Chemical denitrification of water by zero-valent magnesium powder

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Abstract

A laboratory-scale study was conducted in batch mode to investigate the feasibility of using zero-valent magnesium (Mg^0), for removal of nitrate from aqueous solution. Reaction pH, dose of Mg^0, initial nitrate concentration and temperature were considered variable parameters during the study. Strong acidic condition enhanced nitrate reduction and in absence of external proton addition, reaction pH increased rapidly above ten and insignificant nitrate removal (7–16%) was achieved. At $Mg^0:NO_3^-$–N molar ratio of 5.8 and controlled reaction pH of 2, 84% denitrification efficiency was achieved (initial NO_3^-–N 50 mg/L) under ambient temperature and pressure and total nitrogen removal was 70% with 3.2% and 10% conversion of initial NO_3^-–N to NO_2^-–N and NH_4^+–N, respectively. The reaction was first order with respect to nitrate concentration. Nitrate removal rate decreased with solution pH and increased linearly with Mg^0 dose. Nitrate removal was coupled with 96–100% removal of dissolved oxygen and 85–90% generation of soluble Mg^{2+} ion. An activation energy (E_a) of nitrate reduction over the temperature range of 10–50 °C was observed as 17.7 kJ mol^{-1}.
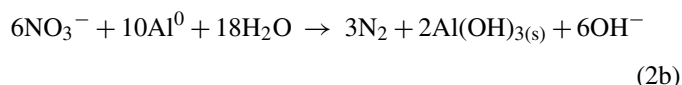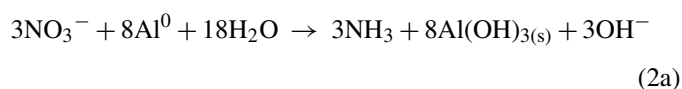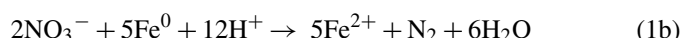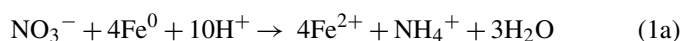© 2005 Elsevier B.V. All rights reserved.

Keywords: Zero-valent magnesium; Nitrate reduction; Reaction pH; Ammonia; Total nitrogen

1. Introduction

Nitrate is a wide spread contaminant of ground and surface waters due to excessive use of nitrogenous fertilizer in agricultural activities and disposal of untreated sanitary and industrial wastes [1–3]. Elevated nitrate concentrations in drinking water are linked to health problems such as methemoglobinemia in infants and stomach cancer in adults and US Environmental Protection Agency (EPA) has set the maximum contamination level as 10 mg/L of NO_3^-–N [4,5]. Current technologies for removal of nitrate like ion exchange, reverse osmosis are neither selective to nitrate, generate secondary brine wastes and require frequent media regeneration and biological denitrification requires intensive temperature control, constant supply of organic carbon with possibilities of contamination from microorganisms [6].

In recent years chemical methods of nitrate removal using zero-valent metals like iron (Fe^0) and aluminum (Al^0) has been studied intensively [7–13]. In aqueous system at acidic pH, Fe^0 is oxidized to ferrous ion (Fe^{2+}) and nitrate ion is reduced to ammonia or nitrogen gas (Eqs. (1a) and (1b)) [14]. At pH above 10.5, Al^0 also reduces nitrate to ammonium ion and is oxidized to Al^{3+} ion (Eqs. (3a) and (3b)) [13,15].

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O \qquad (1a)$$

$$2NO_3^- + 5Fe^0 + 12H^+ \rightarrow 5Fe^{2+} + N_2 + 6H_2O \qquad (1b)$$

$$3NO_3^- + 8Al^0 + 18H_2O \rightarrow 3NH_3 + 8Al(OH)_{3(s)} + 3OH^-$$
$$(2a)$$

$$6NO_3^- + 10Al^0 + 18H_2O \rightarrow 3N_2 + 2Al(OH)_{3(s)} + 6OH^-$$
$$(2b)$$

However, challenges like high dose requirement, long reaction time, presence of anaerobic condition and rapid deactivation of Fe^0 surface due to iron hydroxide precipitation were observed with iron and researches are in progress to enhance the activity of Fe^0 by using palladium/platinum, ultrasound, pretreatment with H_2/acid, using nano-scale Fe^0 [16–21]. Low efficiency (40–50%), ineffectiveness above initial NO_3^-–N higher than 30 mg/L and increase health concern about residual Al^{3+} salt in water are problems with aluminum powder [22]. Thus there is a need to develop a cheap, non-toxic, readily available reducing agent, which can remove nitrate effectively in a wide range of
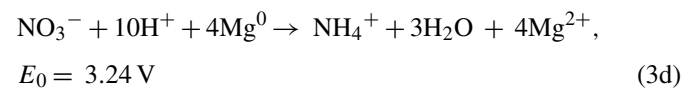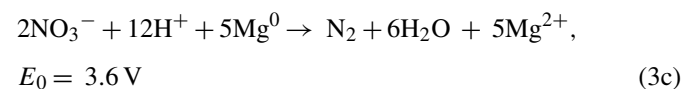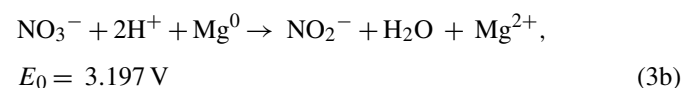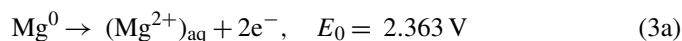
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concentrations under ambient temperature and pressure in aerobic condition, within short reaction time and at moderate dose.
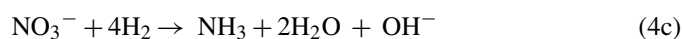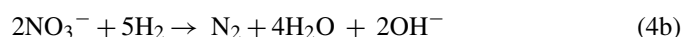
Rapid dechlorination of a persistent organic compound named, DDT is reported by zero-valent magnesium (Mg^0), which is a non-toxic and environmental benign metal, having high reduction potential of 2.363 V as compared to Fe^0 (0.44 V) and Al^0 (1.676 V) [23,24]. Since nitrate reduction by Fe^0 and Al^0 are redox reactions, it seems logical that with increase in reduction potential (E^0) of the metal ion, metal oxidation and nitrate reduction both will increase. Further solubility constant of magnesium hydroxide being much higher than iron [k_{sp} of $Fe(OH)_2$ 7.943×10^{-16} and k_{sp} of $Mg(OH)_2$ 7.08×10^{-12} at 25 °C], surface passivation due to hydroxide precipitation will be less frequent with Mg^0. However, removal of nitrate from water by Mg^0 has been relatively few reported. Therefore, the major objective of the present study was to investigate the feasibility of nitrate removal from water using Mg^0 through a laboratory-scale study under ambient temperature in open system. Reaction pH, dose of Mg^0, initial concentration of nitrate and temperature were selected as variable parameters and attention was given to evaluate the kinetic constants and determination of the reaction products.

2. Theory of nitrate reduction with magnesium (Mg^0)

In Mg^0–H_2O system at neutral and alkaline pH, thin oxide layer forms on the surface of magnesium metal and causes passivation of Mg^0 surface. Under acidic condition this oxide coating is dissolved and surface area of Mg^0 is available for reaction [24,25]. Active Mg^0 surface is oxidized to $(Mg^{2+})_{aq}$ and two electrons are released, which reduce nitrate ion to ammonia or nitrogen gas as shown below (E_0 is the standard state cell potential):

$$Mg^0 \rightarrow (Mg^{2+})_{aq} + 2e^-, \quad E_0 = 2.363 \text{ V} \tag{3a}$$

$$NO_3^- + 2H^+ + Mg^0 \rightarrow NO_2^- + H_2O + Mg^{2+},$$
$$E_0 = 3.197 \text{ V} \tag{3b}$$

$$2NO_3^- + 12H^+ + 5Mg^0 \rightarrow N_2 + 6H_2O + 5Mg^{2+},$$
$$E_0 = 3.6 \text{ V} \tag{3c}$$

$$NO_3^- + 10H^+ + 4Mg^0 \rightarrow NH_4^+ + 3H_2O + 4Mg^{2+},$$
$$E_0 = 3.24 \text{ V} \tag{3d}$$

Alternatively, in acidic solution [H^+] may accept two electrons released by Mg^0 and is reduced to hydrogen gas, which can reduce nitrate to ammonia/nitrogen gas (Eqs. (4a)–(4c)) [13]

$$2H^+ + 2e^- \rightarrow H_2 \tag{4a}$$

$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH^- \tag{4b}$$

$$NO_3^- + 4H_2 \rightarrow NH_3 + 2H_2O + OH^- \tag{4c}$$

In aqueous solution oxygen may compete with nitrate for electrons and is reduced by Mg^0 to water (Eq. (5)) [24]

$$2Mg^0 + O_2 + 4H^+ \rightarrow 2H_2O + 2Mg^{2+}, \quad E^0 = 3.59 \text{ V} \tag{5}$$
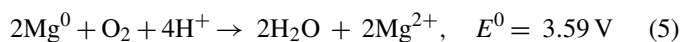
Stoichiometric Eqs. (3b)–(3d) and (4b) and (4c) suggest that 2.5–4 mol of Mg^0 will be necessary for reduction of each mol of nitrate, depending on the extent of nitrate reduction to ammonia/nitrogen gas. However, the actual Mg^0 dose may be higher than theoretical requirement and needs to be determined through experiments.

3. Materials and methods

3.1. Materials

Zero-valent magnesium (Mg^0) powder of 99% purity (density 1.74 g/cm^3) was purchased from Merck, India and used without any pretreatment. Characteristics of Mg^0 powder were analyzed using a particle size analyzer. Specific surface area of Mg^0 particles was 0.0804 m^2/g with effective size of 41.36 μm and coefficient of uniformity 0.50. Potassium nitrate (KNO_3) was used as the source of nitrate in all the experiments and was manufactured by CDH, India. Double distilled water prepared in the laboratory was used for preparation of all reagents and all experimental work.

3.2. Experimental design

Present investigation was carried out in batch mode in open system. All studies were conducted in 2.5 L of glass beaker containing 2.0 L of solution. Predetermined quantities of zero-valent magnesium were added in nitrate containing simulated water and mixing was achieved by a mechanical paddle stirrer (manufactured by Eltek motors) at 1500 rpm. One pH electrode was used for continuous pH measurement during the reaction. Solution pH was maintained by adding HCl of 0.1 N to maintain pH above 3 and 1 N for maintaining pH below 3. Temperature was measured using temperature probe attached with pH meter during the reaction. Liquid samples was pipetted out from the beaker at regular interval of time and collected in specimen tubes (volume 100 mL). Suspended Mg^0 were separated by settling samples for 10 min and decanting the supernatant, which was used for all chemical analysis. Reaction pH, dose of Mg^0, initial concentration of NO_3^-–N and temperature were four variables modified during the study. Total five sets of experiments (sets 1–5) were carried out and details of experimental sets are presented in Table 1. Sets 1–4 experiments were carried out under ambient temperature (20–24 °C). In set 5 experiments temperature was varied from 10 to 50 °C and temperature was controlled in a water bath. All experiments were conducted in duplicate and average values are presented in subsequent section.

3.3. Analytical procedures

The size and specific surface area of Mg^0 powder was estimated by particle size analyzer (Malvern Instruments Ltd., UK).

Table 1
Experimental design during present study

Experimental set	Variable parameter							Controlled parameter
1[a]	Initial pH (pH uncontrolled)	2	3	4	6	–	–	Mg^0 0.7 g/L; initial NO_3^-–N 50 mg/L
2[a]	Controlled pH	2	3	4	5	6	7	Mg^0 0.7, 2 g/L; initial NO_3^-–N 50 mg/L
3[a]	Mg^0 dose (g/L)	0.15	0.35	0.5	0.7	1.0	2.0	Reaction pH controlled at 2; initial NO_3^-–N 50 mg/L
4[a]	Initial NO_3^-–N (mg/L)	30	40	50	75	100	150	Reaction pH controlled at 2; Mg^0:NO_3^-–N molar ratio = 5
5[b]	Temperature	10	25	30	42	50	–	Reaction pH controlled at 2; Mg^0 1 g/L, initial NO_3^-–N 100 mg/L

[a] In sets 1–4 all studies were conducted in open system under ambient temperature varied from 23–26 °C.

[b] In set 5 reaction was conducted in open system with temperature control in water bath.

Surface morphology of Mg^0 powder was estimated by scanning electron microscopy (Scanning electron microscope, Model: LEO, 1430 VP, Carl Zeiss, Germany). All analytical measurements were performed according to APHA [26]. Solution pH was monitored by a digital pH meter (Systronics μpH system 361, India). Nitrate was analyzed at 220 nm wavelength using UV–visible Spectrophotometer (Varian, model Cary 50), ammonia was estimated by phenate method at wavelength of 640 nm after removing di-valent magnesium ion at higher pH, and nitrite was analyzed by sulphanilamide method at 543 nm. Sum of divalent magnesium ion (Mg^{2+}) and divalent calcium ion (Ca^{2+}) was estimated by EDTA titremetric method [26] and concentration of Mg^{2+} was estimated subtracting amount of Ca^{2+} ion. Calcium (Ca^{2+}) was analyzed by flame photometer (Flame Photometer 128 Systronics, India) and concentration of calcium ion was observed zero throughout the study. Dissolved oxygen (DO) was estimated using a DO probe.

4. Results and discussion

4.1. Effects of reaction pH on nitrate reduction

Experiments in sets 1 and 2 were conducted to study the effects of pH on nitrate removal. Initial concentration of NO_3^-–N and dose of Mg^0 were maintained at 50 mg/L and 0.7 g/L in set 1 experiments. In set 1, initial solution pH was adjusted to 2, 3, 4 and 6 and then reaction was conducted without

pH control. Concentrations of residual NO_3^-–N and solution pH with time are shown in Fig. 1(a) and (b), respectively. NO_3^-–N removal of 16% (from initial NO_3^-–N concentration 50 mg/L) was achieved at initial reaction pH 2 and decreased to 12%, 9% and 7% when initial solution pH was adjusted at 3, 4 and 6, respectively. Change in residual NO_3^-–N concentration after 10–12 min was negligible [Fig. 1(a)]. Fig. 1(b) shows that solution pH increased to 10.8 within 10 min irrespective of initial pH and remained constant throughout the study period, suggesting generation of [OH^-] ions during nitrate reduction by Mg^0. Probably, at alkaline pH, $Mg(OH)_2$ precipitation was formed, which caused passivation of Mg^0 surface and nitrate removal ceased [25].

In set 2 experiments, study was conducted at constant reaction pH of 2–7 and initial NO_3^-–N 50 mg/L. At each reaction pH, study was conducted with two doses of Mg^0: 0.7 and 2 g/L. Reaction pH was maintained constant during the reaction by adding HCl (1 N/0.1 N). Concentrations of residual NO_3^-–N are shown in Fig. 2(a) and (b). At reaction pH of 2, equilibrium condition in terms of nitrate concentration achieved within 10–20 min, which increased to 70–90 min at reaction pH ≥ 4. 83–93% removal of NO_3^-–N was achieved, when reaction pH was maintained at 3 and below. Westerhoff [27] reported 50% removal of nitrate (from 140 mg NO_3^-–N/L) by 33 g/L of scrap iron fillings within 23 h at reaction pH of 7. Complete removal of nitrate (initial 100 mg NO_3^-–N/L) was achieved by Fe^0 amount of 33 g/L within 8 h at controlled reaction pH 2 [28]. In the
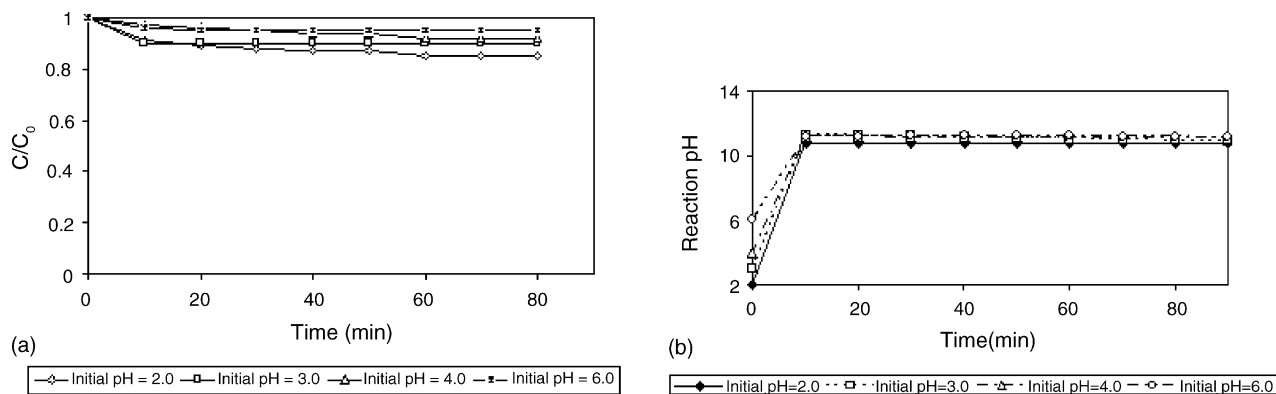

Fig. 1. (a) Nitrate removal without pH control in set 1 experiments [initial NO_3^-–N (C_0) = 50 mg/L, Mg^0 dose 0.7 g/L, initial solution pH adjusted at 2, 3, 4 and 6]. (b) Change in solution pH during nitarate reduction without pH control in set 1 experiments [initial NO_3^-–N (C_0) = 50 mg/L, Mg^0 dose 0.7 g/L, initial solution pH adjusted at 2, 3, 4 and 6].
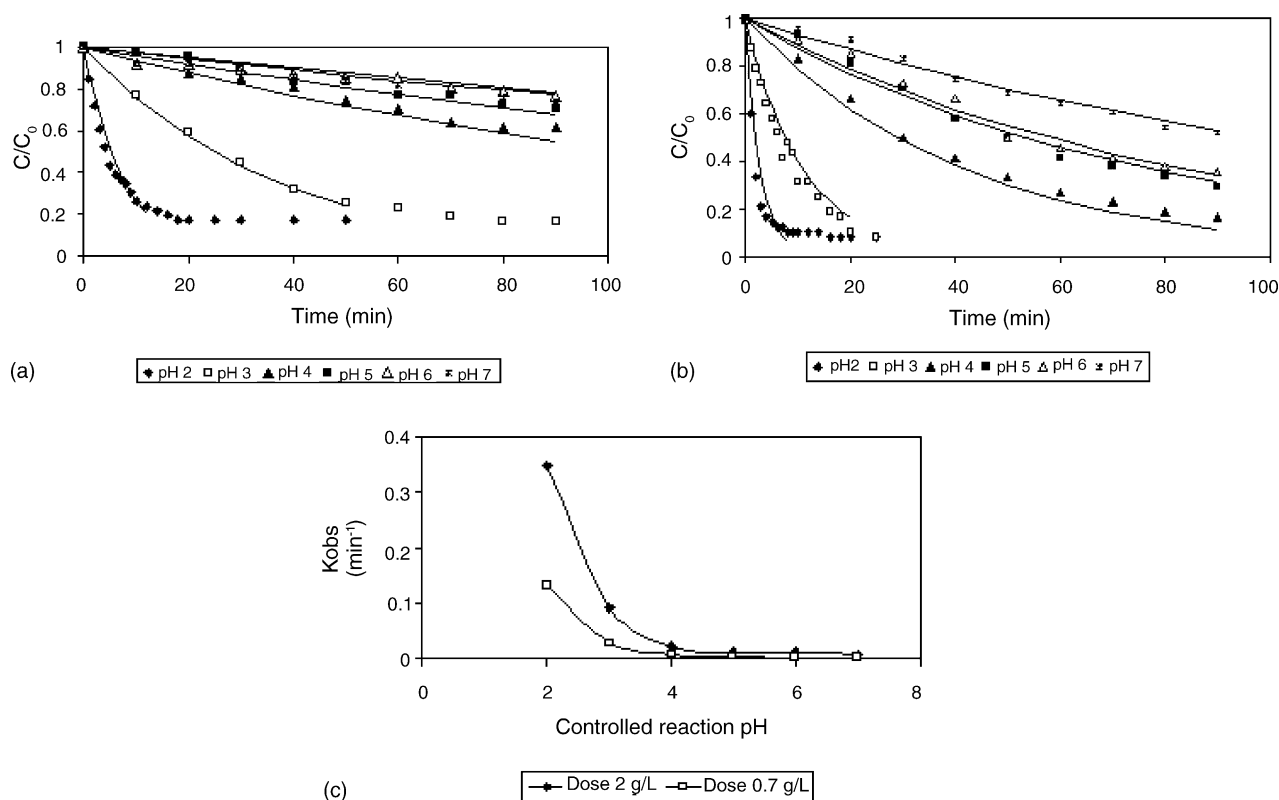
Fig. 2. (a) Nitrate removal reaction with pH control in set 2 [initial NO_3^-–N (C_0) = 50 mg/L, Mg^0 dose = 0.7 g/L, reaction pH controlled at 2–7; solid lines are the first order fitting results]. (b) The effect of controlled reaction pH on removal of nitrate in set 2 [initial NO_3^-–N (C_0) = 50 mg/L, Mg^0 dose = 2.0 g/L, reaction pH controlled at 2–7; solid lines are the first order fitting results]. (c) Relationship between controlled reaction pH and first order nitrate removal rate.

present investigation at Mg^0 amount of 0.7 g/L, 83% nitrate removal was achieved within 20 min, clearly suggesting nitrate removal with Mg^0 was much faster than Fe^0 at strong acidic environment. Fig. 2(a) and (b) indicates that with increase in controlled reaction pH, removal of nitrate decreased. In the present study, 72% and 51% nitrate removals were achieved at Mg^0 dose of 2 g/L at controlled reaction pH of 5 and 7, respectively. At Mg^0 dose of 0.7 g/L, corresponding removals were 26% and 23%, respectively. It is reported that nitrate removal by Fe^0 was negligible at reaction pH above 4.5 [29]. This shows that even at higher reaction pH nitrate removal efficiency of Mg^0 was superior than Fe^0. Present laboratory-scale study shows that during denitrification by Mg^0 proton is consumed as suggested in Eqs. (3b)–(3d) and (4a)–(4c). In the present study, 1 N HCL was used to prevent increase in pH during reaction. For field application also this may be used due to low cost of HCl, alternatively use of a strong acid buffer is recommended.

Fig. 2(a) and (b) shows that residual nitrate concentration can be well described by first order kinetic model (presented with solid lines fitted with Eq. (6))

$$N = N_0 \exp(-k_{obs}t) \qquad (6)$$

where N is the concentration of NO_3^-–N (mg/L) at any time t (min), k_{obs} the first order NO_3^-–N reduction rate (min^{-1}) and N_0 the initial concentration of NO_3^-–N (mg/L).

In Fig. 2(c), the relationship between k_{obs} and controlled reaction pH is presented. k_{obs} decreased non-linearly with increase in solution pH. At controlled reaction pH below 4, the reaction rate increased significantly with decrease in solution pH, whereas above pH 4, the relative change in reaction rate with change in pH was very small.

4.2. Effects of Mg dose on nitrate reduction

Set 3 experiments were conducted at initial NO_3^-–N concentration of 50 mg/L with varying Mg^0 dose (0.15–2 g/L). This was equivalent to Mg^0:NO_3^-–N molar ratio ranging from 1.75 to 23.3. Study was conducted at controlled reaction pH 2 and results are shown in Fig. 3(a). Result of control study is also presented, which was conducted at reaction pH of 2 without Mg^0. Insignificant removal of NO_3^-–N was observed during control study. Nitrate removal was 30% at Mg^0 dose of 0.15 g/L and increased to 82% at Mg^0 dose of 0.7 g/L. With further increase of Mg^0 dose to 1 and 2 g/L, increase in NO_3^-–N removal was relatively less (89% and 91%, respectively). Thus to achieve 80% removal, the Mg^0 dose necessary was observed as 0.7 g/L, at initial NO_3^-–N concentration of 50 mg/L. This was equivalent to 17 g of Mg^0 for each g of NO_3^-–N removal. Corresponding molar dose of Mg^0 for each mol of NO_3^-–N was 9.9. Specific surface area of Mg^0 powder used in present investigation was 0.0804 m^2/g. When Mg^0 dose was converted to surface area, it was observed that 19 m^2 of Mg^0 powder was necessary for removal of each mol of
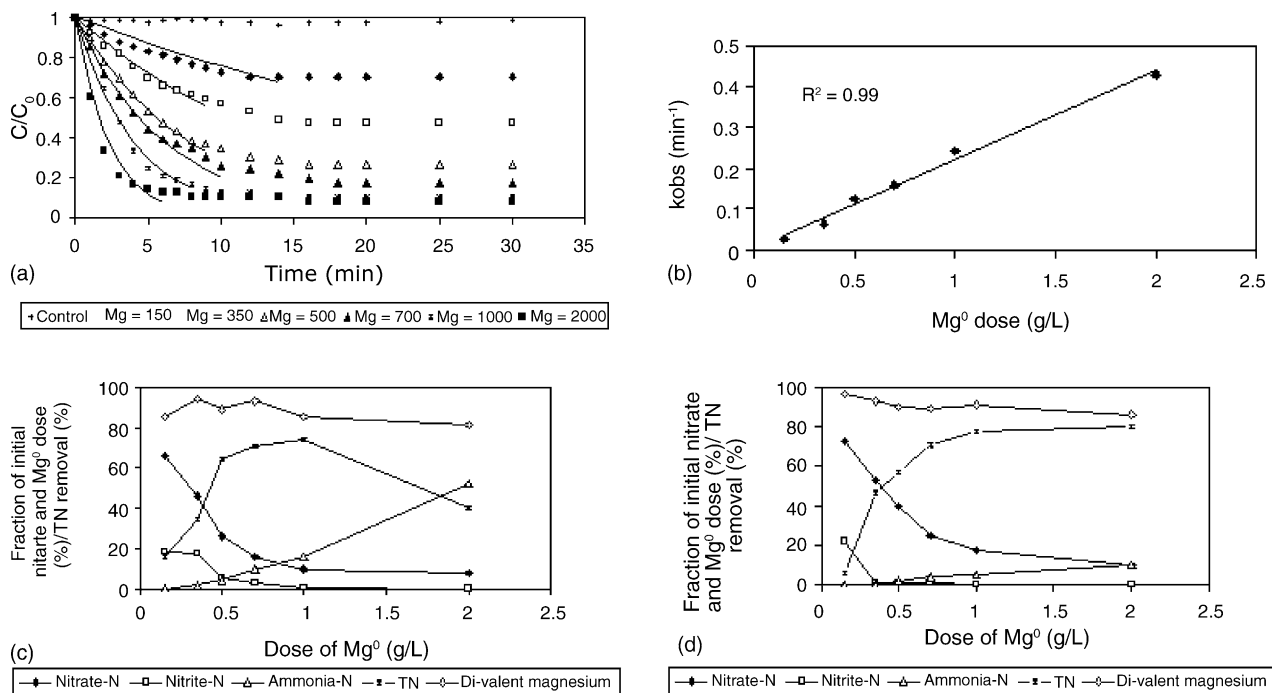
Fig. 3. (a) The effect of Mg^0 loading on nitrate removal in set 3 experiments [initial NO_3^-–N (C_0) = 50 mg/L, reaction pH controlled at 2, control in absence of Mg^0, Solid lines are first order fitting results]. (b) Effects of Mg^0 dose on first order nitrate removal rate in set 3 experiments (initial NO_3^-–N (C_0) = 50 mg/L, reaction pH controlled at 2, Mg^0 dose varied from 0.15–2 g/L). (c) The effect of Mg^0 dose on distribution of end products at initial NO_3^-–N (C_0) = 50 mg/L [nitrate, nitrite and ammonia are shown as fraction of initial NO_3^-–N (%); Mg^{2+} is shown as fraction of initial Mg^0 dose (%) and TN is shown as removal (%)]. (d) The effect of Mg^0 dose on distributions of end products at initial NO_3^-–N (C_0) = 100 mg/L [nitrate, nitrate and ammonia are shown as fraction of initial NO_3^-–N; Mg^{2+} is shown as fraction of initial Mg^0 dose and TN is shown as removal (%).

nitrate from aqueous solution. For comparison, with Al^0 powder 45% nitrate removal was achieved at aluminum [Al^0] dose of 150 mg/L for initial NO_3^-–N concentration of 10 mg/L, equivalent to 33.3 g Al^0 dose for removal of each gram of NO_3^-–N [22]. An iron to nitrate ratio of 120 m^2/mol NO_3^-–N was prescribed for complete removal of nitrate [29], which was more than six times higher than Mg^0:NO_3^-–N ratio observed in the present study. The required molar ratio of nano-sized iron particles for complete nitrate removal was 7.36–14.70 at initial NO_3^-–N concentration of 34 mg/L [14]. In terms of molar dose requirement, Mg^0 provided comparable results as nano-sized iron particles, even though the specific surface area of Mg^0 particles was much smaller than nano-sized particles (37.83 m^2/g as compared to 0.0804 m^2/g for Mg^0 particles). Stoichiometric Eqs. (3b) and (3c) suggest that 2.5–4 mol of Mg^0 is necessary for complete removal of each mol of NO_3^-–N. The actual dose requirement of Mg^0 observed in aerobic open system was two and half to four times higher than theoretical requirement, which suggests that reaction was occurring without significant loss. Fig. 3(a) shows that experimental data on residual NO_3^-–N fitted well with first order model. The first order nitrate removal rate (k_{obs}) increased linearly (R^2 of 0.99) with increase in Mg^0 dose [Fig. 3(b)].

Eqs. (3b) and (3d) suggest that nitrate can be reduced by Mg^0 either to nitrite (NO_2^-), ammonia (NH_4^+) or nitrogen gas (N_2) with generation of soluble divalent magnesium ion (Mg^{2+})$_{aq}$. An attempt was made to establish the effects of Mg^0 dose on concentrations of NO_2^-–N, NH_4^-–N, (Mg^{2+})$_{aq}$ and residual

NO_3^-–N during nitrate removal by Mg^0. Mg^0 doses were varied from 0.15 to 2 g/L at six levels at a controlled reaction pH of 2 for two initial concentrations of NO_3^-–N (50 and 100 mg/L). Concentrations of NO_2^-–N were calculated as fraction of initial NO_3^-–N concentrations using Eq. (7)

Fraction of NO_2^-–N (%)

$$= \frac{\text{Concentration of } NO_2^-\text{–N (mg/L)} \times 100}{\text{Initial concentration of } NO_3^-\text{–N (mg/L)}} \quad (7)$$

Similarly, fraction of NH_4^+–N and residual NO_3^-–N were calculated as fraction of initial NO_3^-–N and presented in Fig. 3(c) and (d). Residual NO_3^-–N as fraction of influent NO_3^-–N decreased with increase in Mg^0 dose (66–72% at Mg^0 dose 0.15 g/L and 2–8% at 2 g/L). For Nitrite-N, 18% and 22% of influent NO_3^-–N (50 and 100 mg/L) were released in solution at Mg^0 dose of 0.15 g/L and decreased with increase in Mg^0 dose. Above Mg^0 dose of 0.7 g/L, NO_2^-–N was almost undetectable in solution. NH_4^+–N fraction increased with increase in Mg^0 dose (2–4% at Mg^0 dose of 0.5 g/L and less and 10–52% at Mg^0 dose of 2 g/L).

The oxidation numbers of nitrogen in nitrate and nitrite are +5 and +3, respectively. With increase in Mg^0 dose, nitrate and nitrite removal increased due to increase in available electron donor [Mg^0]. At lower dose of Mg^0, nitrite fraction was higher due to partial nitrate reduction to intermediate oxidation state +3. Present results demonstrated that ammonia fraction in the effluent increased with increase in Mg^0 dose. With increase

in electron donor, more nitrite reduction to the lowest oxidation state (-3 of ammonia) was favored, thus ammonia fraction increased. Again, when initial NO_3^-–N concentration was increased from 50 to 100 mg/L at Mg^0 dose of 2 g/L, ammonia fraction was significantly less (10% as compared to 52%), due to increase in the concentration of electron acceptor (initial NO_3^-–N). Present results clearly indicate that generation of ammonia during nitrate reduction is governed by concentration of nitrate (electron acceptor) and electron donor (Mg^0). Similar results also reported by Biswas and Bose [30], where ammonia generation increased with increase in metallic iron concentration in a Fe^0 assisted biological autotrophic denitrification system.

Ammonia fraction in solution is also reflected in the removal of total nitrogen (TN). Removal of total nitrogen was calculated using Eq. (8)

$$TN\ removal\ (\%) = \frac{\{Initial\ NO_3^-\text{–}N - \sum(NH_4^+\text{–}N + NO_2^-\text{–}N + Residual\ NO_3^-\text{–}N)\} \times 100}{(Initial\ concentration\ of\ NO_3^-\text{–}N)} \tag{8}$$

At initial NO_3^-–N concentration of 50 mg/L, TN removal increased up to Mg^0 dose of 1 g/L (15.8% at 0.15 g/L dose and 73.64% at 1 g/L dose). At Mg^0 dose to 2 g/L, TN removal declined to 40%, due to presence of high amount of ammonia in solution. When study was conducted at initial NO_3^-–N concentration of 100 mg/L [Fig. 4(d)], TN removal increased with increase in Mg^0 dose (5% at 0.15 g/L and 80% at 2 g/L Mg^0). Removal of total nitrogen clearly indicates generation of species other than nitrite and ammonia during nitrate reduction by metallic magnesium. Present study was conducted at acidic pH, thus volatilization of ammonia from solution as free ammonia can be neglected (ionization constant of ammonia 5.6×10^{-10}). Probably gaseous species like nitrogen gas (N_2), nitric oxide (NO) etc. with oxidation numbers of zero, +2, respectively, were formed [31], which could not be estimated due to open system used for present work. Nitrate can be reduced to nitrite ion (NO_2^-) and then to nitric oxide (NO), which may further reduce to unstable hyponitrite ($N_2O_2^{2-}$). Hyponitrite is finally reduced to nitrogen gas. There might be also possibility of formation of some nitrous oxide (N_2O) in certain conditions from hyponitrite [31].

In the literature reports with zero-valent iron ammonia was the observed end product of nitrate reduction [8,15,22,32]. How-ever, in many studies iron was used in excess with Fe^0:NO_3^-–N molar ratio of 39.68 and 46.14 were used [9,32] and very few study addressed the dose of zero-valent metals on end products formation. Luk and Au-Yeung [22] had reported 41.5% NO_3^-–N, 1.3% NO_2^-–N and 2.5% NH_4^+–N, with TN removal of 55% from initial nitrate–N concentration of 20 mg/L at Al:NO_3^-–N molar ratio 7.8. For comparison, in a study on catalytic nitrate reduction by palladium catalyst on Cu/Mg/Al hydrocalcites reported 23% NH_4^+–N fraction after 200 min of reaction from initial NO_3^-–N concentration of 20.3 mg/L [33].

Present results show that end products of nitrate reduction may be either nitrite, or ammonia or various gaseous species like N_2 and these distribution largely depends on initial NO_3^-–N concentration and Mg^0 dose. Fig. 3(c) shows that for initial NO_3^-–N concentration of 50 mg/L, Mg^0 doses of 0.7 g/L provided more than 80% removal of NO_3^-–N and effluent contained NO_3^-–N 8 mg/L, NO_2^-–N 1.6 mg/L and NH_4^+–N 5 mg/L. It can be seen from Fig. 3(d) that at Mg^0 dose of 1 g/L, 82% removal of NO_3^-–N (initial 100 mg NO_3^-–N/L) was achieved with NO_2^-–N of zero and 5% of initial NO_3^-–N as ammonia. Thus Mg^0 doses of 0.7 and 1 g/L are recommended for initial NO_3^-–N concentrations of 50 and 100 mg/L, respectively, in order to achieve significant removal of nitrate and minimize ammonia formation. This corresponds to Mg^0 and NO_3^-–N molar ratio of 8.1 and 5.8 for initial NO_3^-–N concentrations of 50 and 100 mg/L, respectively.

Concentrations of di-valent magnesium ion $(Mg^{2+})_{aq}$ are also presented in Fig. 3(c) and (d) as fraction of initial Mg^0 dose. It can be seen that almost 85–93% of Mg^0 powder was converted to soluble Mg^{2+} ion. This suggests high corrosion of Mg^0 powder in acidic pH. At initial NO_3^-–N concentrations of 50 and 100 mg/L for Mg^0 doses of 0.7 and 1 g/L, concentrations of $(Mg^{2+})_{aq}$ were 654 and 912 mg/L, respectively at the end of the reaction. Even though $(Mg^{2+})_{aq}$ is non-toxic, it imparts hardness to water, further post treatment is necessary to remove this
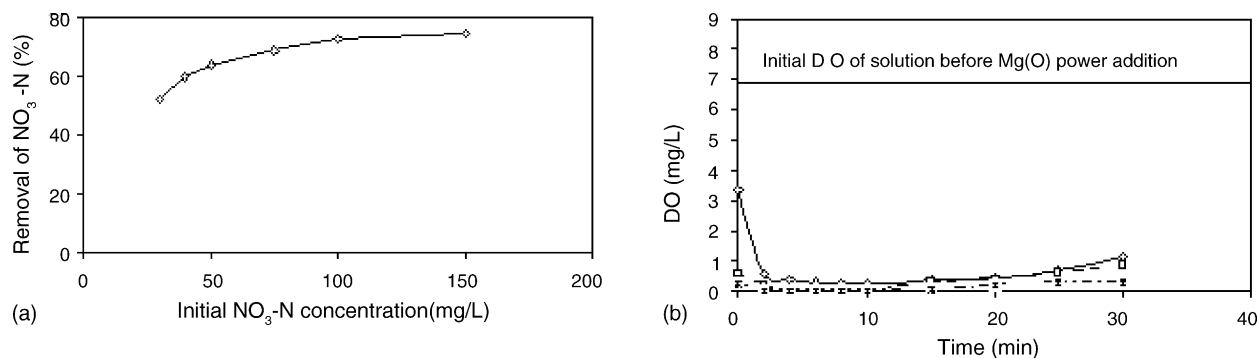
Fig. 4. (a) Effects of initial nitrate concentration on nitrate removal efficiency in set 4 experiments (reaction pH controlled at 2, Mg^0:NO_3^-–N molar ratio constant at 5; initial NO_3^-–N (C_0) = 30–150 mg/L). (b) Profile of DO in presence of nitrate and Mg^0 powder in solution [reaction pH controlled at 2, initial NO_3^-–N (C_0) = 50 mg/L, reaction was conducted in open system with stirring without DO control; time started after addition of Mg^0].

soluble magnesium ion. It is reported that Mg^{2+} is an effective coagulating agent in water/wastewater treatment and can remove many common pollutants like suspended solids, phosphate, turbidity, heavy metal ions, etc., from aqueous solution [34]. Though it is not very commonly used, due to higher cost of it compared to conventional alum treatment. This aspect was not within the scope of the present work, however, further studies are recommended to recover and use this Mg^{2+} salt, generated during denitrification by Mg^0, as coagulating agent.

4.3. Effects of initial nitrate–nitrogen concentration

The functioning range of initial NO_3^-–N concentration that can be reduced by Mg^0 powder was investigated by varying the initial nitrate concentration in a wide range of 30–150 mg NO_3^-–N/L at a constant molar ratio of magnesium to nitrate–nitrogen of 5 in set 4 experiment and results are shown in Fig. 4(a). At initial NO_3^-–N concentration of 30 mg/L, 52% denitrification efficiency was achieved, which increased to 64%, 69% and 73% at initial NO_3^-–N concentrations of 50, 75 and 100 mg/L, respectively. With zero-valent aluminum at Al^0:NO_3^-–N molar ratio of 7.8, denitrification efficiency was only 50% at initial NO_3^-–N concentration of 10 mg/L and decreased to 4% at initial NO_3^-–N concentration of 50 mg/L [22].

Results of set 4 demonstrate that chemical reduction of nitrate using Mg^0 gives better result for higher NO_3^-–N concentration (40 mg NO_3^-–N/L and above). The probable reason was that at lower concentration of NO_3^-–N ions, amount of Mg^0 added in solution was relatively smaller to maintain a constant Mg^0 and NO_3^-–N molar ratio (0.26 g/L for 30 mg NO_3^-–N/L and 0.43 g/L for 50 mg NO_3^-–N/L). This small amount of Mg^0 in aqueous medium was not able to produce favorable environment necessary for nitrate reduction. Again, Eq. (5) shows that reduction of oxygen by Mg^0 is a thermodynamically favorable reaction ($E_0 = 3.59$ V). Present study was conducted in open system hence removal of DO by Mg^0 was likely. In order to confirm that DO profile was developed during nitrate reduction by Mg^0. Reaction was conducted in the open system with stirring without control of DO at varying doses of Mg^0 powder (0.15, 0.7 and 2 g/L) in presence of 50 mg/L NO_3^-–N. Results are presented in Fig. 4(b). Initial DO of solution was 6.9 mg/L. After addition of Mg^0 powder, immediately solution DO declined significantly to 3.4, 0.55 and 0.25 mg/L for Mg^0 doses of 0.15, 0.7 and 2 g/L, respectively. At Mg^0 dose of 0.7 and 2 g/L, within 2–3 min, solution DO was undetectable. Even, for very low dose of Mg^0 (0.15 g/L), DO declined gradually to 0.25 mg/L within 10 min. For all three doses of magnesium powder solution DO started increasing after 10 min. Complete dissolved oxygen removals were reported with macro-scale Fe^0 powder at dose of 50 g/L and with nano-scale Fe^0 at dose of 2 g/L during nitrate reduction [14,16]. Comparing (4b) with (3a) suggest that DO removal was faster than nitrate reduction (since at Mg^0 doses of 0.7 and 2 g/L, almost 74% and 87% nitrate removals were achieved in 18 and 10 min, respectively). In set 4 all experiments were conducted at same identical conditions (same initial DO of solution and same stirring speed). Probably at lower dose of Mg^0 powder, major
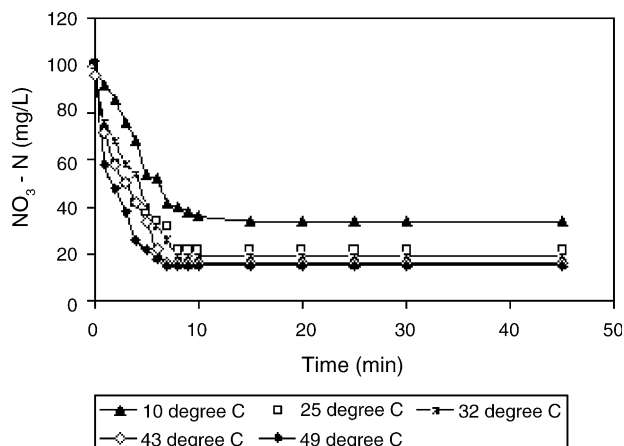

Fig. 5. Effect of temperature on nitrate reduction (reaction condition: Mg^0 dose 1 g/L, reaction pH controlled at 2, initial NO_3^-–N (C_0) = 100 mg/L, temperature maintained constant dining reaction).

amount of metallic magnesium was used for removal of DO and less amount of Mg^0 was available for denitrification. At a constant Mg^0:NO_3^-–N ratio, when initial NO_3^-–N concentration was increased, more amount of Mg^0 was added in solution and higher amount of Mg^0 was available for nitrate reduction, even after significant removal of DO. Previous researchers reported that anaerobic condition enhanced nitrate removal by zero-valent iron [18]. Present result demonstrates that with Mg^0 powder as a reducing agent, the competition for electrons between oxygen and nitrate was successfully overcome by the strong electron donating capacity of metallic magnesium. This observation reinforces the feasibility of Mg^0 powder for nitrate reduction under normal plant operation and eliminates the undesirable restrictions of a closed anaerobic system.

4.4. Effects of temperature

In set 5 experiments, effects of temperature on nitrate reduction by Mg^0 powder was evaluated by varying reaction temperatures at 10, 25, 32, 42 and 50 °C. Reaction temperature was maintained constant in a water bath. Initial NO_3^-–N concentration was 100 mg/L with Mg^0 dose 1 g/L and reaction pH at 2. Effect of temperature on nitrate reduction by Mg^0 is shown in Fig. 5. Residual NO_3^-–N concentrations at 10 and 49 °C were 34 and 16 mg/L (65% and 84% removals, respectively). First order nitrate reduction rates with varying temperature (k_{obs}) are shown in Table 2. Calculated rate constants (k_{obs}) exhibited a

Table 2
First order nitrate reduction rate with varying temperature

Temperature (°C)	k_{obs} (min^{-1})
10	0.108
25	0.158
32	0.182
42	0.237
50	0.271

temperature dependency consistent with Arrhenius Eq. (9) [35]:

$$k_{obs} = A_f(\exp^{-E_a/RT}), \quad or, \quad \ln(k_{obs}) = \ln(A_f) - E_a/RT$$

(9)

where, A_f is the Arrhenius frequency factor ($min^{-1}\,m^{-2}\,L$), E_a is the activation energy ($kJ\,mol^{-1}$), R is the molar gas constant ($0.008314\,kJ\,mol^{-1}\,K^{-1}$) and T is the absolute temperature (K).

The activation energy was determined from the slope of the plot of $\ln(k_{obs})$ and inverse of temperature ($1/T$). The activation energy (E_a) was observed as $17.7\,kJ\,mol^{-1}$. Activation energies of 46, 32, 25.8 and $16.8\,kJ\,mol^{-1}$ are reported during nitrate reduction by non-pretreated Fe^0, hydrogen gas pretreated Fe^0, nano-scale Fe^0 and Cu catalyzed nanoscale Fe^0, respectively [36]. Activation energy (E_a) is the potential energy barrier that must be overcome for a particular reaction to occur, whether a reaction is thermodynamically favorable or unfavorable and an inverse relation exists between activation energy and reaction rate [35]. The lower activation energy observed in the present work was due to faster nitrate reduction by Mg^0 powder than non-pretreated and hydrogen gas pretreated iron.

4.5. Surface characteristics of Mg powder

The morphology of Mg^0 powder surface was analyzed using scanning electron microscope (SEM) and energy dispersive X-ray (EDX) technique. EDX analysis suggests presence of 98.1% magnesium and 1.9% oxygen in original Mg^0 powder. The SEM picture [Fig. 6(a)] shows that original particles were largely rust free on their surface. Mg^0 powder after 10 min reaction with nitrate solution at pH 2, were dried at $102\,°C$ for 4 h and SEM photographs are shown in Fig. 6(b). After reacting with nitrate, surface of Mg^0 powder lost the metallic glaze and color of the surface also turned black. Comparing Fig. 6(a) with (b) it can be said that after reacting with nitrate smaller sized agglomerated particles were formed. The EDX analysis suggests presence of 57.8% magnesium and 42.2% of oxygen in Mg^0 powder after
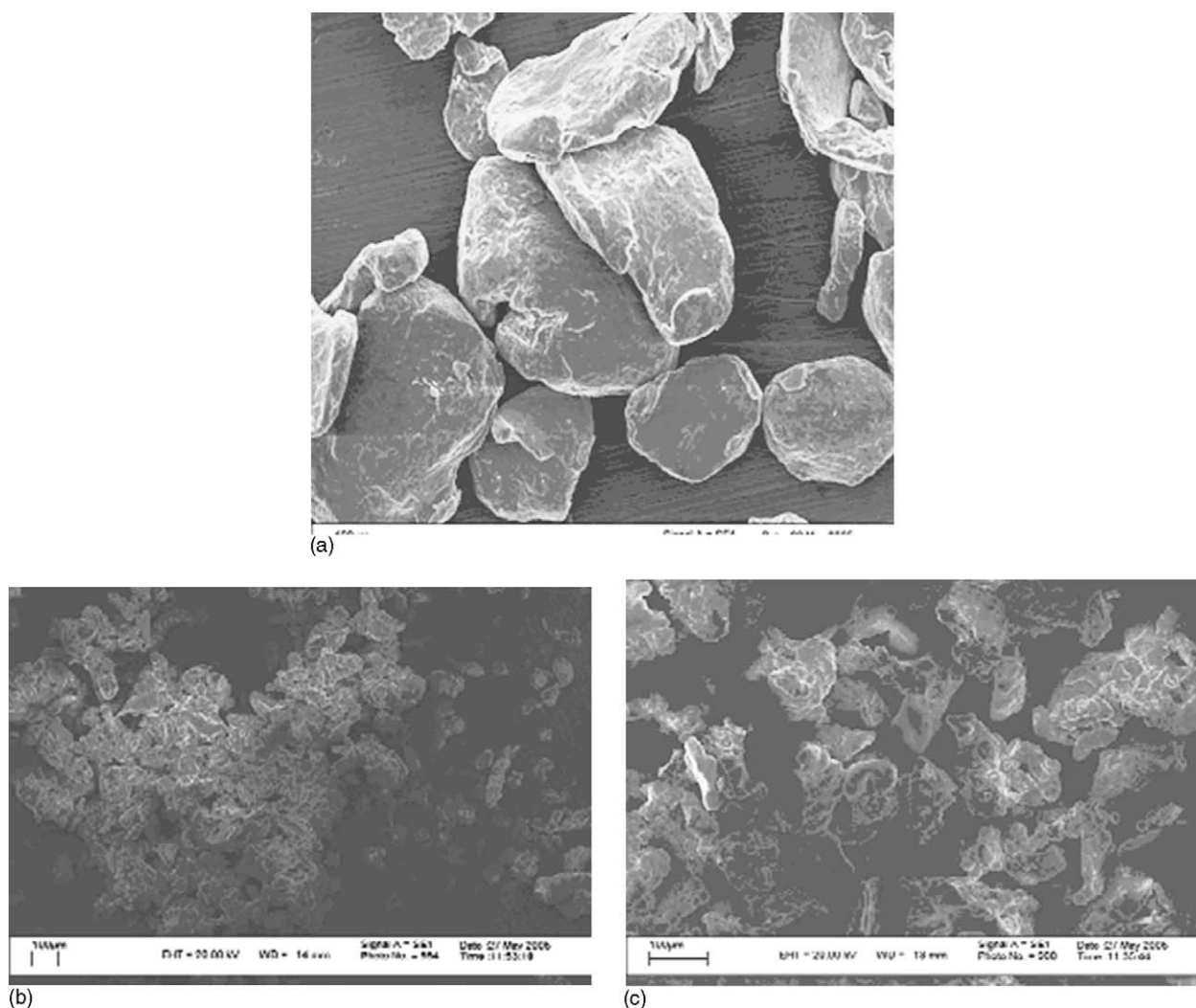

Fig. 6. (a) Fresh zero-valent magnesium powder. (b) Zero-velant magnesium powder after reacting with nitrate solution at acidic pH. (c) Zero-valent magnesium powder after reacting with water (no nitrate) at acidic pH.

reacting with nitrate. In order to verify the effect of nitrate on Mg^0 surface morphology, a SEM picture at same magnification was taken after 10 min of reaction of Mg^0 powder in aqueous solution at pH of 2 in absence of nitrate [Fig. 6(c)]. The particles were slightly black color with size smaller than fresh Mg^0 powder and larger than Mg^0 powder with nitrate. Agglomeration of particles was less in Fig. 6(c) compared to Fig. 6(b). EDX analysis suggests presence of 40% magnesium and 60% oxygen after reaction of Mg^0 powder in aqueous solution without nitrate. It might be possible that some black magnesium oxide formed from Mg^0 powder in aqueous solution at acidic pH. However, further studies are necessary before anything more definitive can be said.

5. Summary and conclusions

In the present work, a new reducing agent named zero-valent magnesium (Mg^0) powder was used for removal of nitrate from water through a laboratory-scale study. Effects of reaction pH, dose of metallic magnesium (Mg^0), initial concentration of nitrate and temperature were studied as variable parameters and based on the findings of this study following conclusions can be drawn.

Solution pH was observed as the major critical parameter during nitrate removal. At solution pH of 3 and below, more than 80% nitrate removal was achieved within 10–20 min from initial concentrations of 50 mg/L, which was much faster than zero-valent iron and aluminum. In absence of external proton addition, nitrate removal was insignificant (7–16%) due to generation of large amount of [OH^-] ion and surface passivation of Mg^0 surface. Careful control of the pH during the reaction possibly with a strong acid buffer or 1 N/0.1 N HCl is highly recommended.

Nitrate removal by Mg^0 occurred through nitrite as intermediate with ammonia/nitrogen gas as end products. Distribution of end products depended on dose of Mg^0 and initial nitrate concentration. At Mg^0:NO_3^-–N molar ratio of 5.8, 84% removal of NO_3^-–N (initial concentration 50 mg/L) and 70% removal of total nitrogen were observed with 3% and 10% of initial nitrate as NO_2^-–N and NH_4^-–N, respectively. Zero-valent magnesium oxidized to soluble di-valent Mg^{2+} ion, hence further post treatment of water is necessary.

Nitrate reduction by Mg^0 followed first order kinetics. First order nitrate reduction rate (k_{obs}) decreased with increase in solution pH in the studied pH range of 2–7. With increase in Mg^0 dose, k_{obs} increased linearly.

Significant removal of dissolved oxygen present in solution was observed during nitrate reduction and removal of DO was function of dose of Mg^0 powder. The method has good potential for use in the field condition as it eliminates the undesirable restrictions of a closed anaerobic system.

Nitrate removal rate increased with increase in temperature in the studied range of 10–50 °C with an activation energy of 17.7 kJ/mol. This method of nitrate reduction was observed as appropriate for initial nitrate concentration varying in a wide range (30–150 mg/L).

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