction rate in GW is likely derived from additional removal of nitrate by chemical reduction involving reductants other than $\text{Fe}(0)$, which is presumed to be green rust formed during the reaction. The XRD diffractogram of the reacted $\text{Fe}(0)$ particles showed a peak with d-spacing of 7.54 Å, which indicates formation of green rust after the reaction (Fig. 2a). The reduction of nitrate by different types of green rust are described (Westerhoff and James, 2003; Choe et al., 2004; Su and Puls, 2004) as:



Green rust is known to form in anoxic environments when partially oxidized Fe^{2+} is precipitated at near or above neutral pH in the presence of anions such as CO_3^{2-} , Cl^- and SO_4^{2-} (Taylor and McKenzie, 1980; Hansen et al., 1996). It has been reported green rust is an active reducing agent for various organic/inorganic contaminants (Hansen et al., 2001; Lee and Batchelor, 2002; Choe et al., 2004; Kim et al., 2008). The GW sample used in this study had high concentrations of those essential anions and appropriate solution chemistry such as reducing condition (Matheson and Tratnyek, 1994) and alkaline pH for the formation of green rust. During the reaction, the greenish suspended particles began to appear approximately 1 h reaction after initiation in the GW containing reactors, and those particles were immediately oxidized upon exposing the solution to atmosphere.

The major product of nitrate reduction was ammonium, consistent with the previous investigations (Cheng et al., 1997; Huang et al., 1998; Westerhoff and James, 2003). The conversion to ammonium ranged 84–93% and 80–89% for DW and GW reactions,

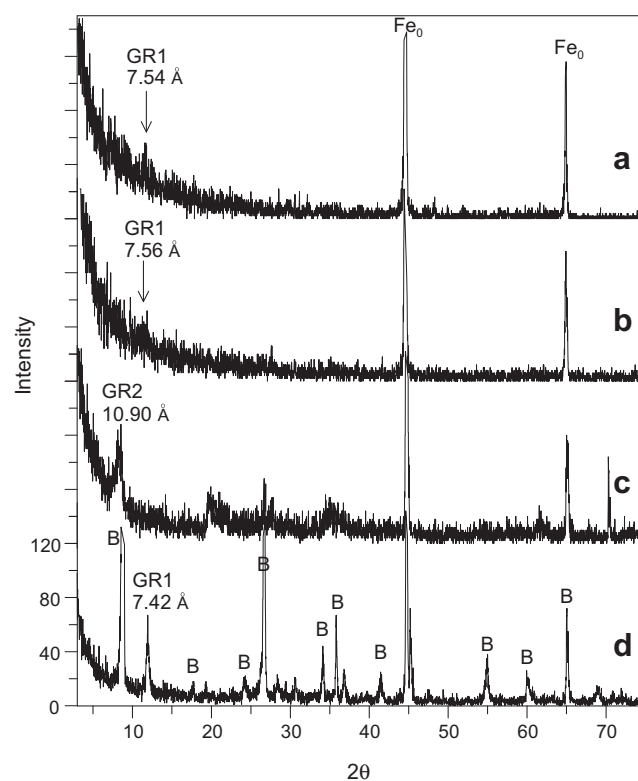


Fig. 2. X-ray diffraction patterns for the reacted materials (a) $\text{Fe}(0)$, (b) $\text{Fe}(0)$ -bentonite, (c) $\text{Fe}(0)$ -fuller's earth, and (d) $\text{Fe}(0)$ -biotite. GR1, GR2 and B represent green rust one, green rust two and biotite, respectively. The peaks representing reflections from basal plane with d-spacing ~ 7.5 Å and ~ 10.9 Å are characteristics of green rust. The d-spacing depends on the crystal structure and the nature of the interlayer anions such as Cl^- , SO_4^{2-} and CO_3^{2-} .

respectively, and these values are similar to those previously reported in the literature (70–90%) (Westerhoff and James, 2003; Yang and Lee, 2005), although some previous batch tests reported nearly 100% conversion of nitrate to ammonium (Hansen et al., 1996; Cheng et al., 1997). Possible explanations for the incomplete mass balance include: (1) evolution of gaseous nitrogen species (N_2 , NH_3) (Choe et al., 2000), (2) adsorption of $\text{NO}_3^-/\text{NH}_4^+$, and (3) analytical error. In the conditions of our study, the most probable sinks for the unaccounted nitrogen would be evolution of gaseous NH_3 and adsorption of NH_4^+ since the pH of the solution increased well above the pKa of ammonium speciation and iron oxide particles will develop negative charge on the surface at elevated pH.

3.2. Effect of minerals type

The effect of the minerals on the reduction of nitrate was investigated by amending the minerals to $\text{Fe}(0)$ reactions both in DW and GW conditions. The overall nitrate removal efficiencies at the end of reaction are presented in Fig. 3, and the timecourses of pH changes during the reactions are given in Fig. SM-3. In DW reactions, the inhibition of nitrate reduction was observed for bentonite and biotite, giving 15% and 7% less removal of nitrate in 64 h reaction, respectively. On the other hand, the amendment of fuller's earth resulted in substantial increase in nitrate removal compared to the $\text{Fe}(0)$ alone reaction. The inhibition effect of bentonite and biotite is attributed to the increase of solution pH due to dissolution of these minerals. It has been reported hydrolysis of bentonite and biotite requires H^+ consumption (Chon et al., 2006; Kaufhold et al., 2008). In this study, dissolution of bentonite and biotite (25 g L^{-1}) in the absence of $\text{Fe}(0)$ in DW raised solution

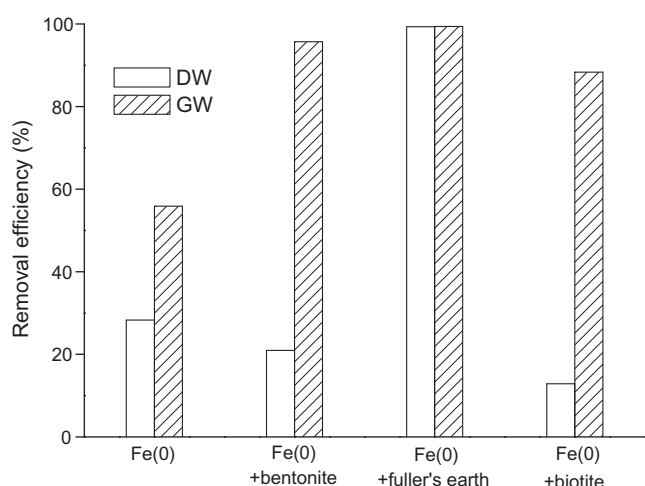


Fig. 3. Comparison of nitrate removal efficiency in DW and GW reactions (Fe(0) dose: 25 g L^{-1} , mineral dose: 25 g L^{-1}).

pH to 9.7 and 9.9, respectively, in 64 h reaction. But, the dissolution of the same amount of fuller's earth initially dropped pH to near 5.0 and steadily increased pH to 7.2 in 64 h. As aforementioned, fuller's earth is an acid-activated calcium montmorillonite that the pH drop is likely due to the rapid release of residual acidity. When used with Fe(0), fuller's earth yielded lower final solution pH than Fe(0)-bentonite and Fe(0)-biotite systems (Fig. SM-3). In addition, the enhanced nitrate removal may also stem from the formation of sulfate green rust that incorporated SO_4^{2-} released from fuller's earth.

Contrary to the reactions in DW, the amendment of bentonite and biotite resulted in enhancement of nitrate removal in GW condition. Compared to Fe(0) alone reaction, nitrate removal efficiencies were 41% and 33% higher for the reactions amended with biotite or bentonite, respectively. Examination of the GW pH data in Fe(0) alone (Fig. SM-1), Fe(0)-bentonite and Fe(0)-biotite (Fig. SM-3), despite some variations, the pH values of mineral amended reactions were higher than those of Fe(0) alone reaction throughout the reaction period. This suggests that pH was not an influencing factor in the rate enhancement in mineral amended reactions. As the formation of green rust in GW was suggested to cause an increase in rate, the further rate enhancement in the presence of the minerals may be attributed to the formation of green rust associated with the mineral surfaces. In other words, as mineral surfaces become negatively charged in alkaline pH condition, they readily adsorb Fe^{2+} and Fe^{3+} produced by oxidation of Fe(0), leading to formation of surface bound green rust by incorporating necessary anions from GW.

The XRD analyses of the reacted particles showed that, although diffraction peaks were broad and weak in some samples, peaks with d-spacing of either ~ 7.5 or $\sim 10.9 \text{ \AA}$ were detected for all the samples, an indicative of the presence of two types of green rust after the reaction (Fig. 2b–d). The weak and board signals of green rust may be attributable to highly amorphous nature of the produced green rust. The crystal structure of green rust is classified in green rust one (GR1, space group $R\text{-}3m$ with d-spacing $\sim 7.5 \text{ \AA}$) and green rust two (GR2, space group $P\text{-}3m1$ with d-spacing $\sim 10.9 \text{ \AA}$), according to the sequence of stacking of $\text{Fe}(\text{OH})_2$ brucite-like layers that depends on the shape and type of inserted anions such as Cl^- , SO_4^{2-} and CO_3^{2-} (Génin et al., 2005; Trolard et al., 2007). For Fe(0)-fuller's earth sample, formation of GR2 after the reaction is likely caused by sufficient supply of SO_4^{2-} from fuller's earth surface.

In GW reactions, the overall removal of nitrate were 56%, 88%, 99%, 88% and molar sum of nitrate and ammonium at the final

sampling time were 83%, 50%, 51%, and 91% of the initial nitrate for Fe(0) alone, Fe(0)-bentonite, Fe(0)-fuller's earth, and Fe(0)-biotite, respectively. The significantly lower recoveries from the reactions involving bentonite and fuller's earth indicate that a large portion of the ammonium was adsorbed on these minerals. Such a removal of ammonium was not apparent for the reaction involving biotite, which may be attributed to its low CEC (Table SM-1). The pH values of the Fe-bentonite system increased to above the pKa value (9.23) of ammonium in first 12 h (Fig. SM-3). This high pH causes shift of ammonium speciation to ammonia and that one could imagine that cation exchange reaction with exchangeable cations will no longer be effective. However, it has been reported clay minerals with cation exchange capability are capable of ammonia adsorption, although the extent of ammonia adsorption varies depending on the clay type and origin. For example, Dontsova et al. (2005) suggested ammonia at the interface of exchangeable cations is protonated by acidic water molecule in contact with exchangeable cations, and ammonium subsequently enters into cation exchange reaction with the clay. Control reactors containing the mineral and nitrate solution showed little changes in nitrate concentrations in both DW and GW conditions, indicating the minerals have no adsorption capacity for nitrate (Fig. SM-4).

3.3. Effect of minerals dose

The effect of minerals dose on nitrate reduction in GW was investigated by varying the amount of mineral from 0.5 to 25 g L^{-1} while keeping the Fe(0) dose constant at 0.5 g . In general, nitrate removal increased with the increase of the mineral dose, and the enhancement effect was the greatest for fuller's earth, followed by bentonite and biotite (Fig. 4a). For bentonite and fuller's earth, the reaction sharply increased until the mineral dose increased to 5 g L^{-1} , which corresponds to Fe(0):mineral mass ratio of 5:1. Further additions of the minerals substantially slowed down the increase of reaction rate, showing a sign of saturation at high doses. On the other hand, the reaction rate of biotite-amended reactions showed a pattern of linear increase with increasing mineral doses.

Assuming green rust plays a major role in the removal of nitrate, the saturation effect observed for bentonite and fuller's earth suggests the reactions become limited by formation of green rust as sufficiently large amount of mineral surfaces are provided. In other words, the reactions at high doses of minerals could be limited by the amount of soluble iron species adsorbed to mineral surfaces to form green rust. The absence of such saturation in the reactions involving biotite suggests availability of surface sites is the limiting factor for the rate increase and this appears to be related to relatively low surface area of biotite.

The ammonium concentrations obtained at the final sampling time for the reactions with varying doses of the minerals are shown in Fig. 4b. In the reactions involving bentonite and fuller's earth, ammonium concentration continuously increased with increase in mineral doses to 5 g L^{-1} , but started to decrease at higher mineral loadings. Nitrogen mass balances (nitrate-N + ammonium-N) in the mineral dose range of 0.5 , 2.5 , and 5 g L^{-1} were 89%, 87%, and 85% and 90%, 90%, 91% of the initial nitrate concentration for bentonite and fuller's earth systems, respectively. These were not smaller than that of Fe(0) alone reaction (83%), which suggests little ammonium removal by the minerals occurred with a dose less than 5 g L^{-1} . This low ammonium removal efficiency is probably due to competition effect from divalent cations present in the solution (Ca^{2+} , Mg^{2+} , Fe^{2+}). It has been reported that montmorillonite has preferential affinity for divalent Ca^{2+} and Mg^{2+} over monovalent NH_4^+ if none of the ions had overwhelmingly high concentration (Talibudeen, 1981).

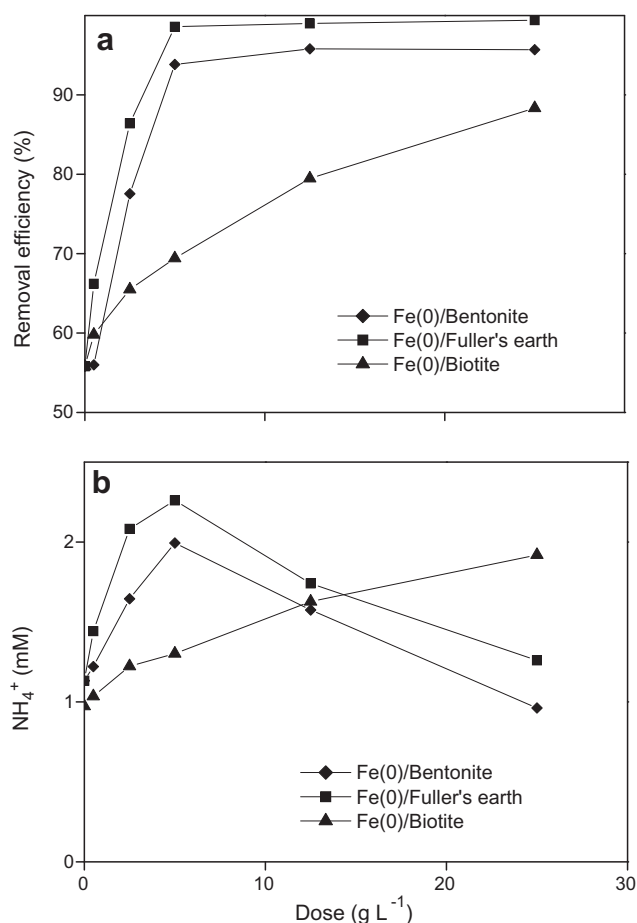


Fig. 4. (a) Effect of clay mineral dose on nitrate removal efficiency, and (b) ammonium release at varying doses of the minerals.

However, higher doses of bentonite and fuller's earth apparently had an effect on ammonium removal, showing increasing removal with increasing dose (Fig. 4b). The sum of nitrate-N and ammonium-N was 68% and 70% at 12.5 g L⁻¹ dose, and further decreased to 50% and 51% at 25 g L⁻¹ dose for bentonite and fuller's earth, respectively. The pH values measured at the end of reaction in varying dose of minerals indicated, for the reactions involving bentonite or fuller's earth, there was a slight increase of pH with the increase in mineral dose up to 5 g L⁻¹, and started to decrease when the dose was further increased to 12.5 and 25 g L⁻¹, with the extent of decrease much greater for fuller's earth (Fig. SM-5). This change of pH may have possibly contributed to the enhanced removal of ammonium due to increased speciation to charged ammonium, but its effect may not be significant, especially for the reaction involving bentonite. On the contrary to fuller's earth and bentonite, ammonium concentrations in biotite-amended reactions kept increasing within the same range of mineral dose, suggesting very weak adsorption capability of biotite.

3.4. Adsorption isotherms

Equilibrium adsorption experiments were performed with varying concentrations of ammonium to demonstrate the adsorption capacities of the minerals in controlled conditions, and the adsorption isotherms are shown in Fig. SM-6a. As seen in the figure, isotherms of bentonite and fuller's earth showed initial rapid increase, indicating that plenty of readily accessible sites are available in the beginning of the adsorption. But, as ammonium concentration in-

creased, isotherms started to plateau, an indication of saturation of sites on the minerals. In terms of efficiency, bentonite showed much better performance for ammonium removal than fuller's earth despite the lower surface area, with the value of maximum adsorption capacities of bentonite and fuller's earth 5.6 and 2.1 mg g⁻¹, respectively. This is consistent with the result reported by Rožić et al. (2000) who claimed acid treatment of a clay decreased the efficiency of ammonium removal.

Compared to bentonite and fuller's earth, ammonium adsorption on biotite was considerably low and showed weak dependence on the ammonium concentration, confirming the negligible ammonium removal in the Fe(0) combined reaction. Despite its structural similarity to montmorillonite clay minerals, biotite lacks swelling property with cations (K⁺) tightly held with the interlayer (Malmström and Banwart, 1997), which prevents exposure of an additional mineral surface capable of cation adsorption. The experimental data were fitted to linearized form of Langmuir equation for equilibrium modeling (Snoeyink, 1990) (Fig. SM-6b). The values of Langmuir constants, maximum monolayer capacity (q_m , mg g⁻¹) and energy of adsorption (b , M⁻¹), obtained from the slope and intercept are given in Table SM-2. The q_m values of the minerals are comparable to the maximum adsorption obtained from the adsorption isotherms.

4. Conclusions

The reduction of nitrate by Fe(0) under DW and GW conditions proceeded at different rate, with the removal efficiency far greater in GW than in DW. In both conditions, rapid reaction occurred in initial phase of reaction, which accounted for significant portion of the total nitrate removal. Inactivation of Fe(0) surface became apparent with the increase of pH. The higher removal of nitrate in GW was attributed to the formation of green rust resulting from coprecipitation of partially oxidized Fe²⁺ and essential anions contained in GW under alkaline condition. XRD analysis revealed the presence of green rust within the reacted materials despite the weak detection at the target angle, which presumed to arise from high amorphousity of the produced green rust.

In DW reactions, nitrate reduction slowed down in the presence of bentonite and biotite due to the pH raising effect of the minerals while rate enhancement was achieved by the addition of fuller's earth. In GW reactions, rate enhancement was observed for all the minerals and presumed role of the minerals was to provide the reactive sites for formation of surface bound green rust. In addition, ammonium produced from nitrate reduction was effectively removed from the solution by bentonite and fuller's earth.

Increasing dose of the minerals resulted in increase of nitrate removal, with the enhancement effect being the highest for fuller's earth, followed by bentonite and biotite. But, for bentonite and fuller's earth, the reaction rates reached a plateau when the dose of the minerals increased above Fe(0) to mineral ratio of 5:1, while biotite-amended reactions kept increasing with the increase of dose up to 1:1 Fe(0) to mineral ratio. Ammonium concentrations at varying dose of the minerals indicated relatively small ammonium removal occurred until the dose was increased to 5 g L⁻¹ (5:1 ratio), but the removal became apparent with the further additions of bentonite and fuller's earth. On the contrary, ammonium concentrations in biotite-amended reactions kept increasing with the increase of dose, suggesting very weak adsorption capability of biotite for ammonium. Equilibrium adsorption experiments with the minerals showed 5.6 and 2.1 mg g⁻¹ as the maximum adsorption capacity for ammonium on bentonite and fuller's earth, respectively. Biotite had very low ammonium adsorption capacity, probably due to non-swelling property.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.08.005.

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