Effect of metallic iron in reducing nitrate mobility in alkalizes soils

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Abstract –

Reducing the mobility of nitrate in soils is therefore important in controlling nitrate contamination of groundwater. For this way using zero-valent iron as a nitrate reductant is being assessed as a potential method for reducing nitrate mobility in soils. Alkaline Soil samples were collected from a cereals soil at the Enfidha region, Sousse, Tunisia (35°54′N10°36′E). A series of laboratory batch experiments were carried. Results so far indicate that in the presence of zero-valent iron, 16, 5 % nitrate was reduced to ammonium and the 69% of ammonium produced is partitioned between the soil surface and the solution phase. The amount of ammonium partitioned to the soil surface is dependent on the cation exchange capacity of the soil as well as the concentration of ammonium in the solution phase. The addition of Fe $^{(2+)}$ enhanced nitrate reduction and was also accompanied by an increase in pH.

Keyword: nitrate; zero-valent iron; alkaline soil;

ammonium

1. INTRODUCTION

Nitrate (NO_3^-) is an important inorganic nitrogen species, key to the healthy growth of all crops either through direct uptake or indirectly through processes involving a range of bacteria within the soil and root systems. But as the intense agricultural activity excessive use of nitrogen fertilizer to improve food output for increasing population and the evolution of industrial waste effluent discharge and tourism development sectors induced increasingly nitrate contamination in the groundwater [1]. High level of NO_3^- within potables waters becomes dangerous. It can be including an increased risk of a number of diseases such cancers [2]. Many technologies to eliminate nitrate from

water contamination due to human activity such as biological denitrification, ion exchange, reverse osmosis and chemical reduction was investigated. But all these technologies have shown a different effect to reduce NO_3^-. In addition, previous studies have indicated that there are other processes of NO_3^- reduction in nature that do not rely directly on bacteria [3,4] but by oxidation-reduction (redox) active heavy metals such as iron (Fe). The ability of zero-valent iron (Fe^0) to chemically reduce nitrate and chlorinated organic contaminants has long been known [5, 6] and has been successfully utilized in several pilot-scale and full-scale groundwater remediation efforts to remove these contaminants [7]. Nitrate reduction by Fe0 is a redox reaction in which the oxidation of Fe^0 to Fe^{2+} or Fe^{3+} releases electrons which are accepted by NO_3^-, leading to the reduction of NO_3^- to ammonium (NH_4^+) [8,9]. Nitrate reduction to ammonium of 70 -100 % has been reported in groundwater [10]. It is the Fe^{2+} or Fe^{3+} and NH_4^+ produced during the reaction and their fate that are significant in the retardation of N mobility [11]. Soils generally have significantly higher cation-retention capacity than anion-retention capacity, and therefore, would retain NH_4^+ more readily than NO_3^-. Hence ammonium is less likely to leach in soils. Ammonium is also preferentially fixed by micro-organisms, rendering the NH_4^+ unavailable for leaching. The NH_4^+ can also enhance microbial denitrification. Numerous studies [12, 13, and 14] have shown that the reduction of nitrates by Fe $^{(0)}$ was a spontaneous process in acidic soil conditions and using catalysts to neutrality conditions. In alkaline soils, abiotic reduction of NO_3^- has not been adequately addressed. To our knowledge, this is the first study to evaluate the potential use of Fe $^{(0)}$ to reduce the

mobility of NO_3^- in these soils in the Mediterranean region and especially in the Tunisia region where water resources are scarce and groundwater has a main water resource for people, agricultural and industrial use.

2. MATERIAL AND METHODS

2. 1. Site description

Soil samples were collected from a cereals soil at the Enfidha region, Sousse, Tunisia (35°54′N10°36′E). This region belongs to semi-arid bioclimatic stage characterized by sweet winter and cool summer. The mean maximum and minimum temperature are 10°C (January) and 38°C (August) respectively. The annual rainfall recorded is above 300 mm. Relative humidity ranges from 20 to 80%. The site into which the trial was done was previously cultivated with cereals.

2. 2. Chemical analysis

Soil samples were sampled to a depth surface of 25cm. Samples were air-dried and ground to pass a 2mm sieve. Soil pH was determined in 1: 2 soil: water suspension; organic matter (OM) determined by the wet oxidation method (Walkley and Black); particle-size distribution by the pipette method; cation exchange capacity (CEC) by the $BaCl_2$ extraction method. Mehlich-III, P, Ca, Mg, Fe, Al, Cd, Cu, and Mn were determined by equilibrating 2.5g of air-dried soil sample with 25mL of Mehlich-III extracting solution for 5min and filtering through Whatman no. 40 filter paper. The different concentrations in the extracts were measured using an inductively coupled plasma optical emission spectrometer (Perkins Elmer, Model 4300DV).

Soil NO_3^- and NH_4^+ concentrations were analyzed using the steam distillation method.

2. 3. Batch Study

A soil 5g mass is suspended in a bottle containing a volume of 100 ml NO_3^- solution at a concentration of 50mg.L^{-1}. To this mixture, 1 g of Fe $^{(0)}$ was added. A solution of NO_3^- was prepared using the solution of $NaNO_3$. The particles of $Fe^{(0)}$ used have a diameter of about 60-100 microns and irregular in shape and it was pretreated with HCl (0.5M) for a period of 5 minutes to remove any impurities. The resulting system is closed and placed under magnetic stirring (200 tr.min^{-1}) at a temperature T = 20 ° C ± 2. To create an anaerobic environment in groundwater, the deionized water used for the preparation of the nitrate solution was boiled and the reactor was purged with nitrogen gas to remove dissolved oxygen before and during the reaction. Two drops of toluene were added to each mixture to prevent any biological transformations. After stirring for predetermined time intervals (0, 25; 0, 5; 0, 75, 1, 1, 5 and 2hours), approximately 5 ml of the suspension was extracted using a syringe. The supernatant is separated from the liquid phase by filtration. The filtrate was collected for measurements of pH and concentrations of NH_4^+ and NO_3^-. Two repetitions were performed for all tests.

3. RESULTS AND DISCUSSION

3.1. Soil proprieties

Nitrate mobility in soil was influenced by some soil properties at varying levels. Soil properties that correlated nitrate mobility were pH, organic matter, exchangeable cation and texture of soil. Table 1 summarizes the physico-chemical properties of soil at the Enfidha site. The physical proprieties were characterized by highly content of clay (43.3%), the field capacity was ranged from 7 and 13.2 % and the Wilting point was ranged from 4 and 9.1%. Additionally the value of pH is 8.26 indicated that is an alkaline soil. Other soil chemical analyses gave values of 3.48 % organic matter (OM), 90 total nitrogen (N) and 4 phosphorus (P) and exchangeable cation 294 potassium (K), 193 calcium (Ca) and 22 magnesium (Mg) (mg.kg^{-1} soil). For this result it can be suggested that the exchangeable cations concentrations in the soil were all high indicating this soils is calcareous in nature and had a weakly sorption capacity of nitrate. On the other hand, the presence of organic matter reduces nitrate sorption capacity due to result of competition for sorption sites between nitrate and negatives charges of organic legands.

Table 1: Soil characteristic

	Chemical proprieties (mgkg^{-1})							Physical proprieties (%)			
pH	OM (%)	N	P	K	Mg	Ca	Clay	Sand	loam	Field capacity	Wilting point
8.26	3.48	90	4	294	22	193	43.3	36	20.7	7-13.2	4-9.1

3.2. Nitrate reduction by iron

The residual NO_3^- concentration in solution as a function of reaction time was indicated in Fig. 1. The NO_3^- concentration showed a decreasing trend throughout the experiment, whereby the general process could be divided into three phases. The first phase spreads during initial 60 min, adequate contact of Fe $^{(0)}$ with NO_3^- occurred and the NO_3^- concentration rapidly reduced; during second phase the process weakly declined until 90 min. However, after 90 min (third phase), NO_3^- reduction level increased again. About 16, 5 % of nitrate concentration decreased after 2 hours of reaction by Fe $^{(0)}$ indicating that the NO_3^- adsorbed obviously increased in the presence of Fe $^{(0)}$. Additionally Figure 1 shows that over time the concentration of ammonium (NH_4^+) on the exchange surface increases. This is consistent with an increase in NO_3^- reduction and NH_4^+ production. These observations are also confirmed by studies of Hwang et al, [15] and Tee et al., [16]. On other hand many studies ([17 18 19] were indicated that Fe $^{(0)}$ acts as electron donor responsible for triggering the reaction of reduction of NO_3^- to NH_4^+ following the below reactions (Eq1, Eq2):

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \quad (Eq1)$$

$$NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O \quad (Eq2)$$
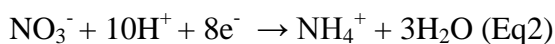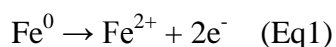
Nevertheless, this reduction is relatively low because the amount of NO_3^- transformed into two hours of contact time has an average value of about 10%. Moreover the NH_4^+ concentration production in the solution was 1.45mg / l indicating that the rate of NH_4^+ was about 69%. For this results it can be suggest that as reduction proceeds NH_4^+ is partitioned to the soil surface exchange sites and can be trapped. There is also the potential for this NH_4^+ to become adsorbed in the interlayer of some clay such smectite [20]. Also for these results it can be revealed that the adsorption of NH_4^+ ions thus

seems easy but the transformation of NO_3^- ions is low. Generally the results implied that NO_3^- reduction by Fe^0 could occur at pH > 8.0. Previous studies showed that nitrate reduction by Fe^0 was effective under acidic condition (pH < 7.0) but negligible in alkaline condition (pH > 8.0) [21, 22 23].

3.3. Effect of Fe^{2+} dosage on nitrate reduction by Fe^0

In order to investigate the effect of the addition of Fe^{2+} in the increasing nitrate reduction a 50 mg L^{-1} of Fe was added in the previous solution. The results were shown in Fig. 1. It can be showed that the nitrate reduction by $Fe^0 + Fe^{2+}$ was enhanced and continuous at initial pH. The NO_3^- concentration showed a decreasing trend throughout the experiment, whereby the general process could be divided into three phases. During initial 20 min, adequate contact of Fe^0 and Fe^{2+} with NO_3^- occurred and the NO_3^- concentration quickly reduced; during second phase the process smoothly declined until 60 min. However, after 60 min (third phase), nitrate reduction rate increased again. It can be observed from Fig. 1 that addition of the Fe^{2+} always favors the NO_3^- reduction in the presence of Fe^0. These findings are also confirmed by the works of Huang et al, [24 25], which also indicated the importance of Fe (0) and Fe^{2+} in reducing NO_3^-. The result of the Fig1 was indicating that the level of NO_3^- reduction increase turned into two hours of contact time was 36.3%. Simultaneously the level of NH_4^+ produced was 1.17 (mgL^{-1}) in the soil solution. Also it can be revealed that the 72% of NH_4^+ was adsorbed in the surface soil. The decisive role of Fe $^{2+}$ as shown by the following equations (Eqs 3, 4 and 5) reveled by Tsang et al., [26]

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \quad (Eq3)$$

$$NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O \quad (Eq4)$$
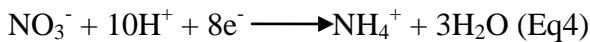
The addition of these two reactions leads to the following reaction (Eq5):

$$NO_3^- + 10H^+ + 8Fe^{2+} \longrightarrow 8Fe^{3+} + NH_4^+ + 3H_2O$$
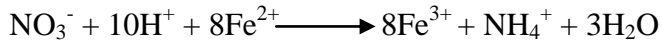
Wang et al., [27] indicate that the ion of H^+ indicate in the previous equations was produced from the

interlayer spaces of clay and silicate structures and the organic fraction after the reaction of dissociation and it was played a role of the release of the reduction NO_3^- and NH_4^+ production reaction [28].
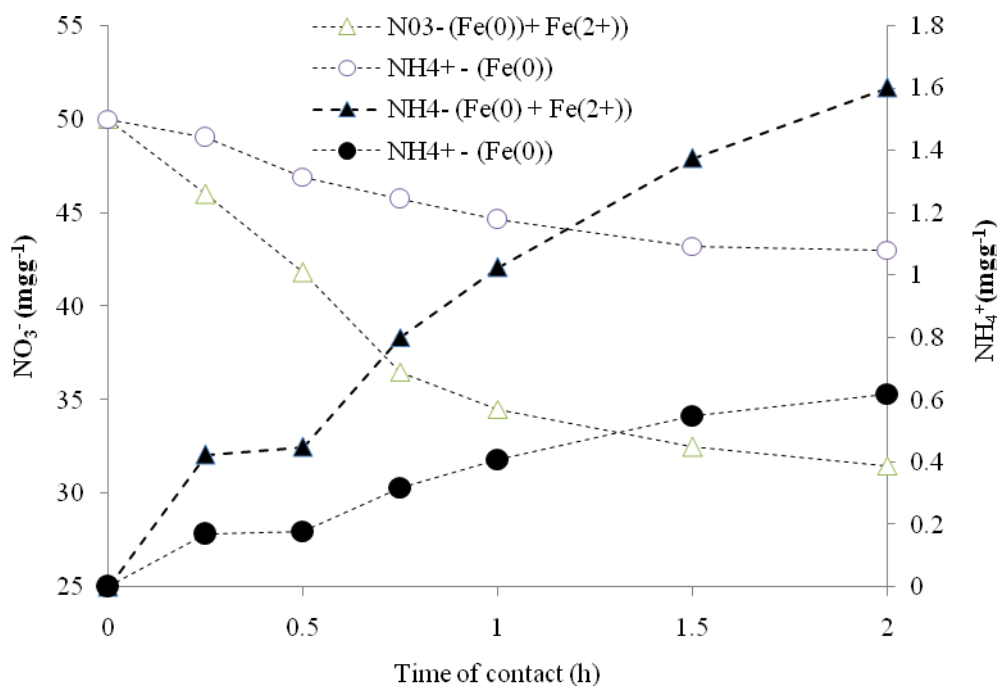

Fig1. Effect of Fe^0 and Fe^{2+} on NO_3^- reduction and NH_4^+ production (V= 50ml; m $_{Soil}$= 5g; $m_{Fe(0)}$ = 1g;

$[NO_3]$=50mgL^{-1}; $[Fe^{(2+)}]$ =50mgL^{-1}

3.4. Effect of the ratio

In order to optimize the reduction of nitrates NO_3^- by Fe^0, the study of the variation ratios (Fe0 /soil) was carried. Therefore, the (Fe^0/soil) following ratios (0.1, 0.2, 0.5 and 1) were used and the results obtained are shown in Fig 2. It can be show that the increasing of the ratio (Fe^0 / soil) of 0.1 to 1% was increased NO_3^- reduction in the solution from 4.1% to 59%. For this it can be suggested that the

increase level of Fe^0 enhance NO_3^- reduction. The increasing of Fe^0 level indicates the increase of electrons donor responsible for nitrate reduction. This finding was be revealed by other work such Harvey et al., [29]. These authors showed that for (1: 1) (Fe^0/soil) ratio the NO_3^- reduction and NH_4^+production were seemed total.
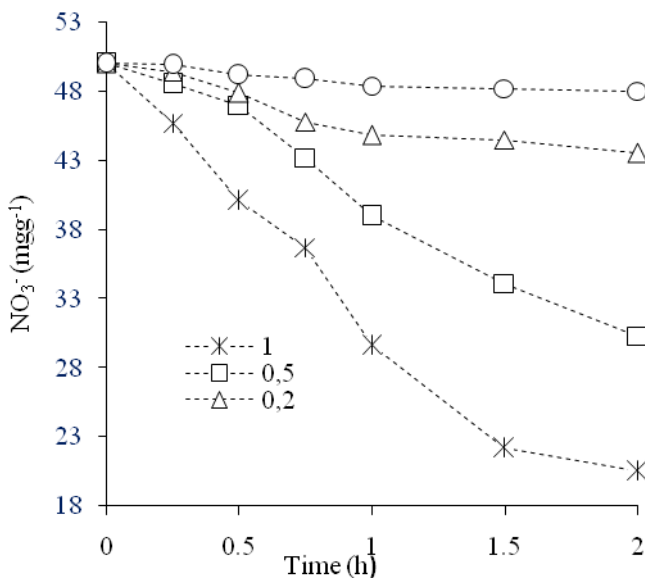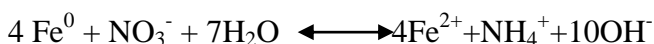
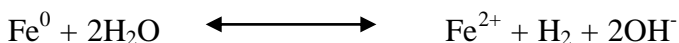Fig2. Effect of Fe$^{(0)}$ /soil ratios on NO$_3^-$ reduction

(V= 50ml; [NO$_3^-$] =50mgL^{-1})

3.5. Influence the addition of Fe $^{(0)}$ and Fe $^{(2+)}$ on the change in pH

The pH measurement during the contact time was carried and the results are shown in Fig 3. It can be show that the production of NH$_4^+$ ion in solution from the reduction of NO$_3^-$, was increasing the initially value of pH. In the presence of NO$_3^-$ the oxidation of Fe^0 by water proceeds through reaction with consumption of H + ions and the increasing of OH$^-$ in the solution (Eqs 6 and 7).

Eq (6):

$$4 Fe^0 + NO_3^- + 7H_2O \longleftrightarrow 4Fe^{2+} + NH_4^+ + 10OH^-$$

Eq (7):

$$Fe^0 + 2H_2O \longleftrightarrow Fe^{2+} + H_2 + 2OH^-$$

This increase in pH was also found by previous others studies. Su et al, [30] showed that NO$_3^-$ reduction of about 9% after the addition of Fe$^{(0)}$ resulted in an increase pH of 6.2 to 9.3. Similarly Harvey et al, [29] reported that the reduction nitrate to ammonium is also accompanied by an increase of the pH of 7 to 8.1 and the decreasing of the oxygen concentration (O$_2$) of 8.3 to 8, 1 (mgL^{-1}). Xu et al, [31] indicate that the reaction of the NO$_3^-$ reduction by Fe $^{(0)}$ was associated with increasing of the consumption of H$^+$ ions and the increasing of OH$^-$ in the solution [32].
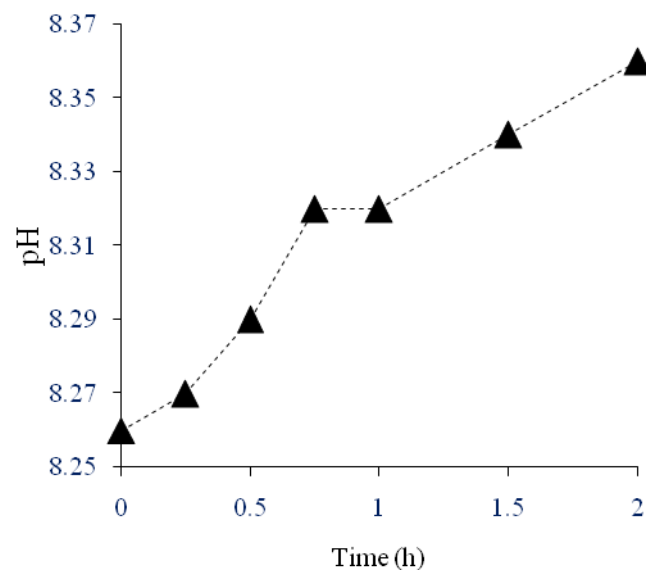
Fig1. Effect of Fe $^{(0)}$ and Fe $^{(2+)}$ on pH variation
(V= 50ml; m $_{Soil}$= 5g; m$_{Fe(0)}$ = 1g; [NO$_3^-$]=50mgL^{-1}, [Fe$^{(2+)}$]=50mgL^{-1})

CONCLUSION

The study reveals that Fe^0 play a key role in nitrate reduction in the solution and also in reducing the contamination of groundwater due to high level of nitrate. The study further suggests that the zero-valent iron reduction shows potential for reducing nitrate mobility in soils through the partitioning of the produced ammonium-N to soil surface exchange sites. Three phases were evident throughout the declining concentrations of NO$_3^-$. The addition of Fe^{2+} obviously was accelerated the electron transfer enhanced the reduction of nitrate. The initial pH was rise due the consumption of H$^+$.

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