EXPERIMENTAL INVESTIGATION OF THE CHEMICAL REDUCTION OF NITRATE IN WATER BY Mg^{o} AND Cu/Mg BIMETALLIC PARTICLES IN THE ABSENCE OF ANY PH- CONTROL MECHANISM

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ABSTRACT

Batch experiments revealed that magnesium (Mg^{o}) and copper/magnesium (Cu/Mg) particles had the potential for being used in the removal of nitrate from aqueous solutions. This study suggested that the reductive denitrification of nitrate by Mg^{o} and Cu/Mg bimetals depended on a number of parameters including reductant dose, solution temperature, initial nitrate concentration and contact time. The values of the activation energy (E_a) of nitrate reduction over a temperature range of 5-60 °C were 20.39, 20.34, 12.77 and 12.13 kJ/mol for Mg^{o}, 0.1% Cu/Mg, 1% Cu/Mg and 5% Cu/Mg, respectively. The predominant by-product depended strongly on the initial pH of the solution and the reductant type. When the initial pH was 4, Mg^{o} produced more nitrite and ammonium than the Cu/Mg bimetals. The time required for the removal of 70% of NO_3^- from a 100 mg/L solution was about 80 min when the experiments were conducted using Mg^{o} particles and it was about 5 min when the reaction was conducted under the same conditions using bimetallic 1% Cu/Mg. Thus, bimetal Cu/Mg had a greater potential for being used as a reductant during the denitrification of water in comparison with Mg^{o} as far as the generation of toxic by-products is concerned.

KEYWORDS:
Magnesium/ copper, Bimetal, Denitrification, Nitrate

1. INTRODUCTION

In recent years, nitrate pollution of groundwater and surface water has turned to the widespread concern in many parts of the world due to the overuse of nitrogenous fertilizers, animal wastes and untreated industrial wastes [1-4]. High nitrate concentrations in drinking water are related to many health threats such as blue baby syndrome and cancer [5-7]. Furthermore, the release of nitrate to water bodies can promote algal blooms [8] and it was stated previously that fertilization with excessive amount of nitrogen can cause nitrate accumulation in different vegetables [9]. For these reasons, both the World Health Organization (WHO) and the Environmental Protection Agency (USEPA) recommend a maximum nitrate concentration of 10 mg/L (calculated based on nitrogen) in drinking water [3,5,10]. Additionally, the demand for water is increasing worldwide; therefore, decreasing the nitrate concentration in drinking water is imperative. The most popular methods of removing nitrate levels from drinking water are biological denitrification and physical- chemical processes. Physical-chemical processes such as ion-exchange, reverse osmosis, electrodialysis and sorption are nitrate selective and efficient; however, these processes cannot convert nitrate into harmless compounds. Although biological denitrification has been widely applied to remove nitrate, this method is complex and difficult to perform practically [11-13]. Therefore, the use of zero-valent metals such as zinc, aluminum and especially iron in the chemical method of nitrate removal has been evaluated intensively through the last decade [14-16].The reduction of nitrate by Fe^{o} poses many challenges, compared with other metals like Mg^{o} , including the need for a high dose, the possibility of Fe^{2+} entering the water, blocking the reaction by $Fe(OH)_3$ precipitation and low standard potential (E^{o}) (Eqs.1-3) [17-21].

$$Mg^{2+} + 2e^- \longrightarrow Mg^{o} \qquad E^{o}=-2.363\ \text{V} \tag{1}$$

$$Fe^{2+} + 2e^- \longrightarrow Fe^{o} \qquad E^{o}=-0.44\ \text{V} \tag{2}$$

$$Zn^{2+} + 2e^- \longrightarrow Zn^{o} \qquad E^{o}=-0.76\ \text{V} \tag{3}$$

Magnesium is one of the most abundant elements in seawater and the crust of the earth, which is environmen-tally acceptable (nontoxic) and has a high hydroxide solubility; therefore, releasing Mg^{2+} ions during the treatment does not pose any environmental threat (MCL 150 mg/L according to the USEPA) [1,22]. Accordingly, zero-valent magnesium has a better potential for nitrate reduction than iron.

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In the present study, the use of bimetallic Cu/Mg particles consisting of a core metal (magnesium) and a second metal (copper) was investigated in the removal of nitrate from water. In several studies, magnesium in a bimetallic form was used for the dechlorination of chlorinated hydrocarbons and dye removal [19, 23, 24]. These studies revealed that magnesium in a bimetallic form enhanced reactivity toward chlorinated organic compounds and nitrate when compared to zero-valent magnesium. However, Chackraborty and Kumar [1] addressed the area of chemical denitrification of water by zero-valent magnesium powder and concluded that further research was still necessary before any definitive answer could be made regarding the use of this metal for the removal of nitrate from water.

For the treatment with a bimetallic compound, a small amount of copper was coated onto the surface of magnesium particles to generate Cu/Mg, which enhances the reactivity of magnesium with nitrate solution. Lin et al. [6] conducted batch experiments and effectively demonstrated that nitrate can be rapidly reduced by Fe/Cu particles. However, to the best of our knowledge, the effectiveness of bimetallic Cu/Mg particles for the removal of nitrate from water has not been reported to date.

Thus, the overall objectives of this study were to: (a) assess the effectiveness of Mg^o and Cu/Mg bimetallic particles during denitrification; (b) evaluate the effect of several parameters including reductant dose, solution temperature, initial concentration of nitrate and contact time on nitrate removal efficiency; (c) discuss the possible effects of the presence of dissolved oxygen on nitrate reduction by Mg^o and Cu/Mg particles; and (d) obtain several mechanisms of denitrification from batch studies that may provide improved input parameters for the design of full scale remediation operations.

2. MATERIALS AND METHODS

2.1. Chemicals

All chemicals used in this study, including potassium nitrate, magnesium particles (< 0.1 mm), copper(II) chloride, Nessler's reagent and hydrochloric acid, were of analytical reagent grade. Synthetic nitrate contaminated water was prepared from potassium nitrate.

2.2. Preparation of Cu/Mg Bimetallic Particles

In this study, bimetallic magnesium was synthesized by mixing a solution of secondary metal (copper) with zero-valent magnesium particles. The copper metal stock solution was prepared by dissolving $CuCl_2$ in deionized (DI) water (0.01 wt. %, 0.1 wt. %, 1 wt. %, 5 wt. % and 10 wt. %). Bimetal Cu/Mg was prepared using the copper bulk loadings of 0.01-10 wt. % by diluting the appropriate amount of copper stock solution to 100 ml with DI water, and then adding this solution to 100 g of fresh magnesium particles according to the following redox reaction:

$$Mg^o + Cu^{2+} \rightarrow Mg^{2+} + Cu^o \qquad (4)$$

The samples were then shaken by hand for 3 min after which they were allowed to remain at 25 °C for 5 min in order to enable the reduction of Cu^{2+} to Cu^o. After discarding the clear aqueous phase, the resulting Cu/Mg particles were rinsed with purified water and acetone. The prepared bimetal was then completely dried in a drying oven (60-65 °C) for 6-7 h after which it was cooled down to the room temperature and stored in vials [23,25]. The bimetal Cu/Mg was found to be green gray with no visual oxide formation on the surface.

2.3. Experimental Design

All experiments were performed in the batch mode in 75 ml serum bottles. Specifically, 0.25-2.5 g/L Mg^o and Cu/Mg particles were added to the water containing nitrate at the concentrations of 50, 100, 150 and 200 mg/L and then mixed at 125 rpm using a rotary shaker (Glas-col) under ambient conditions and various initial pH values. The pH of the solution was adjusted to 4, 6 or 7 by adding 0.1 N HCl. In another experiment, the temperature was varied from 5 to 60 °C in a water bath while maintaining the nitrate content, solution pH and contact time at 100 mg/L, 6 and 20 min, respectively. Thirty ml aliquots of the samples were then collected from the serum bottles by pipette at various time intervals and filtered through 0.42 µm filters. All experiments were conducted in duplicate and the average values are presented.

2.4. Analytical Method

The size of the Mg^o particles was estimated using a particle size analyzer (Malvern Instruments Ltd., UK). All analytical measurements were conducted according to the APHA [26]. The concentrations of nitrite and nitrate were analyzed using a UV spectrophotometer (UV 2100, Shimadzu, Japan) while the concentration of ammonia was determined by the phenate method at 640nm after increasing the pH of the solution and removing the Mg^{2+}. The level of divalent magnesium ions (Mg^{2+}) was obtained by subtracting the total hardness ($Mg^{2+} + Ca^{2+}$) from the Ca^{2+} ion concentration. The calcium ion concentration (Ca^{2+}) was determined using a flame photometer (Flame photometer, FP-6410, China). In addition, the dissolved oxygen (DO), oxidation-reduction potential (ORP) and pH of the solution were measured using a DO meter (WTW, Oxi340, Germany), ORP meter (Suntex, TS-2, Taiwan) and pH meter (Suntex, TS-1, Taiwan), respectively.

3. RESULTS AND DISCUSSION

3.1. Characteristics of Mg^o and synthesized Cu/Mg bimetallic particles

The synthesized Cu/Mg bimetallic particles prepared in this study were found to have a specific surface area of 0.0671 m^2/g and a size range of 86 – 97 µm.

The morphology of the bare Mg^o and Cu/Mg surface were obtained using Scanning Electron Microscopy (SEM).

SEM images [Figs 1 (a), (c) and (e)] of fresh Mg^o particles, 1% Cu/Mg and 5% Cu/Mg were taken. The Mg^o particles were rust-free and gray in color. Bright spots which were present on the surface of the bimetallic magnesium (Cu/Mg 1 and 5%) were likely to be the deposits of the second metal; however, some bright spots had a relatively low intensity on the surface of 1% Cu/Mg. The images of the particles after reacting with the nitrate are shown in Figs 1 (b), (d) and (f). The surface of Mg^o and Cu/Mg bimetal lost the metallic glaze, the surface color slightly turned black and small agglomerated particles were found.

The EDX analysis was also used to obtain information regarding the elemental composition of the Mg^o and Cu/Mg (1 and 5%) before and after reacting with nitrate. The results are presented in Table 1. The results of the EDX analysis suggested the presence of 45.4%, 44.1% and 42.8% oxygen in the Mg^o, 1% Cu/Mg and 5% Cu/Mg systems, respectively, before the reaction with nitrate. These findings indicate that increasing oxygen values on the surface of all reductants after reaction with nitrate may indicate oxidation conditions in aqueous solution.

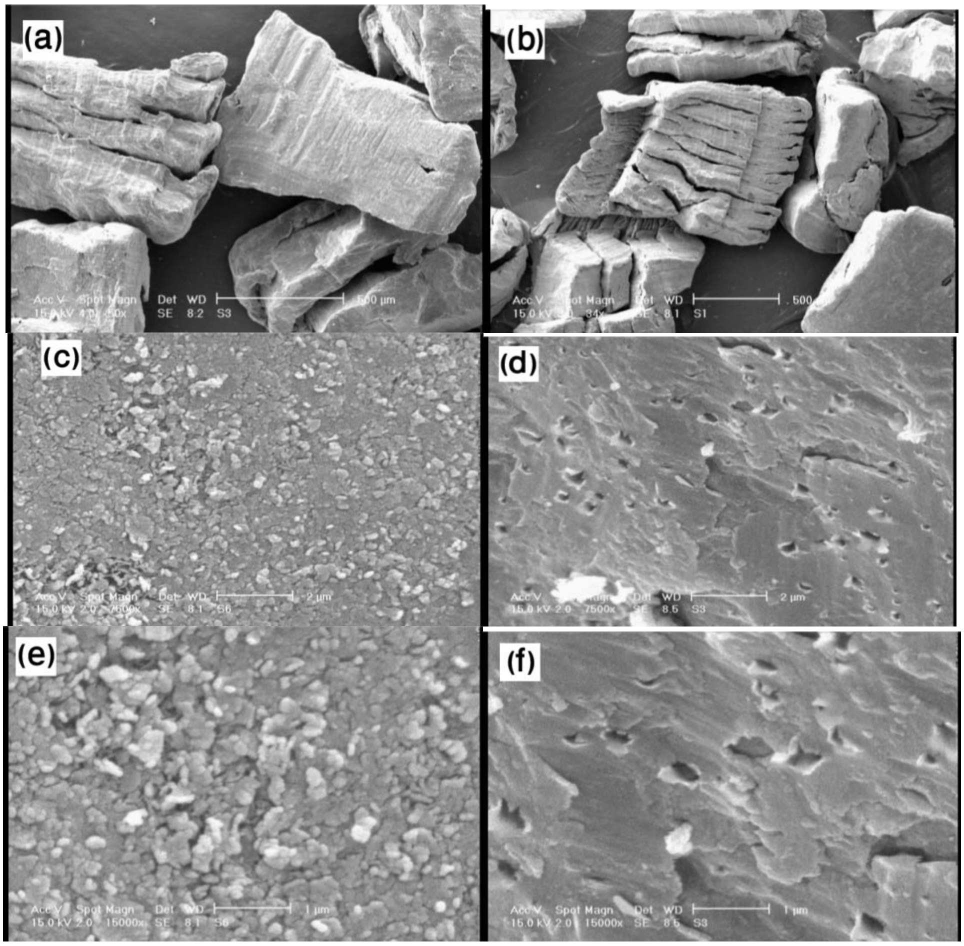


FIGURE 1 - Scanning electron microscopy (SEM) images for (a) fresh Mg^o particles; (b) Mg^o particles reacted with 100 mg/L- NO_3^- for 20 min at the initial pH of 4; (c) fresh bimetallic 1% Cu/Mg particles; (d) bimetallic 1% Cu/Mg particles reacted with 100 mg/L- NO_3^- for 20 min at the initial pH of 4; (e) fresh bimetallic 5% Cu/Mg particles; and (f) bimetallic 5% Cu/Mg particles reacted with 100 mg/L- NO_3^- for 20 min at the initial pH of 4.

TABLE 1 - Elemental composition of Mg^o, 1% Cu/Mg and 5% Cu/Mg particles before and after the reaction with nitrate [nitrate content, 100 mg/L; initial solution pH, 4; contact time, 20 min].

Reductants	Composition (%)					
	Before reacting			After reacting		
	magnesium	oxygen	copper	magnesium	oxygen	copper
Mg	54.6	45.4	0	42.9	57.1	0
1% Cu/Mg	54.2	44.1	1.7	32	66.8	1.2
5% Cu/Mg	51.8	42.8	5.4	32.9	62.3	4.8

3.2. Effect of Cu loading on denitrification efficiency

The effect of Cu loading on the denitrification efficiency was investigated and the results are shown in Fig. 2. It is clearly observable that the denitrification efficiency depends on the Cu loading. In other words, low Cu loading (≤ 0.5 wt.%) or high Cu loading (5 and 10 wt.%) was not beneficial to the reduction of nitrate and the optimum loading was obtained at the second metal content 1 wt.%. According to the hypothesis, the denitrification of nitrate would occur once they were adsorbed on the Cu/Mg surface; Cu on zero-valent magnesium surface played the role of a collector of hydrogen gas that resulted from the corrosion of magnesium. Similar results were reported for the effect of the loading of the second metal on dechlorination [3]. An increase in the second metal content in bimetallic particles could promote the magnesium oxidation and, consequently, the rate and extent of denitrification.

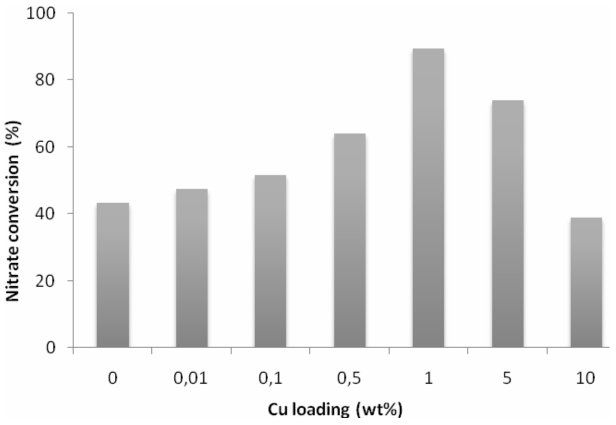


FIGURE 2 - Effect of Cu loading content on the NO_3^- conversion [initial nitrate concentration, 100 mg/L; reductant dose, 2 g/L; pH, 4; contact time, 20 min].

A higher catalytic metal loading could increase the number of catalytic metal 'islands' (i.e., galvanic cells) and/or the total cathodic areas on the magnesium surface. Interestingly, the experimental data showed that increased Cu loading resulted in the decreased denitrification efficiency when Cu loading was more than 1wt%. The increased amount of Cu coating on Mg^0 might hinder the formation of H_2 by Mg^0 corrosion. Denitrification reaction depended on an active magnesium surface and, presumably, the number of active sites on the surface was not large enough for an effective denitrification; therefore, the denitrification efficiency decreased when Cu loading was more than 1wt%.

3.3. pH variation of the solution in the Mg^o and Cu/Mg systems

During the nitrate reduction experiments, the reaction pH was monitored in the Mg^o and Cu/Mg system for 80 min (Fig. 3). The initial nitrate concentration and reductant dose (Mg^o and Cu/Mg) were maintained at 100 mg/L and 1.5 g/L, respectively. The pH variation in the Mg^o, 0.1% Cu/Mg, 1% Cu/Mg and 5% Cu/Mg systems without any pH control were 4-10.42, 4-10.24, 4-10.41 and 4-10.29, respectively. The pH of the solution in the Mg^o and Cu/Mg system increased to greater than 10, which was similar to the previously observed results in Mg^o and Fe^o systems [1,6]. Overall, the pH of the solution increased rapidly within 10 min and then remained stable for the remainder of the study period in all systems, especially in the Mg^o system. Additionally, the increase in pH in Mg^o was greater than the increase observed in the systems that employed the Cu/Mg bimetals. An increase in pH of the solution was commonly reported in previous studies in which a zero-valent metal was used for the reductive degradation [25,27-29]. This increase may be due to the consumption of protons (H^+) and the generation of hydroxide ions (OH^-) as shown in the following equations (5, 6 and 7):

$$Mg^{\circ} + 2H^{+} + NO_3^{-} \rightarrow Mg^{2+} + NO_2^{-} + H_2O \qquad (5)$$

$$4Mg^{\circ} + 10H^{+} + NO_3^{-} \rightarrow 4Mg^{2+} + NH_4^{+} + 3H_2O \qquad (6)$$

$$5Mg^{\circ} + 12H^{+} + 2NO_3^{-} \rightarrow 5Mg^{2+} + N_2 + 6H_2O \qquad (7)$$

A high pH accelerates the formation of $Mg(OH)_2$ and may lead to problems such as the formation of a passivation layer on the surface of the reductants and blockage of further nitrate reduction, especially for Mg^o [30,31].

The concentration of residual nitrate with time is shown in Fig. 4. The Cu/Mg bimetals were found to lead to a rapid and effective reduction of nitrate. Specifically, the Mg^o and Cu/Mg systems removed 68.3% and 77.8-91.9%

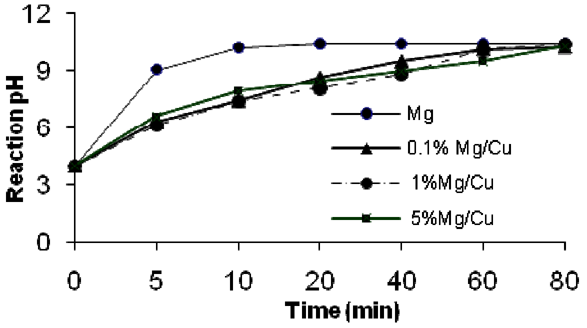


FIGURE 3 - Variation in the pH of the solution during nitrate removal by Mg^o and Cu/Mg bimetals [initial nitrate concentration, 100 mg/L- NO_3^-; initial solution pH, 4; reductant dose, 1.5 g/L].

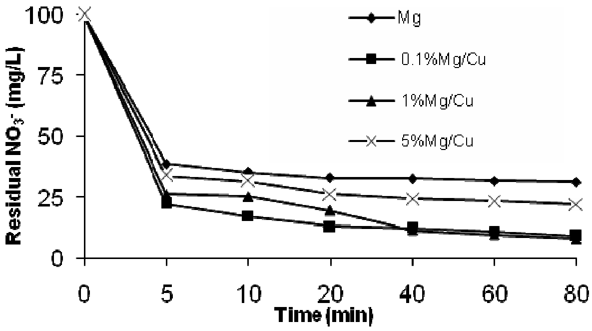
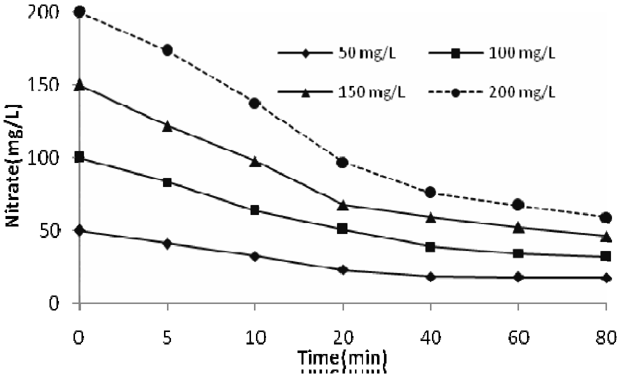
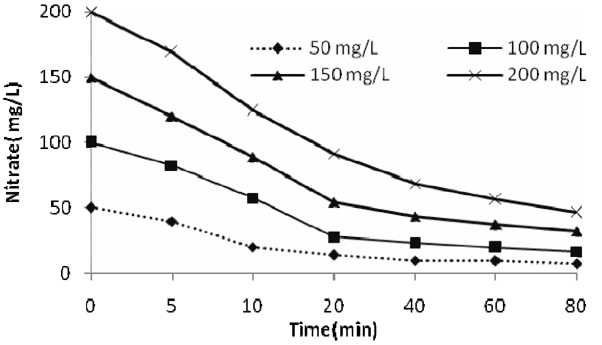


FIGURE 4 - Time course profile for the removal of nitrate using Cu/Mg bimetals and Mg^o alone [nitrate content, 100 mg/L- NO_3^-; initial solution pH, 4; reductant dose, 2 g/L].

of the nitrate, respectively, within 80 min. The conversion of nitrate began to decrease after 5 min in the Mg° system and after 20 min in the Cu/Mg systems. These changes may have been due to the precipitation of magnesium hydroxide onto the surface of the reductants due to an increase in solution pH. However, based on the results presented in Figs 3 and 4, it is clear that the influence of the formation of magnesium hydroxide on the surface of the Cu/Mg bimetals was not great. Therefore, other mechanisms such as the generation of nascent hydrogen $(2H^{+}+2e^{-}\rightarrow 2H^{*})$ were involved in the remarkable nitrate removal rate, which was observed in the Cu/Mg bimetallic systems.



(a)Mg°



(b) 1%Cu/Mg

FIGURE 5 - Effect of initial nitrate concentration on nitrate reduction a) by Mg° and b) by 1% Cu/Mg [initial solution pH, 6; Mg°:NO_3^--N molar ratio constant at 5

3.4. Effect of initial nitrate concentration

Figs 5(a) and (b) show the nitrate reduction profiles obtained for the Mg° and 1% Cu/Mg bimetal systems when different initial nitrate concentrations (50- 200 mg/L- NO_3^-), an initial solution pH of 6 and a constant molar ratio of magnesium to nitrate of 5 were used. The highest rate of denitrification (70.5%) was achieved by Mg° particles with the highest initial concentration of nitrate. The conversion efficiency observed when the initial concentration of nitrate was 200 mg/L was greater than the efficiencies observed when the initial concentrations were 150, 100 and 50 mg/L-NO_3^-. Therefore, the lowest rate of denitrification by Mg° particles was obtained when the initial nitrate concentration was 50 mg/L. There are two probable reasons for the lower denitrification rate observed when there was a lower initial nitrate concentration in the Mg° system. The first is that there may have been insufficient Mg° available for maintaining the constant Mg: NO_3^- molar ratio at 5 (0.097 g/L for 50 mg/L - $NO_3^-$and 0.387 g/L for 200 mg/L - NO_3^-), which would prevent the occurrence of a favorable reaction for reducing nitrate. The second possible reason is that the production of nitrite and ammonium (according to Fig. 6) which may have decreased the nitrate transport to the Mg° surface. However, further studies are required to identify possible inhibitory and side effects of intermediates (NH_4^+ and NO_2^-) on the reduction of nitrate by Mg° and to develop methods for solving this problem.

As shown in Fig. 5(b), higher nitrate reduction rates (85.8%) were observed in the 1% Cu/Mg bimetal system when there were lower initial nitrate concentrations. Specifically, the zero-valent aluminum and magnesium maximum denitrification efficiencies were 50% and 73% when there were initial nitrate concentrations of 50 and 100 mg/L-NO_3^-, respectively [1,14]. These results indicate that the mechanism responsible for the reduction of nitrate by 1% Cu/Mg differs from the mechanism responsible for the reduction by Mg°. In other words, a rapid nitrate reduction by 1% Cu/Mg bimetal may be explained by the mechanisms such as the formation of metal-hydride (M-H) complexes with the copper and the dissociation of molecular hydrogen or other hydrogen sources on the second metal surface (Cu) serving as a direct reductant for nitrate.

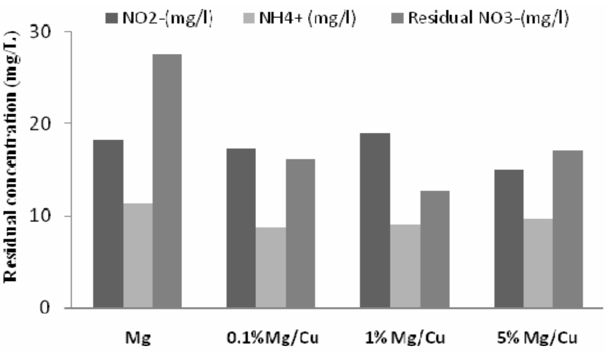


FIGURE 6 - By-product generation during nitrate removal by Mg° and Cu/Mg [initial nitrate concentration, 100 mg/L- NO_3^-; contact time, 20 min; initial solution pH, 4; reductant dose 1.5 g/L].

The identification of intermediate and final products formed during nitrate reduction was one of the focuses of this paper. As shown in Eqs. 5-7, nitrate can be reduced by Mg° and Cu/Mg to nitrite, ammonia or nitrogen gas and divalent magnesium ion (Mg^{2+}). Figs. 6 and 7 show the concentration profiles of residual nitrate, nitrite and ammonium for the Mg°, 0.1% Cu/Mg, 1% Cu/Mg and 5% Cu/Mg systems. The results indicated that the values of nitrite and ammonium as intermediate products of nitrate reduction largely depend on the initial pH of the solution and the reductant type. When the initial pH was 4 (Fig. 6), Mg° produced more nitrite and ammonium than the Cu/Mg bimetals. However, 37.56% of initial nitrate was released to the solutions in the Mg^o system under these conditions. Additionally, as shown in Fig. 6, remarkable amounts of nitrite and ammonium persisted in each system that contained Cu/Mg bimetallic particles at about 15-19 mg/L-NO_2^- and 8.7-9.6 mg/L-NH_4^+, respectively. The greater nitrate removal by the Cu/Mg bimetals may be explained by the lower nitrite accumulation and acidic pH of the solution.

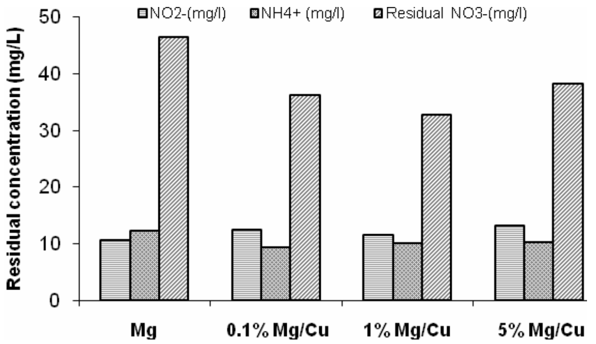


FIGURE 7 - By-product generation during nitrate removal by Mg^o and Cu/Mg [initial nitrate concentration, 100 mg/L- NO_3^-; contact time, 20 min; initial solution pH, 7; reductant dose, 1.5 g/L].

As shown in Fig. 7, at an initial solution pH of 7, the major intermediate of the nitrate degradation reaction was ammonium. The generation of nitrite and ammonium generated from the incomplete nitrate reduction by Fe^o and Mg^o was reported at low or neutral pH [6,14]. Obviously, the differences in the mechanisms of denitrification by bimetallic particles and magnesium alone also need to be considered. Direct electron transfer can play a primary role in reduction by metal alone, but in bimetallic systems, such as the Cu/Mg system, direct electron transfer by adsorbed hydrogen atoms may result in the reduction of nitrate. Adsorbed hydrogen atoms are formed via the reduction of protons from water at the second metal (Cu) surface, and these atoms reduce nitrate more rapidly than direct electron transfer. Indeed, it was reported that a variety of organohalides can be reduced by the adsorbed hydrogen atoms [12,32].

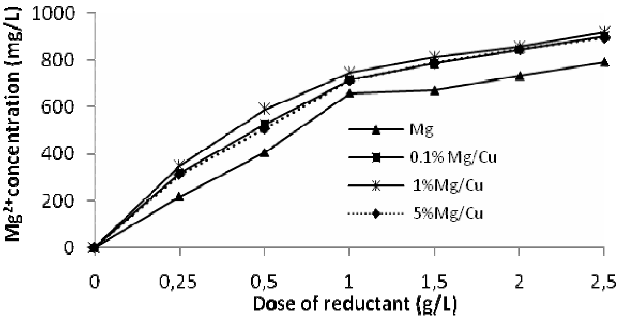


FIGURE 8 - The effect of Mg^o and Cu/Mg dose on Mg^{2+} concentration as a by-product [nitrate content, 100 mg/L- NO_3^-; initial solution pH, 4; contact time, 20 min].

Based on the results of this study, di-valent magnesium can be released into the solution during the reduction of nitrate by Mg^o and Cu/Mg systems. Therefore, an effort was also made to identify the relationship between Mg^{2+} ion and Mg^o and Cu/Mg dose. As shown in Fig. 8, the high level of magnesium ion accumulation suggests that a high level of Mg^o and Cu/Mg corrosion occurred when the initial pH was 4. Typically, when the initial dose of Mg^o, 0.1% Cu/Mg, 1% Cu/Mg and 5% Cu/Mg systems was 1.5 g/L, the concentrations of Mg^{2+} ion in solution were 671.88, 786.05, 811.76 and 788.32 mg/L, respectively, after 20 min. Although the maximum contaminant level (MCL) of Mg^{2+} ion in drinking water is high when compared with the systems that use other metals for nitrate reduction (i.e. Fe^{2+}, Zn^{2+} and Al^{3+}), it results in hard water. Therefore, further studies should be conducted to evaluate the methods of removing this soluble Mg^{2+} ion, such as coupling this process with cation ion exchange. Semerjian and Ayoub [33] reported that Mg^{2+} is an effective coagulating agent in water and wastewater treatment that can enhance the removal of many common pollutants such as total suspended solids, turbidity, color, COD, nutrients and metals. Despite these findings, magnesium ion is not commonly used because of its higher total operation and maintenance costs and greater requirements for sludge handling and processing when compared to the conventional alum treatment. However, these concepts are beyond the scope of the present paper; therefore, further studies should be conducted to develop methods of recovering and using Mg^{2+} salts produced during the nitrate reduction by Mg^o and Cu/Mg bimetallic particles as coagulating agents.

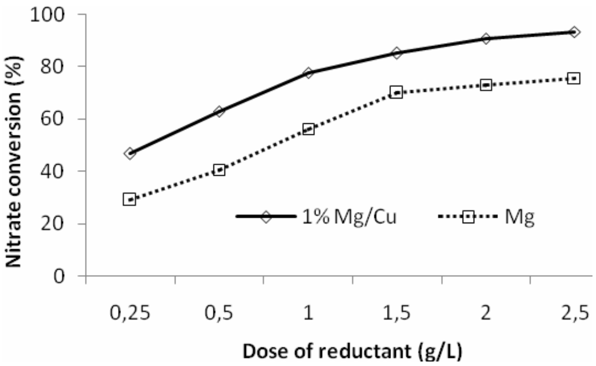


FIGURE 9 - Effect of Mg^o and 1% Cu/Mg dose on the nitrate removal efficiency [nitrate content, 50 mg/L- NO_3^-; initial solution pH, 6; reaction time; 20 min].

3.5. Effect of Mg^o and Cu/Mg dosage

Because the reduction of nitrate by Mg^o and Cu/Mg occurs during a reaction at the reductant surface, it was suggested that the quantity of metal or bimetal strongly influenced the rate of nitrate reduction. Increasing the dose of Mg^o or Cu/Mg particles in the solution would increase the reductant surface area. Fig. 9 presents the effects of Mg^o and 1% Cu/Mg (0.25-2.5 g/L) on the nitrate removal efficiency at an initial nitrate concentration of 50 mg/L, solution pH of 6 and reaction time of 20 min. The nitrate removal efficiency increased from 29% for Mg^o and 0.25 g/L to more than 69.84% for Mg^o and 1.5 g/L while further increase of Mg^o to 2 and 2.5 g/L did not lead to a remarkable increase in the nitrate removal (73.14 and 75.62, respectively). The trend in the 1% Cu/Mg system was consistent with that of the Mg^{o} system although, at doses greater than 1.5 g/L, a relatively lower nitrate reduction was observed. Similar results were reported by Li and Chen [29] and Chackraborty and Kumar [1].

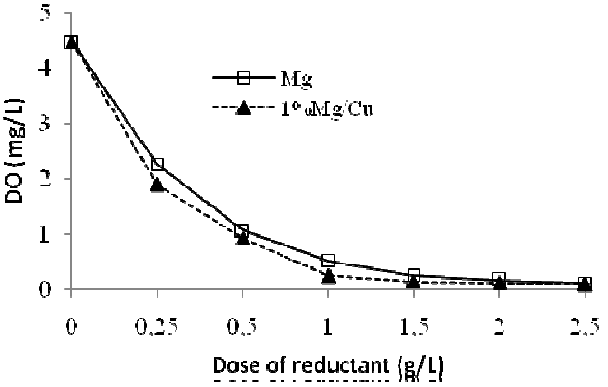
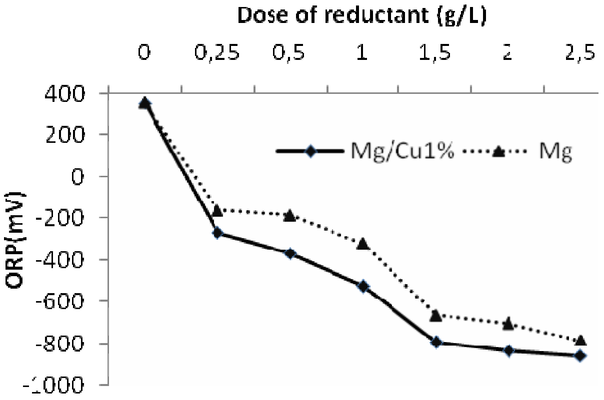


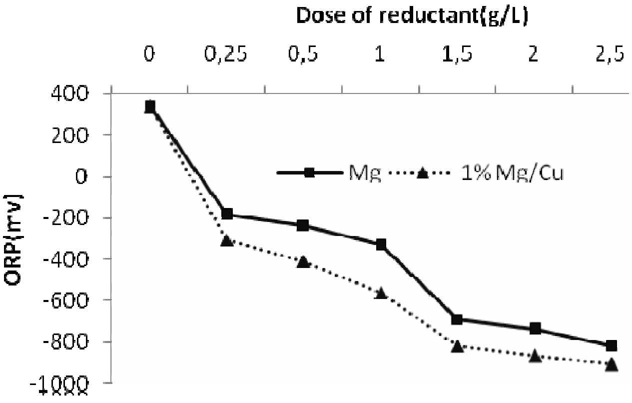
FIGURE 10 - Effect of Mg^{o} and 1% Cu/Mg dose on the dissolved oxygen [nitrate content, 50 mg/L- NO_3^-; initial solution pH, 6; reaction time, 20 min].

It has been reported that the main advantage of systems that use Mg^{o} and Cu/Mg particles is their ability to conduct reactions under atmospheric oxygen conditions [1, 23, 24, 31]. To confirm this concept, the reaction was conducted under aerobic conditions without any control of DO using varying doses of Mg^{o} and Cu/Mg particles and 50 mg/L NO_3^- (Fig. 10). Twenty min after adding Mg^{o} particles, the initial DO of the solution (4.47 mg/L) declined remarkably to 2.26, 1.07 and 0.52 mg/L when the initial doses of Mg^{o} were 0.25, 0.5 and 1 g/L, respectively. For other Mg^{o} doses (1.5, 2 and 2.5 g/L), the DO was very low or near zero after 20 min. Additionally, the DO decreased to zero within 20 min when 1% Cu/Mg bimetal was used at doses 1, 1.5, 2 and 2.5 g/L. Based on a visual comparison of Fig. 10 and Fig. 9, the DO removal occurred more rapidly than the nitrate reduction for both the Mg^{o} and 1% Cu/Mg particles. Because all experiments in Figs 9 and 10 were conducted under the same conditions, the solution DO may have affected the nitrate reduction when low doses of Mg^{o} and 1% Cu/Mg bimetallic particles (<1.5 g/L) were used. However, the anaerobic environment enhanced the nitrate removal by Mg^{o} and Cu/Mg.

Figs 11 (a) and (b) show the ORP plots during nitrate reduction for varying doses of Mg^{o} and 1% bimetallic Cu/Mg with and without DO purging, respectively. Dissolved oxygen was purged using H_2 gas prior to the addition of Mg^{o} and 1% Cu/Mg particles. It should be noted that the values of ORP under the DO purged conditions were slightly higher than the values observed without DO purging for both Mg^{o} and 1% Cu/Mg. Additionally, the values of ORP in Cu/Mg were higher than the values of Mg^{o} regardless of DO purging. This was because more negative ORP led to a more reductive condition which created a more rapid nitrate reduction, thereby allowing the nitrate removal in the Cu/Mg bimetal system to proceed in an efficient and rapid manner. However, these results also confirmed that the presence of oxygen may not affect the nitrate reduction by Mg^{o} and 1% Cu/Mg bimetallic particles.



a) Without DO purged



b) DO purged

FIGURE 11 - Effect of Mg^{o} and 1% Cu/Mg dose on ORP a) without DO purging and b) with DO purging [nitrate content, 100 mg/L- NO_3^-; initial solution pH, 6, reaction time, 20 min].

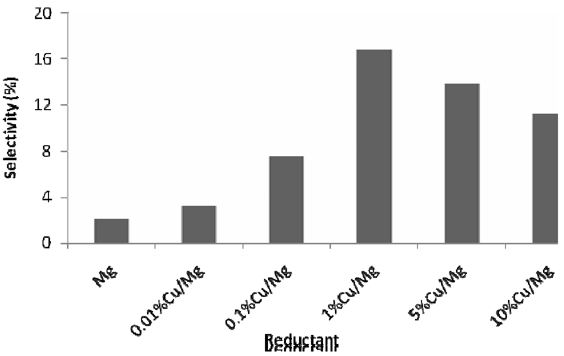
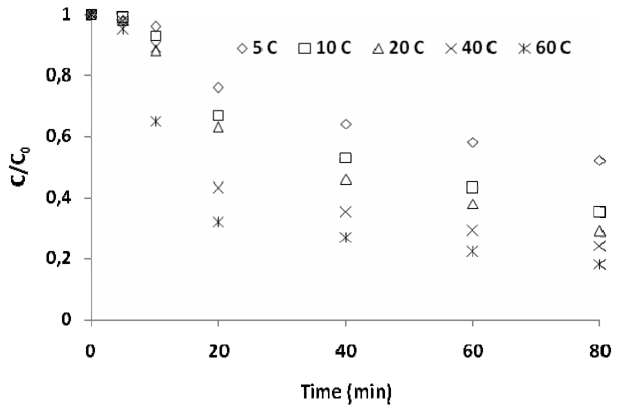


FIGURE 12 - Nitrogen formation selectivity for nitrate reduction by Mg^{0} and Cu/Mg reductants [nitrate content, 100 mg/L- NO_3^-; initial solution pH, 4; reductant dose, 2 g/L; reaction time, 40 min].

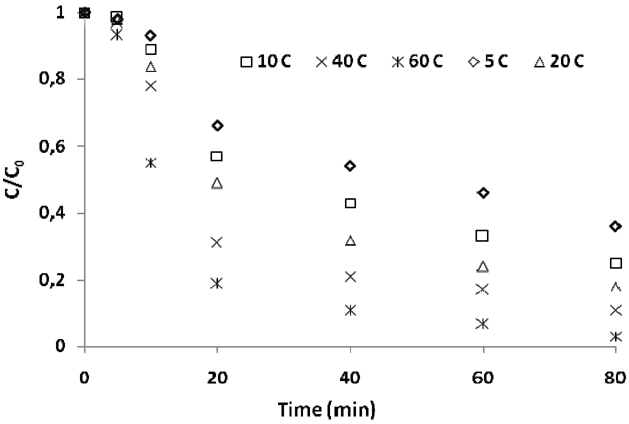
Fig. 12 shows the selectivity for six reductants. Selectivity was calculated by the equation:

$$\text{Selectivity} = \{1-[(NO_2^-)_t+(NH_4^+)_t]/[(NO_3^-)_0-(NO_3^-)_t]\}\times 100\% \quad (8)$$

The selectivity of reductants had the following order: 1% Cu/Mg > 5% Cu/Mg > 10% Cu/Mg > 0.1% Cu/Mg > 0.01% Cu/Mg > Mg. The maximum selectivity (16.81 %) was achieved by 1% Cu/Mg. Due to the relatively low selectivity for nitrate reduction by Cu/Mg, more attempts are still necessary before applying this reductant to water treatment process.



(a) Mg^0



(b) 1%Cu/Mg

FIGURE 13 - Kinetics of nitrate reduction as the function of reaction time in the presence of (a)Mg^0 and (b)1%Cu/Mg over the temperature range of 5-60 °C [nitrate content, 150 mg/L- NO_3^-; initial solution pH, 4; reductant dose, 2 g/L].

3.6. Temperature effect

Temperature is an important factor involved in chemical reduction which may provide some insights into the mechanisms of the reactions evaluated in this study [34]. Controlled chemical reactions are often sensitive to changes in temperature whereas processes limited by mass transport are not strongly influenced by temperature. In the present study, the effects of temperature on nitrate reduction by Mg^o and Cu/Mg particles were measured by conducting the reactions at 5, 10, 20, 40 and 60 °C (Fig. 13 (a) and (b)). First order nitrate reduction rates (k_{obs}) by Mg^o, 0.1% Cu/Mg, 1% Cu/Mg and 5% Cu/Mg in batch experiments exhibited a temperature dependency consistent with the Arrhenius equation:

$$k_{obs} = A(\exp\frac{-Ea}{RT}) \quad (9)$$

where A is the Arrhenius frequency factor (L/(min.m^2), E_a is the activation energy (kJ/mol), T is the absolute temperature (K) and R is the molar gas constant (0.008314 kJ/(mol.K)). The E_a for the reaction was determined from the slope of a plot of ln(k_{obs}) versus inverse temperature (1/T). Activation energies of 42.5, 25.8 and 16.8 kJ/mol were reported during the nitrate reduction by microscale Fe^o, nano-Fe^o and 5% nano-Cu/Fe, respectively [6]. The E_a is a potential energy that must be overcome to enable the reduction of nitrate and oxidation of Mg^o and Cu/Mg bimetals. In the present study, the nitrate reduction in batch experiments using Mg^o resulted in E_a=20.39 and 20.34 kJ/mol for 0.1% Cu/Mg, 12.77 kJ/mol for 1% Cu/Mg and E_a=12.13 kJ/mol for 5% Cu/Mg at temperatures ranging from 5 to 60 °C (Table 2). A literature review revealed that the typical mass transport-controlled chemical reaction in water is considered to be 10-20 kJ/mol [35,36]. Because the activation energy values for all reductants was within the range of 10-20 kJ/mol, the kinetics of nitrate reduction showed the characteristics of a mass transport-controlled reaction. Furthermore, the lower values of E_a provided further evidence that faster denitrification rates occurred in systems employing Cu/Mg (1 and 5%) than in those containing Mg^o particles.

TABLE 2 - Activation energy for nitrate reduction by Mg^o, 0.1% Cu/Mg, 1% Cu/Mg and 5% Cu/Mg [nitrate content, 150 mg/L- NO_3^-; initial solution pH, 4; reductant dose, 2 g/L].

Reductants	K_{obs} (1/min)					Activation energy (kJ/mol)
	5 °C	10 °C	20 °C	40 °C	60 °C	
Mg	0.094	0.106	0.149	0.248	0.289	20.39
0.1%Cu/Mg	0.096	0.107	0.155	0.252	0.296	20.34
1%Cu/Mg	1.16	1.39	1.67	2.21	3.08	12.77
5%Cu/Mg	1.09	1.14	1.28	1.94	2.8	12.13

4. CONCLUSIONS

In this paper, the effects of several parameters including the dose of Mg^o, three bimetallic Cu/Mg systems (0.1, 1 and 5%), initial concentration of nitrate and temperature were described on the denitrification of 50-200 mg/L-NO_3^- at initial pH values of 4-7 while focusing on the reactions conducted under aerobic conditions. The following results can be derived from the experimental findings of this study:

1. Nitrate reduction by Mg^o and Cu/Mg particles occurred through nitrite and ammonium as intermediates with the nitrogen gas as the end product. The distribution of the intermediate products appeared to depend on the initial pH and reductant type. At an initial pH of 4, the rate of producing ammonia ion was greater than when the initial pH was 7 and there was an adverse effect on

the production of nitrite ions. The Mg^o and Cu/Mg particles were oxidized to soluble Mg^{2+} ion; hence, further post treatment such as cation ion exchange is needed.

2. As the dose of the reductant increased, the ORP decreased by the desired amount, thereby resulting in a significant rate of nitrate removal (>85% efficiency).
3. The E_a values of Mg^o and Cu/Mg ranged from 10 to 20 kJ/mol indicating that the denitrification in these systems occurred via a mass transport-controlled reaction.
4. Based on the experimental batch data, the following can be concluded:
   - The nitrate removal efficiency of Cu/Mg bimetals is greater than that of Mg^o.
   - The nitrate removal efficiency by 1% Cu/Mg bimetal is greater than that of other bimetals (0.1 and 5%).
   - The influence of $Mg(OH)_2$ precipitation on blocking nitrate removal by the Cu/Mg bimetals was low.
   - In addition to the rapid reduction of Mg^o to Mg^{2+}, generation of nascent hydrogen ($2\ H^+ + 2e^- \rightarrow 2\ H^*$) may play a role in the nitrate removal rate by the Cu/Mg bimetallic systems.

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