Study of different methods for enhancing the nitrate removal efficiency of a zero-valent metal process

S.F. Cheng*, C.Y. Huang** and J.Y. Liu*

*Department of Environmental Engineering and Management, Chaoyang University of Technology, 168 Gifeng E. Rd., Wufeng, Taichung County 41305, Taiwan (E-mail: shufen@mail.cyut.edu.tw)

**Ordnance Readiness Development Center, 91034-2 Ji Ji Mail Box, Nantou County, Taiwan (E-mail: sanada@ms18.hinet.net)

Abstract This study explores the effect of several enhancing methods, namely acid wash pretreatment, ultrasound treatment and addition of nickel catalyst on the nitrate removal efficiency of three zero-valent metals – iron, aluminium and zinc. It is hoped that by learning about the major reaction pathways of nitrate removal with zero-valent metals and the main factors influencing the reactivity of those zero-valent metals, optimum process conditions may be identified. The study results show that direct transfer of electrons is the major reaction pathway. Thus increasing a clean, fresh metal surface and decreasing the thickness of the diffusion layer to accelerate mass transfer are the main determinants of reaction rate. In the absence of a clean, fresh metal surface, the catalytic reaction of nickel becomes the primary removal pathway.

Keywords Acid wash; catalyst; ultrasound

Introduction

Following the Green Revolution in the 1970s, massive use of fertilisers helped boost the yield of crops and solve the food shortage crisis. After the heavy use of N fertilisers, there has been a rising trend in recent years of increasing nitrate level in groundwater around the world, including Taiwan (Pintar et al., 2001; Prüsse and Vorlop, 2001). Moreover, with the advancement of technology, the livestock industry is opting for high-density, large-scale farming. As a result, contaminants in the soil exceed its carrying capacity and leach to the groundwater, resulting in increasingly higher nitrate levels in groundwater (Pintar and Batista, 1999; Choe et al., 2004).

Based on information currently available, the direct harm of nitrate to human health is not clear. However, if groundwater containing high levels of nitrate serves as the source of drinking water, nitrate might be converted to nitrite in the digestive system. An excessive amount of nitrite affects the oxygen-carrying function of haemoglobin, leading to methaemoglobinaemia, or the so-called “blue baby syndrome”. Research results in recent years also show that nitrite might cause damage to the liver and is potentially carcinogenic (World Health Organisation, 1985; Prüsse and Vorlop, 2001; Choe et al., 2004). Thus the presence of nitrate in drinking water poses a significant health concern.

Zero-valent iron has been used extensively in the research and the process for treating groundwater contaminated with chlorinated organic compounds (Gillham and O’Hannesin, 1994; Matheson and Tratnyek, 1994; Muftikian et al., 1995; Wang and Zhang, 1997; Lien and Zhang, 1999). Owing to the presence of chlorine, carbon in the chlorinated organic compounds is in a highly oxidised state. With its reductive capacity, zero-valent metal can remove chlorine by reduction. The nitrogen in the nitrate exists in the valence state of +5, the highest oxidised state, and using the reductive capacity of zero-valent metal to remove nitrogen has been proved feasible based on the theory of thermodynamics and empirical
studies (Siantar et al., 1996; Cheng et al., 1997; Chew and Zhang, 1998; Huang et al., 1998; Choe et al., 2000; Liao et al., 2003; Westerhoff and James, 2003).

Many factors influence nitrate removal rate of zero-valent metals, including characteristics of the water sample, such as pH (Zawaiden and Zhang, 1998; Choe et al., 2004), content of organic matter (Liao et al. 2003) and the presence of other dissolved components in water, e.g. hardness, chloride and silicate (Pintar et al., 1998; Klausen et al., 2001). The characteristics of the zero-valent metal itself, such as its reactivity, size of the particle’s surface area and freshness of the metal surface are the major influencing factors. Moreover, the addition of catalyst might change the reaction pathway of nitrate removal and affect the reaction rate. Matheson and Tratnyek (1994) suggest three possible pathways for the degradation of chlorinated organic compounds by zero-valent metals: (1) transfer of electrons via direct contact with the surface of iron metal; (2) reductive dechlorination by ferrous ion Fe$^{+2}$ produced from the reaction of zero-valent metal with water, which is generally believed to be a minor reaction pathway; (3) dechlorination by hydrogen produced from the reaction of zero-valent metal with water under the activity of the metal catalyst. The primary degradation pathway might differ under different conditions, and the reaction rate is dependent upon the major limiting steps in reaction mechanisms, which could be the reaction rate itself or the mass transfer rate.

The high-speed vibration of ultrasound assures uniform agitation, increases the chance of collision and helps strip the oxidised build-up on metal surface. It also reduces the thickness of the diffusion layer on the metal surface, thereby increasing the rate of mass transfer (Lauterborn and Bolle, 1975; Leighton, 2001; Geiger et al., 2002).

Using acid-wash pretreatment, addition of the nickel catalyst and ultrasound vibration, this study hopes to identify the major reaction pathways and main factors influencing the reaction rate of nitrate degradation by iron, aluminium and zinc, and thereby identify an economical, fast and effective process for treating excessive nitrate in water supplies.

**Materials and methods**

The zero-valent metals iron (Fe), aluminium (Al) and zinc (Zn) were used for the experiment. The Fe used included iron powder and iron ingot; the iron powder, identified as Fe(A) and Fe(B), was more than 99% pure and supplied by Riedel-de Haen and Shimakyu, respectively; the industrial-grade iron ingot identified as Fe(C) was supplied by Shimakyu with a grain size similar to 1-cm long iron nail. The Al used was of high purity and also came from Shimakyu, and contained columnar grains 1-cm long and about 0.2 cm in diameter. The zero-valent Zn was a granular, highly pure reagent supplied by Aldrich with grain size ranging from 10 to 50 mesh and purity greater than 99.8%.

In the batch experiment, a 400-mL water sample containing 20 mgL$^{-1}$ nitrate was placed into a 500 mL serum bottle and added to 50 g of test zero-valent metal. The nitrate water sample was prepared manually in the laboratory by diluting 1,000 mgL$^{-1}$ nitrate standard solution from Merck (prepared with sodium nitrate) with ultra-pure water. The study examined the removal of nitrate by various zero-valent metals without any pretreatment and compared the changes in removal efficiency after acid-wash pretreatment. For acid wash pretreatment, 1:2 (HCl:H$_2$O) hydrochloric acid was poured directly into a vessel that contained the test metal and agitated thoroughly for about 3 min. Subsequently, the test metal was rinsed profusely with water, dried, and then placed into the reaction flask for testing.

For addition of the nickel catalyst, nickel powder was added directly into the reaction flask. Taking into account that nickel powder does not distribute uniformly, this
experiment required a large amount of nickel, i.e. 25 g in each reaction flask. The nickel powder used came from Acros with 99.9% purity and grain size of 325 mesh.

To learn about the determinants of the reaction rate, the study compared the effect of mechanical agitation and ultrasound vibration; the mechanical agitation was carried out at the rate of 500 rpm, and ultrasonic cleaner commonly used in the laboratory was used for ultrasound vibration.

The residual concentrations of nitrate and its decomposition product nitrite were measured using ion chromatography (Dionex, DX-120) outfitted with AS12A, 4-mm column.

**Results and discussion**

**Effect of acid-wash pretreatment on the rate of nitrate degradation by zero-valent metals**

In the nitrate degradation tests using Fe, Al or Zn without any pretreatment, it was found that zero-valent Al and industrial-grade iron ingot Fe(C) exhibited practically no degradation activity against nitrate, while Fe(A), Fe(B) and Zn degraded nitrate in a manner that approximated zero-order decay. The changes in the nitrate degradation of respective metals are shown in Figure 1. The rate constant of zero-order reactions of Fe(A), Fe(B) and Zn are depicted in Table 1. Their correlation coefficient $R$-value based on zero-order reaction model reached 0.98, suggesting approximation to zero-order reaction. Zero-order reaction means the reaction rate was independent of the concentration of nitrate, and the major factor influencing reaction rate could be mass transfer (Siantar et al., 1996). In this study, the reaction took place under ultrasound vibration. Thus, the transfer of nitrate between the aqueous solution and metal surface should not have been the main rate-limiting factor. Based on the situation observed in this study, the primary determinant of reaction rate was possibly the number of active sites provided by the zero-valent metal.

Both Fe(A) and Fe(B) used in the study were more than 99% pure and both had similar grain sizes (about 300 mesh) and specific surface areas (1.37 and 1.52 m$^2$g$^{-1}$). The Fe(A) had been unpacked for more than six months, while Fe(B) came in as a new package for this experiment and was used immediately after opening. It was found that their nitrate removal rate was four times apart. Such a result implies that the reactivity of zero-valent

![Figure 1](https://iwaponline.com/wst/article-pdf/53/11/81/432044/81.pdf)
metal was not singularly determined by the size of its specific surface area. The primary determinant was whether the surface area possesses reactivity, while the reactivity of zero-valent iron decreased significantly after repeated exposure in air.

Figure 1 also illustrates nitrate degradation by acid-washed Fe(A), Fe(B), Al and Zn under ultrasound vibration. As shown, the degradation rates were markedly different from those of unwashed metals, exhibiting pseudo first-order decay. The rate constants $k_1$, and correlation coefficient $R$-values are also illustrated in Table 1. As shown, when the reactions were simulated based on a pseudo first-order model, their correlation coefficient $R$-values were over 0.99, suggesting close approximation of pseudo first-order reaction.

The experimental results show that the rate constant $k_1$ of nitrate degradation by acid-washed Fe(A) and Fe(B) was similar. By comparing the results of Figure 1, it is clear that acid wash produced the most conspicuous changes in Al in terms of nitrate degradation rate. As shown in Figure 1, Al not acid washed showed virtually no degradation activity on nitrate. However, the acid-washed Al exhibited activity that approximated pseudo first-order reaction with an average rate constant around 1.22 (h$^{-1}$).

This study particularly used industrial-grade iron ingot with low purity and large grain size (Fe(C)) to investigate its nitrate degradation activity with and without acid-wash pretreatment and under different added amounts. No degradation effect was observed with unwashed Fe(C) even though a large amount of iron ingot at 300 g per 400 mL was added, while acid-washed Fe(C) at the amount of 50, 100, 200 and 300 g per 400 mL showed marked nitrate removal effect, although with different removal efficiency. When the addition of Fe(C) was under 200 g, the nitrate degradation approximated zero-order reaction. As shown in Table 1, which depicts the rate constants and correlation coefficient $R$-values of Fe(C) reactions, the correlation coefficient $R$-values based on zero-order reaction model all reached 0.98. When 300 g of Fe(C) was added, the nitrate degradation approximated pseudo first-order reaction. Its correlation coefficient $R$-value based on the pseudo first-order model reached 0.99, and its rate constant $k_1$ was approximately 0.349 (h$^{-1}$).

According to the experimental results, industrial-grade and low-purity iron, such as Fe(C), could produce a nitrate degradation effect similar to that of reagent grade, highly pure iron powder, such as Fe(A) and Fe(B), provided it is acid washed and supplied in sufficient quantity. Thus, this study found that as long as the surface of zero-valent iron is fresh, neither its purity nor grain size is a main factor influencing its treatment efficiency. Using large-grain iron ingot and treating it with intermittent acid wash

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### Table 1 Reaction model, rate constants and $R$-values of nitrate degradation by Fe, Al and Zn, according to Figure 1

<table>
<thead>
<tr>
<th>Material</th>
<th>RM</th>
<th>Rate (h$^{-1}$)</th>
<th>$R$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(A)</td>
<td>Zero</td>
<td>0.020</td>
<td>0.987</td>
</tr>
<tr>
<td>Fe(B)</td>
<td>Zero</td>
<td>0.087</td>
<td>0.991</td>
</tr>
<tr>
<td>Zn</td>
<td>Zero</td>
<td>0.107</td>
<td>0.989</td>
</tr>
<tr>
<td>Fe(A)/aw</td>
<td>Pseudo-first</td>
<td>0.278</td>
<td>0.998</td>
</tr>
<tr>
<td>Fe(B)/aw</td>
<td>Pseudo-first</td>
<td>0.318</td>
<td>0.999</td>
</tr>
<tr>
<td>Zn/aw</td>
<td>Pseudo-first</td>
<td>0.788</td>
<td>0.998</td>
</tr>
<tr>
<td>Al/aw</td>
<td>Pseudo-first</td>
<td>1.219</td>
<td>0.993</td>
</tr>
<tr>
<td>Fe(C)/aw</td>
<td>Pseudo-first</td>
<td>0.349</td>
<td>0.995</td>
</tr>
</tbody>
</table>

aw: acid wash; RM: reaction model; $R$-value: correlation coefficient
and ultrasound vibration to keep its surface fresh is a more convenient and feasible approach than using iron powder.

**Various methods for enhancing nitrate degradation by zero-valent metals**

Changes in the nitrate degradation rates of Fe, Al and Zn under acid-wash pretreatment, ultrasound vibration or addition of a nickel catalyst are depicted in Figure 2. The nitrate degradation reactivity of unwashed Fe(A) under ultrasound vibration or the addition of a nickel catalyst was close to zero-order reaction. The rate constant \( k_0 \) of unwashed Fe(A) alone was 0.020 (h\(^{-1}\)), 0.107 (h\(^{-1}\)) under ultrasound vibration and 0.114 (h\(^{-1}\)) with nickel catalyst added. As shown, the ultrasound and nickel treatment enhanced the reaction rate by 4.7 and 5.0 times, respectively. After Fe(A) was acid washed, its nitrate degradation approximated pseudo first-order decay under ultrasound vibration. Similarly, it was found that nitrate degradation of unwashed Fe(B) and Fe(C) under ultrasound vibration or the addition of nickel catalyst approximated zero-order reaction. After the Fe(B) and Fe(C) were acid washed, their reaction rate approximated pseudo first-order kinetics under various promoting methods. As seen in Figure 2, for Fe(B) that had

![Figure 2](https://iwaponline.com/wst/article-pdf/53/11/81/432044/81.pdf)

**Figure 2** Nitrate degradation rates
stronger reactivity, the addition of nickel catalyst did not enhance its reaction rate significantly. For unwashed industrial-grade Fe(C) under ultrasound vibration, the addition of nickel enhanced its nitrate removal performance markedly. However, after Fe(C) was acid washed, the addition of nickel not only failed to boost its nitrate removal efficiency, but also had a retarding effect as shown by the experimental results. The same phenomenon was observed with zero-valent Zn and zero-valent Al. For zero-valent Zn, as shown, ultrasound vibration could significantly enhance the nitrate removal efficiency of Zn, while the addition of nickel did not show a noticeable effect. It was found that unwashed Al displayed virtually no removal activity, while with the addition of nickel, nitrate concentration decreased markedly with time. The acid-washed Al displayed fast nitrate degradation. When modelling the pseudo first-order reaction, its rate constant $k_1$ was 1.041 (h$^{-1}$); under the same conditions, the addition of nickel resulted in conspicuous slow-down of the reaction rate, and when modelling the pseudo first-order reaction, its rate constant $k_1$ was 0.315 (h$^{-1}$).

Based on the results discussed above, it was found that acid-wash pretreatment, coupled with ultrasound vibration, provides the most effective method for enhancing the nitrate degradation performance of various zero-valent metals. For acid-washed metal, the reaction-limiting factor due to the presence of less active sites on the metal surface resulted in a zero-order relationship between nitrate degradation rate and residual concentration of nitrate. However, if the zero-valent metal is acid washed and subjected to ultrasound vibration, the metal surface is kept fresh and provides sufficient reactivity. Under the circumstances, the reaction rate is determined by the residual concentration of nitrate, exhibiting pseudo first-order reaction kinetics. As for the activity of the nickel catalyst, the study finds that for metals with lower reactivity, such as unwashed Fe(A), Fe(C) and Al, the addition of nickel had a relatively prominent enhancement effect. However, for zero-valent metals with higher reactivity, such as Fe(B), the enhancement effect of nickel on nitrate degradation is not conspicuous. In fact, for other zero-valent metals having a higher reactivity, such as Zn as well as acid-washed Fe(C) and Al, the addition of nickel retarded the nitrate degradation rate. Based on the findings discussed above, the primary reaction pathway of nitrate degradation by zero-valent metals is direct transfer of electrons. The catalytic reaction mechanism as suggested by Matheson and Tratnyek (1994) made some contribution, but its reaction rate is apparently lower than direct contact of electrons, possibly because that catalytic reaction is a multi-step reaction. Thus keeping the surface of zero-valent metal fresh and highly reactive through acid wash and ultrasound vibration produces the fastest degradation rate, while the addition of nickel interferes with the direct contact reaction, hence slowing down the reaction rate.

**Conclusions**

This study found that zero-valent metals iron and aluminium tend to lose their reactivity under natural conditions. Thus, pretreatment with acid wash is an effective means of enhancing the reactivity. The high-speed vibration of ultrasound assists the mass transfer between reactants. The vacuolation it produces also aids the removal of oxidants and buildup on the metal surface. Pretreatment with acid wash coupled with ultrasound vibration is the most effective approach to enhance the reactivity of zero-valent metals according to this study.

Based on the findings, we surmise that the mechanism of nitrate removal by zero-valent metal is direct transfer of electrons upon contact. The catalytic reaction of nickel, as demonstrated in the study, also enhances the removal efficiency, but its reaction rate is relatively slow as compared with direct transfer of electrons. Thus, the addition of nickel catalyst produces a more noticeable effect in zero-valent metals with lower reactivity.
When the zero-valent metal has a higher reactivity, the addition of nickel produces a competing reaction, which interferes with the direct contact of electrons and retards the reaction.

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References


