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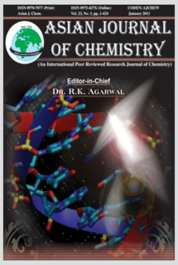

# Use of Mechanicaly Prepared Iron Nano Particles for Nitrate Removal from Water

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Zero-valent iron powder has been found to be potentially useful for the removal of nitrate in the water environment. This research is aimed at subjecting the reduction of nitrate by iron nanoparticles produced *via* physical method. Iron nanoparticles with an average diameter of 25 nm which are characterized by the large specific surface area (40-60 $m^2 g^{-1}$) reduced about 95 % of nitrate within a period of 3 h in the controlled pH = 2-4. Compared with iron nanoparticles produced *via* chemical method, requirement to acid addition is the most drawback of this iron nanoparticles.

**Key Words: Nitrate reduction, Iron nanoparticles, Groundwater, Nanoscale iron particles, pH.**

## INTRODUCTION

Nitrate pollution of groundwater and surface water has become environmental problems in many parts of the world. Anthropogenic sources as nitrogen fertilizers, nitrogen pesticides, animal wastes and septic systems account for most nitrate contamination of groundwater. Nitrate itself is relatively non-toxic. However, it can be microbially reduced to nitrite, which poses several health threats to human being including methemoglobinemia, liver damage and cancers[1,2]. Current technologies to remove nitrate from water include ion exchange (IE), reverse osmosis (RO), biological denitrification (BD) and chemical reduction (CR). Ion exchange and reverse osmosis require frequent regeneration of the media and generate secondary brine wastes. Biological denitrification, the most widely used method, requires intensive maintenance and a constant supply of organic substrate. Moreover, the microbial process is generally slow and sometimes incomplete compared to chemical reduction. Environmental application of metallic iron have been enthusiastically accepted by many users and regulatory agencies, largely due to the low costs and absence of any known toxicity reduced by the use of iron.

Use of metallic iron in the form of packed bed reactors and permeable reactive barriers has been widely reported. Despite their minuscule status, nanoscale particles may hold the potential to cost-effectively address some of the challenges of site remediation[3]. Interest in $Fe^o$ as an alternative for nitrate removal from water has emerged only recently[4,5].

Nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost effective solution to some of the most challenging environmental clean up problems. Nanoscale iron particles have large surface area and high surface reactivity. Equally important, they provide enormous flexibility for *in situ* application.

Nanoparticles can be transported effectively by the flow of groundwater. Due to this attribute, the nanoparticle-water slurry can be injected under pressure and/or by gravity to the contaminated plume where treatment is needed. The nanoparticles can also remain in suspension for extended periods of time to establish an *in situ* treatment zone. Equally important, they provide enormous flexibility for both *in situ* and *ex situ* applications. For example, nanoparticles are easily deployed in slurry reactors for the treatment of contaminated soils, sediments and solid wastes. Alternatively, nanoparticles can be anchored onto a solid matrix such as activated carbon and/or zeolite for enhanced treatment of water, wastewater or gaseous process streams[6].

Direct subsurface injection, whether under gravity-fed or pressurized conditions, has already been shown to effectively transform chlorinated organic compounds[7,8]. The technology holds great promise for immobilizing heavy metals and radionucleide as well.

## EXPERIMENTAL

Denitrification experiments were performed in strictly anaerobic batch systems. The initial nitrate concentrations ranged was 50-300 mg $NO_3^- L^{-1}$. Each 250 mL sample of 50, 100, 200 and 300 mg $NO_3^- L^{-1}$ aqueous solution and 1 g of dry iron nanoparticles was charged into sample. Oxygen was removed by purging argon gas into the nitrate solution as well as in period of experiment. The samples passed through a 0.45 μm membrane filter and the concentration of unreacted nitrate were determined by UV spectrophotometer (UV 2100, Shimadzu) control experiments containing no Fe particles were also prepared. A constant mixing rate of 240 rpm was used throughout the study and was not interrupted by sampling.

Iron nanoparticles were purchased from nanostructure and nanoamorphous Company and used without further purification. These nanoparticles are produced *via* physical method. Table-1 shows the characteristics of iron nanoparticles. Potassium nitrate and HCl were used for synthetic solutions and pH adjustment purchased from Merck. Deionized water was used for preparation of all reagent solutions expect where noted otherwise.

TABLE-1
CHARACTERISTICS OF IRON NANOPARTICLES

| | |
|---|---|
| Purity | 99.6 % |
| Average particle size (APS) (nm) | 25 |
| Specific surface area ($m^2 g^{-1}$) | 40-60 |
| Bulk density ($g cm^{-3}$) | 0.10-0.25 |
| True density ($g cm^{-3}$) | 7.87 |
| Color | Black |
| Morphology | Spherical |

## RESULTS AND DISCUSSION

**Nitrate reduction by iron nanoparticles without pH control:** When no pH control was provided, the extent of nitrate removal by iron particles was strongly dependent on the initial pH of solution (Fig. 1). The pH tested ranged from 2-11. Nitrate removal within 3 h was negligible at initial pH > 4 (data not shown) whereas 49 % of nitrate was removed in less than 5 min at initial pH = 3.

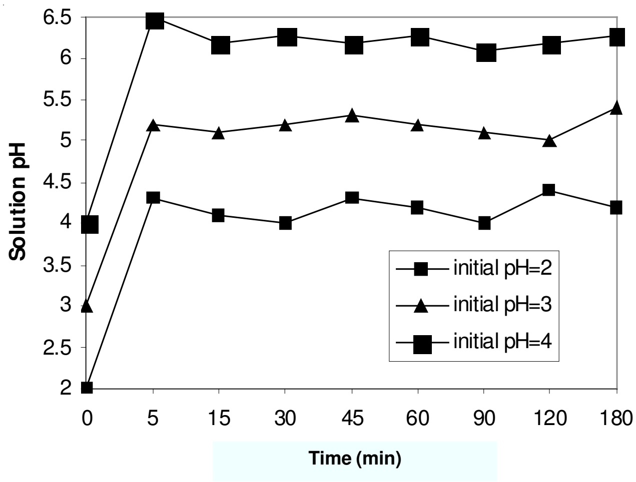

Fig. 1. Solution pH change after addition of 4 g $L^{-1}$ iron nanoparticles

Present results contradict with the previous study which indicated that complete denitrification in an aqueous solution can be achieved in a few minutes by contacting the solution with iron nanoparticles produced by chemical method under ambient conditions with no pH control[9], this is due possibly to the method used for nanoparticles production for nitrate reduction.

As shown in Fig. 2 at pH 2, 3 and 4, nitrate reduction stopped shortly after Fe was added. Coincidently, the pH solution also increased by about 2.0-2.5 pH units in 5 min and remained constant thereafter.

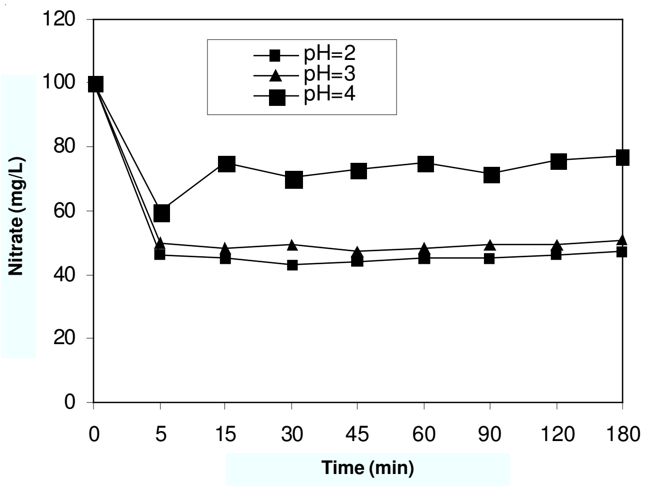

Fig. 2. Reduction of nitrate in different initial pH after addition of 4 g $L^{-1}$ iron nanoparticles

This suggests that the rapid inactivation was probably caused by solution pH increases, which occurred when Fe was oxidized by proton (eqn. 1) and nitrate (eqn. 2).

$$2H_3O^{3+} + Fe^o = H_2(g) + Fe^{2+} + 2H_2O \quad (1)$$

$$NO_3^- + Fe^o + 2H_3O^+ = Fe^{2+} + NO_2^- + 3H_2O \quad (2)$$

A closer examination of the reaction in the first few minutes revealed that nitrate reduction (and pH increase) was rapid but stopped completely in less than 5 min (Fig. 3).

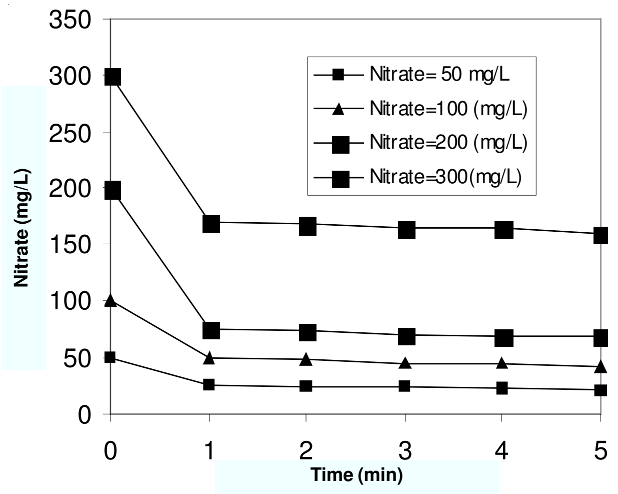

Fig. 3. Nitrate reduction within 5 min after addition of 4 g $L^{-1}$ iron nanoparticles in the initial pH = 2

Present data indicate that nitrate reduction is enhanced by low pH and is probably related to iron corrosion. Cheng *et al.*[10] also suggested that iron corrosion (325 mesh) is a necessary ingredient for nitrate reduction. Chin *et al.*[2], observed that the iron corrosion rate was pH insensitive at circum neutral pH but greatly enhanced by low pH at pH < 4. It should be noted that the rate of nitrate reduction by $Fe^o$ in unbuffered deionized water (pH not reported but probably close to 7) has been measured[5].

**Nitrate reduction by iron nanoparticles with pH control:** Compared to the pH unbuffered experiments, significantly enhanced nitrate removal was achieved when the pH solution maintained constant using a pH meter. During the experiments, pH solution did not vary by more than 0.5 pH unit at any time.

Fig. 3 shows the effect of pH on nitrate removal. All nitrate reduction rates were almost identical at $pH < 4$. In contrast, only negligible removal was observed at $pH > 4$. This abrupt change in nitrate reduction rate suggests that the mechanism responsible for rapid nitrate reduction at low pH dose not exist at $pH > 4$.

It is clearly shows that not only the initial pH of the solution but also the change of pH during reaction play a very important role for the reduction and that the pH of solutions need to be maintained below 4 for complete reduction of nitrate.

**Mechanism of nitrate reduction:** A mechanism for nitrate reduction by $Fe^o$ has not been proposed. However, as has been discussed for other reductive reactions[11] involving $Fe^o$. The electrons required to reduce nitrate must come from $Fe^o$ either directly or indirectly through the corrosion products, $Fe^{2+}$ and hydrogen.

In a study on nitrate reduction by $Fe^o$ in pH-buffered solution, Cheng *et al.*[10] proposed that corrosion was necessary for nitrate reduction to occur and that a corrosion product of $Fe^o$, rather than $Fe^o$ itself was responsible for nitrate reduction. These authors considered ferrous species, $Fe(OH)_2$ and aqueous $Fe^{2+}$ to be the reductants which react with nitrate.

The data shown in Fig. 4 suggest that the mechanism responsible for the rapid reduction of nitrate at $pH \leq 4$ is not important at $pH \geq 5$ the reaction immediately took place upon addition of $Fe^o$. These observations strongly suggest that nitrate reduction by $Fe^o$ is an acid-driven process and that proton either directly participates in the reaction or indirectly facilitates it.

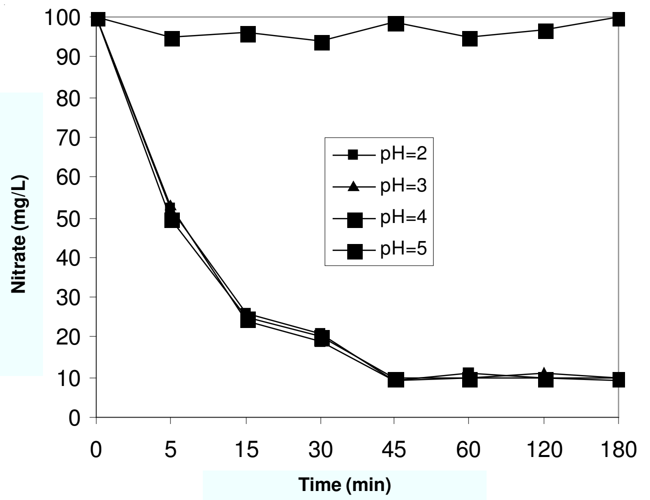

Fig. 4. Reduction of nitrate *versus* time at controlled pH. Feocontent = 4 g $L^{-1}$ for all experiment

It is likely that aqueous proton is first reduced by Fe to form reduced hydrogen species, such as hydrogen atom (H), which then reacts with nitrate or evolves as $H_2$.

The role of hydrogen in nitrate reduction by Fe has been noted. In contrast to our finding that nitrate reduction by $Fe^o$ was slow at neutral pH, Siantar *et al.*[4] reported that iron powder stored fewer than 10 % $H_2$ degraded nitrate and nitrite within minutes at pH 7. Apparently, pre-exposure to $H_2$ enables $Fe^o$ to rapidly reduce nitrate. Iron may activate sorbed $H_2$ similar to catalytic metals such as palladium[12,13]. Cheng *et al.*[14] proposed that the hydrogen gas intercalated in a Pd lattice is a strongly reductant which reductively dechlorinates 4-chlorophenol. In like manner, but to lesser extent, $Fe^o$ may convert sorbed $H_2$ gas or aqueous proton (through reduction) to atomic hydrogen, which then reduces nitrate.

It has been adsorbed[15] by $Fe^o$. $H_2$ enters into the bulk of the metal presumably as individual hydrogen atoms rather than diatomic molecules[16].

Alternatively, nitrate may be reduced directly by $Fe^o$ and lowering pH facilities the reaction by dissolving away ferrous hydroxide and other protective layers at the $Fe^o$ surface.

## Conclusion

Present results indicate that pH is a critical parameter which controls nitrate reduction by iron nanoparticles that produced *via* physical method. No significant nitrate removal was observed in 3 h at $pH \geq 5$. At $pH \leq 4$, pH control *via* acid addition greatly enhanced the rate and the extent of nitrate reduction.

Under the experimental conditions, nitrate was reduced either by surface hydrogen derived from proton or directly by $Fe^o$, $Fe^{2+}$ and $Fe(OH)_2$ did not appear to be involvel. Other factors such as mass transfer, surface precipitation and sorption of products[17-19] may become important under different conditions.

More research is needed to understand the mechanism of electron transfer and the possible inhibitory effects in treatment systems involving $Fe^o$. As an alternative technology to treat nitrate-contaminated water, chemical reduction using iron nanoparticles produced by physical method requires an acidic condition that is not practical in field application but application of iron nanoparticles produced by chemical method is a fast, simple, reliable and relatively inexpensive way to remove nitrate.

Optimization of chemical reduction of nitrate using iron nanoparticles produced by chemical method can be a cost effective way to treat water or wastewater containing high level of nitrate.

## ACKNOWLEDGEMENTS

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