

Nitrate Reduction without Ammonium Release using Fe-loaded Zeolite

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ABSTRACT

Nitrate reduction with zero valent iron (Fe^0) has been extensively studied, but the proper treatment for ammonium by-product has not been reported yet. In groundwater, however, ammonium is regarded as contaminant species, and particularly, its acceptable level is regulated to 0.5 mg-N/L for drinking water. This study is focused on developing new material to reduce nitrate and properly remove ammonium by-products. A new material, Fe-loaded zeolite, is derived from zeolite modified by Fe(II) chloride followed by reduction with sodium borohydride. Batch experiments were performed without buffer at two different pH to evaluate the removal efficiency of Fe-loaded zeolite. After 80 hr reaction time, Fe-loaded zeolite showed about 60% nitrate removal at initial pH of 3.3 and 40% at pH of 6 with no ammonium release. Although iron filing showed higher removal efficiency than Fe-loaded zeolite at each pH, it released a considerable amount of ammonium stoichiometrically equivalent to that of reduced nitrate. In terms of nitrogen species including NO_3^- -N and NH_4^+ -N, Fe-loaded zeolite removed about 60% and 40% of nitrogen in residual solution at initial pH of 3.3 and 6, respectively, while the removal efficiency of iron filing was negligible.

Key words : Fe-loaded zeolite, Zero valent iron, Nitrate reduction, Ammonium

요 약 문

영가 철을 이용한 질산성 질소 환원에 대한 연구는 지금까지 활발히 진행되어 왔지만, 이 반응에서 생성된 암모늄 부산물에 대한 적절한 처리과정은 아직 보고되지 않았다. 하지만, 암모늄은 먹는 물 수질기준에 의해 지하수 오염물로 분류되고 있어 (허용치 0.5 mg-N/L), 질산성 질소로 오염된 지하수 정화에 영가 철을 단독으로 사용하는 것에는 한계가 있다. 따라서, 본 연구의 목적은 질산성 질소를 환원함과 동시에 이 과정에서 발생하는 암모늄을 제거할 수 있는 반응물질을 개발하는데 있다. 본 연구에 사용한 Fe-loaded zeolite는, 제올라이트와 Fe(II) 용액을 교반시켜 제올라이트 구조 안으로 Fe(II)를 흡착유도하고, 이를 sodium borohydride로 환원하는 과정을 통해 제작되었다. Fe-loaded zeolite 제작에 사용된 Fe(II) 용액의 농도를 실험을 통해 산정하고, 이를 통해 Fe-loaded zeolite를 제작한 후, Fe-loaded zeolite의 질산성 질소 제거 성능을 확인하기 위해 두 가지 pH 조건에서 회분식 실험을 수행하였다. 80시간의 반응을 통해 Fe-loaded zeolite는 초기 pH가 3.3인 경우 약 60%의 질산성 질소를, pH가 6인 경우는 약 40%의 질산성 질소를 제거하였고, 암모늄 부산물은 전혀 검출되지 않았다. 영가 철의 경우, 각 초기 pH 조건에서 Fe-loaded zeolite 보다 뛰어난 질산성 질소 제거성능을 보였지만, 반응 후 상당량의 암모늄 부산물을 생성하였다. 질산성 질소와 암모늄을 포함한 질소(-N)제거 효능의 관점에서 Fe-loaded zeolite의 경우 pH 3.3과 6의 경우에서 각각 60%와 40%의 제거효율을 보인 반면, 영가 철의 제거효율은 무시할만한 수준으로 나타났다.

주제어 : Fe-loaded zeolite, 영가 철, 질산성 질소 환원, 암모늄

1. Introduction

Nitrate contamination in groundwater by agricultural runoff, unexploded ordnance and industrial process is a pervasive environmental problem (Cheng *et al.*, 1997). Nitrate is reduced to nitrite in the human gut and may

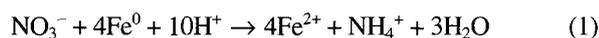
cause methemoglobinaemia in newborn infants (blue baby syndrome) and in adults deficient in glucose-phosphate dehydrogenase; chronic health risks also exist (Westerhoff, 2003). To alert this potential risk, the U. S. Environmental Protection Agency has set a maximum contaminant level (MCL) of 10 mg-N/L for nitrate.

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Various remediation strategies have been applied so far to treat nitrate in water, including reverse osmosis, ion exchange and bio-tower treatment (Clifford and Liu, 1993; Liessens *et al.*, 1993). Recently, with the successful application of zero valent iron (ZVI) in the permeable reactive barriers (PRBs) against chlorinated solvents (Gillham and O'Hannesin, 1994; Yabusaki *et al.*, 2001), the reduction of oxo-anion like nitrate has been extensively studied using ZVI. Results from the studies have shown that pH was a critical factor in nitrate reduction (Alowitz and Scherer, 2002), and using buffers could enhance the removal rate of ZVI (Cheng *et al.*, 1997). For by-product species, most studies have reported that ammonium was the primary by-product of the reaction (Cheng *et al.*, 1997; Westerhoff, 2003; Huang *et al.*, 1998; Huang *et al.*, 2002; Kielemoes *et al.*, 1998; Till *et al.*, 1998). Nitrate reduction by ZVI could be described as the following equation.



As mentioned by Cheng *et al.* (1997), one of the main disadvantages in nitrate reduction using ZVI is the production of ammonium ion (Cheng *et al.*, 1997). When applying ZVI in PRBs to remediate nitrate, this disadvantage is even more critical because ammonium (NH_4^+) produced in this reaction is considered as another contaminant in groundwater. Moreover, in Korea, the acceptable level of ammonium in drinking water is much lower than nitrate as 0.5 mg-N/L, while that of nitrate is 10 mg-N/L.

The current study focuses on developing new materials which can reduce the nitrate and properly remove the ammonium by-product. The new material, Fe-loaded zeolite, is derived from zeolite modified by Fe(II) chloride followed by reduction with sodium borohydride. In this study, the optimal conditions for making Fe-loaded zeolite were determined, and the performance of Fe-loaded zeolite for nitrate removal was verified by performing batch experiments.

2. Material and Methods

2.1. Materials

Zeolite was obtained from Wangpyo Co. in Pohang, one of the largest zeolite deposits in Korea. X-ray diffraction analysis showed that the zeolites were about 60% clinoptilolite, and the remainder consisted of feldspar, quartz, calcite and illite. The zeolite had a BET surface area of 24 m²/g.

2.2. Fe(II) loading on zeolite

FeCl_2 solutions were prepared by dissolving the ferrous

chloride (FeCl_2 , extra pure reagent, Yakuri Pure Chemicals Co. Ltd., Japan) in the deionized water (18.2 M Ω , Milli-Q Water, Milli Pore, USA) with stock concentrations ranging from 3 to 450 mM. Three grams of zeolite and 30 mL of FeCl_2 solution (solid : solution by weight = 1 : 10) were contained in 37-mL screw-cap glass tubes, and were shaken for 24 hours at ambient temperature with rotary shaker. Duplicates were prepared for each initial concentration. After shaking, the supernatant in tube was decanted, and the remaining solids were washed with deionized water three times. Then, Fe(II) in zeolite was extracted by injecting 30 mL of 1.0 M KCl (assay 99.0%, Showa Chemicals Inc., Japan) solution in the tube, and shaking for 1 hour (Li and Li, 2001). After shaking, the solution was used for Fe analysis. And, HNO_3 digestion was performed on the solids remaining after KCl extraction (Li and Li, 2001). The KCl-treated zeolite was shaken with 10 mL of HNO_3 for 1 hour, and the supernatant was used for Fe analysis.

2.3. Preparation of Fe-loaded zeolite

Fifty grams of zeolite was stirred with 500 mL of 350 mM ferrous chloride solution (solid : solution by weight = 1:10) for 24 hours at ambient. The Fe(II)-sorbed zeolite was washed several times with deionized water and stirred in 500 mL of 20 mM sodium borohydride (NaBH_4 , 98%, Sigma, USA) solution for 30 min. The borohydride-reduced zeolite was washed several times with deionized water, dried in the vacuum dry oven at 90°C for 1 hr, and stored in anaerobic condition. The material-making processes are summarized in Fig. 1.

2.4. Batch experiments

Nitrate solution was prepared by dissolving $\text{Na}(\text{NO}_3)$ in deionized water with initial concentration of 1.61 mM and pH of 6. The solution pH was varied to 3.3 with 1 M HCl or used as unadjusted. Then, 3 g of Fe-loaded zeolite and 30 mL nitrate solution were placed in the 37-mL amber tube without buffer. The tubes were shaken at 36 rpm with vertical rotary shaker for 80 hrs at ambient temperature. Parallel experiments were performed with no material (blank), 40-mesh iron filing (Fisher, USA), Fe(II)-sorbed zeolite without reduction, and pure zeolite. During shaking, at pre-determined time interval, each tube was taken, and supernatant was separated from solid materials by filtering through 0.45 μm -pore membrane. Duplicates were prepared at each time intervals. And the supernatant was used for estimating the concentration of nitrate and ammonium.

2.5. Nitrate and ammonium analysis

Fe was analyzed by atomic absorption spectrometer

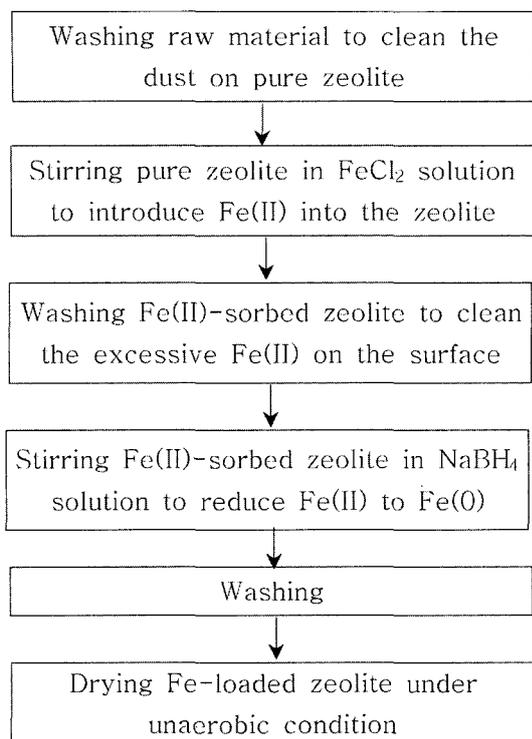


Fig. 1. Processes for Fe-loaded zeolite production.

(vario 6[®], analytic jena). Nitrate was analyzed by Ion Chromatography (Waters 432, USA) using IC-Pak anion column (4.6 mm×5 cm) with the diluted solution of sodium borate/gluconate concentrate as the mobile phase at the flow rate of 1.2 mL/min. Nitrate retention time was 4.2 min. Ammonium was analyzed by IC (Waters 432) using IC-Pak Cation M/D (3.9 mm×150 mm). The mobile phase was 0.1 mM EDTA/3.0 mM HNO₃, and flow rate was 1 mL/min. The retention time of ammonium was 4.05 min.

3. Results and Discussions

3.1. Fe(II) loading on zeolite

The processes for making Fe-loaded zeolite involve stirring zeolite in FeCl₂ solution to introduce Fe(II) into zeolite matrix, followed by borohydride reduction to convert Fe(II) in zeolite to Fe(0). So, the optimal concentration of FeCl₂, which produced maximum loading of Fe(II) in zeolite, was determined by ion exchange experiment.

As shown in Fig. 2, the amount of Fe(II) sorbed in zeolite by ion exchange, which was directly estimated by extracting with KCl solution, increased as the initial concentration of FeCl₂ increased, and stabilized at approximately 350 mM. It possibly indicated that Fe(II) exchange capacity of zeolite was saturated. Nitric acid digestion for Fe-loaded zeolite after KCl extraction showed

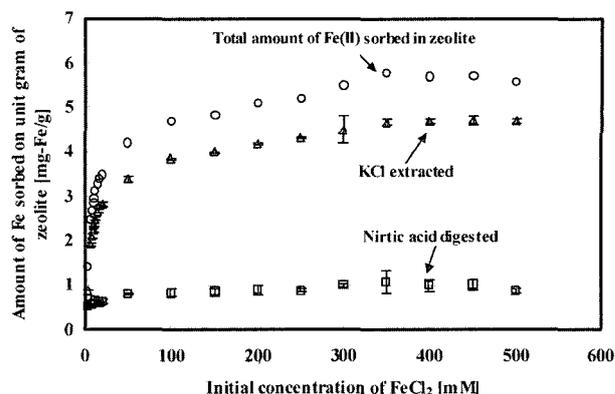
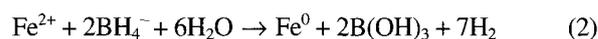


Fig. 2. Estimation on sorbed amount of Fe(II) in zeolite by KCl extraction and nitric acid digestion. Total amount of Fe(II) was calculated by adding the digested amount to the extracted amount.

that Fe(II) could be sorbed to zeolite by the mechanisms other than ion exchange (Fig. 2). The amount of Fe(II) sorbed by non ion-exchange mechanism was relatively small compared to that by ion exchange (4.8 mg/g), and almost constant as 1 mg/g over the range of 50 to 450 mM of FeCl₂.

From the test results, the concentration of FeCl₂ solution used in the first step of Fe-loaded zeolite making process, was determined as 350 mM, where the maximum sorption of Fe(II) in zeolite occurred. At this concentration, the loaded Fe(II) amount was estimated as 5.8 mg/g (0.1 mmol/g), and the stoichiometric requirement of NaBH₄ was calculated from Eq. (2) to fully reduce the sorbed amount of Fe(II) in zeolite to Fe(0).



Therefore, 100 mmol of borate was contained in 5 L of deionized water for fully reacting with 500 g of Fe(II)-loaded zeolites (0.1 mmol/g×2×500 g = 100 mmol). Consequently, the concentration of NaBH₄ solution was determined to be 20 mM (100 mmol/5 L).

3.2. Nitrate reduction and ammonium production

Fig. 3(a),(b) show the results of nitrate reduction at initial pH of 3.3 and 6, respectively.

Removal efficiency decreased at higher pH, which was consistent with the results in previous studies (Cheng *et al.*, 1997; Huang *et al.*, 1998; Alowitz and Scherer, 2002). This decrease in Fe-loaded zeolite and iron filings might be explained with H⁺ consumption during the overall reaction (Eq. (1)) and the greater likelihood of precipitation of iron oxides (Alowitz and Scherer, 2002). In Fig. 3, Fe-loaded zeolite showed about 60% and 40% removal efficiency at pH 3.3 and 6, respectively through 80 hr

reaction. During early period of reaction within 5 hrs, removal rate (tangent slope of the curve) of Fe-loaded zeolite was similar with iron filing, but afterwards decreased more rapidly than iron filing. The rapid decrease in removal rate of Fe-loaded zeolite might be responsible for the small amount of Fe in Fe-loaded zeolite (Table 1). Consequently, Fe-loaded zeolite showed lower removal efficiency than iron filing. However, considering the small fraction of Fe in Fe-loaded zeolite (2.77 Fe-wt%) as shown in Table 1, it could be speculated that Fe in Fe-loaded zeolite have higher reactivity than that of iron filings.

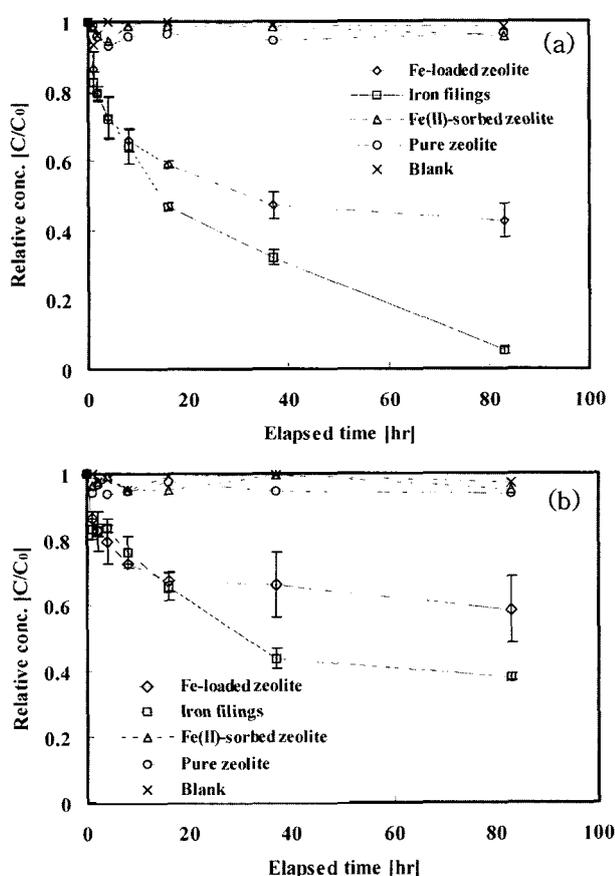


Fig. 3. (a) Nitrate removal efficiency of each material at initial pH of 3.3, (b) Nitrate removal efficiency of each material at initial pH of 6.

Table 1. Chemical composition estimation on materials by X-Ray Fluorescence (XRF) analysis

	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	LOI	Total
P.Z	66.51	12.93	0.25	1.50	0.68	1.75	2.93	2.55	0.04	0.05	11.27	100.46
FL.Z	66.07	12.85	0.23	2.77	0.59	1.60	3.01	2.39	0.06	0.05	11.11	100.72
I.F	0.15	0.01	0	98.26	0.01	0	0	0	0.01	0		
Fe(II)	66.22	12.90	0.24	2.76	0.60	1.74	2.24	2.53	0.04	0.06	10.92	100.25

P.Z: Pure zeolite, FL.Z: Fe-loaded zeolite, I.F: Iron filing, Fe(II): Fe(II)-sorbed zeolite, LOI: Loss on ignition

For identifying the reaction by-products, ammonium concentrations were measured for the residual solution containing Fe-loaded zeolite and iron filing, as shown in Fig. 4.

Ammonium accumulation in iron filing-system increased as the reaction proceeded, i.e., the amount of reduced nitrate increased. However, in Fe-loaded zeolite system, ammonium was not detected at any time interval although noticeable amount of nitrate was removed (Fig. 4). It was hypothesized that ammonium produced in Fe-loaded zeolite system might be sequentially sorbed to Fe-loaded zeolite by ion exchange. This suggestion could be supported by the fact that Fe-loaded zeolite contained similar amount Na with that of zeolite (Table 1), which is one of the most exchangeable ion in zeolite, and that the concentration of Na was extraordinarily high in Fe-loaded zeolite system than in iron filing system.

In terms of nitrogen (-N) contamination including NO₃⁻-N and NH₄⁺-N, Fe-loaded zeolite showed about 60% and 40% removal at initial pH of 3.3 and 6, whereas nitrogen removal by iron filing was negligible. The removal efficiencies of Fe-loaded zeolite and iron filing against nitrogen contaminants were summarized in Table 2, which indicated that Fe-loaded zeolite showed about 8-fold higher nitrogen removal efficiency than iron filings.

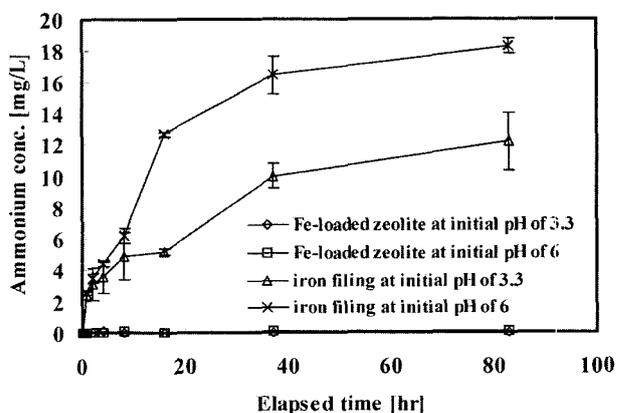


Fig. 4. Ammonium concentration in residual solution during nitrate reduction.

Table 2. Removal efficiency of ZanF and iron filing for nitrogen contaminants at initial pH of 3.3 and 6

	ZanF at 3.3	ZanF at 6	Iron filing at 3.3	Iron filing at 6
Removal efficiency ^a	62%	41%	8%	5%

^aRemoval efficiency(%) = (amount of NO₃-N + NH₄⁺-N)/(amount of initial NO₃-N) × 100

4. Conclusion

With the test results, it could be concluded that Fe-loaded zeolite remediate nitrogen species in residual solution more efficiently and properly than iron filing.

When applying iron filings in PRBs, iron filing alone is not an appropriate and sufficient reactive material for treating nitrate contaminant in groundwater. For nitrate removal applications, PRBs must hence incorporate an additional reactive barrier for ammonium behind ZVI barrier, or another reactive material should be mixed with iron filing in the barrier for treating the undesirable by-product. However, PRBs in series could increase construction costs and process complexities, and the mixed materials in the barrier could become segregated due to differences in bulk density and gradation. Therefore, the newly developed materials, Fe-loaded zeolite could possibly be an alternative to iron filing in PRBs for nitrate-contaminated groundwater. However, prior to a field application, additional investigations have to be performed on Fe-loaded zeolite including removal efficiency enhancement, column experiment with simulated groundwater and longevity estimation. Particularly, the dramatic decrease in material reactivity by time elapsed should be considered in field design, and should be reflected in barrier material replacements.

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