

CHEMICAL DENITRIFICATION OF NITRATE FROM GROUNDWATER VIA SULFAMIC ACID AND ZINC METAL

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ABSTRACT

Nitrate contamination in drinking water can cause methemoglobinemia, which is especially detrimental to infants and nursing mothers. Batch experiments in two units for catalytic reduction of nitrate from groundwater with Zn catalyst and sulfamic acid were conducted. The system includes chemical denitrification (ChemDen reactor) and electrolytic recovery reactors. A batch study was conducted to optimize parameters like pH, sulfamic acid concentration, Zn concentration, temperature and reaction time governing the ChemDen process. The concentrations of remained nitrate and Zn were measured at the end of the reactions. Results showed that near to 100% of nitrate decreased and the quantity of remained nitrate was <1 mg/L. pH and agitation had great effect on denitrification, and the nitrate removal rate changed rapidly when pH value ranged between 3-4. Two water quality parameters which limit this process were sulfate and chloride ions concentrations in nitrate contaminated water.

Key words: Chemical denitrification, groundwater, zinc, sulfamic acid, electrolytic reactor

INTRODUCTION

Nitrate (NO_3^-) concentrations in groundwater have increased globally (Kapoor and Viraraghavan 1997). Wastewater, fertilizers, and livestock farming are major sources of nitrate in groundwater supplies. Groundwater in many locations is used as a supply for drinking water, and high nitrate concentrations present a potential risk to public health, particular to infants (Gangolli *et al.*, 1994). In the United States, the Environmental Protection Agency has set a maximum contaminant level (MCL) for nitrate in drinking water of 0.71 mM (10 mg of $\text{NO}_3^- \text{N L}^{-1}$) (Pontius, 1993). There are many methods for nitrate removal from water. Biological denitrification reduces nitrate to a gaseous nitrogen species. The gaseous product is primarily nitrogen gas, but it may also be nitrous oxide or nitric oxide. A broad range of bacteria, including many in the genera *Pseudomonas*, *Micrococcus*, *Archromobacter*, *Thiobacillus*, and *Bacillus* can reduce nitrate. Natural biological denitrification occurs, although not extensively, in aquifers in which a sufficient source of reducing

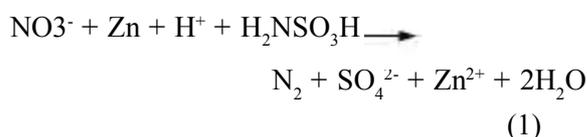
organic carbon is present. Water treatment processes stimulate denitrification by injection of nutrients. Such organic compounds as methanol, methane, glucose, and starch or mixtures of these (e.g. a sugary brewery waste) can be used as carbon sources (Soresen and Jorgensen, 1993). The feasibility of biologically removing nitrate from groundwater had tested by using cyanobacterial cultures. Results demonstrated that nitrate contaminated groundwater, when supplemented with phosphate and some trace elements, can be used as growth medium supporting vigorous growth of several strains of cyanobacteria. As cyanobacteria grew, nitrate was removed from the water (Qiang *et al.*, 2001). Nitrate removal by hydrogen coupled denitrification was examined using flow through, packed-bed bioreactors for treating nitrate contaminated drinking-water supplies. Nitrate removal was accomplished using a *Rhodocyclus* sp., strain HOD 5, isolated from a sole-source drinking-water aquifer (Smith *et al.*, 2005). Chemical methods for decomposing nitrate can be divided into two groups: nonspecific methods and methods designed for nitrate decomposition.

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There is no simple chemical method that would reduce nitrate to nitrogen gas at low temperature and pressure. It is relatively easy to reduce nitrate to ammonia, but it is much more challenging to stop the reduction at molecular nitrogen. Many metals, such as magnesium, manganese, Zn, chromium, iron, cadmium, tin, aluminum, and lead will reduce nitrate. The final reduction products are governed by the temperature, the pH, and the metal used.

Zhang and coworkers (2003) had conducted a batch experiment on catalytic reduction of nitrate from groundwater with Pd and Cu catalysts. It was found that Pd-Cu combined catalysts at a ratio of 4 can maximize the nitrate reduction into nitrogen; above 80% total nitrogen removal efficiency was achieved (Zhang *et al.*, 2003). At Los Alamos National Laboratory (LANL), Dr. Dziewinski had invented a simple and robust chemical process that converts nitrate in water into environmentally benign gaseous nitrogen. In this process, nitrate-contaminated water is added to a simple chemical reactor, where it is contacted with two inexpensive chemical reagents: sulfamic acid and Zn. These two reagents reduce the nitrate to gaseous nitrogen according to the following overall reaction (Dziewinski and Barber, 1999):



The generated Zn cations were subsequently electrolytically reduced back to the metallic state. Thus Zn was not a consumed reagent; it considered as a mediator or catalyst. The system consisted of a simple reaction vessel, an agitator, and an electrolytic cell. Sulfamic acid was a consumable reagent, and Zn was a reusable reagent. Based on the nitrate concentration in the waste, appropriate quantities of sulfamic acid were added while Zn remains in excess in the reactor. Zn is oxidized to form Zn^{++} ion and then reduced back to Zn metal by electrolysis.

The process begins immediately after nitrate is introduced to the reactor and bubbles of nitrogen gas are released to the atmosphere. When the reaction is complete, the treated water can be safely released to the environment.

The process can be configured in two ways. The electrolytic cell is installed as a separate unit, or it is built into the denitrifying reactor. In the second case, the reactor first performs the denitrification and then is switched to the Zn recovery mode. A power supply provides a low-voltage DC current for Zn recovery in the reactor (Dziewinski and Barber, 1999).

MATERIALS AND METHODS

Sulfamic Acid 99% (Merck), Zn Metal Powder (Merck), KNO_3 (Merck), NaCl (Merck), CaCO_3 (Merck). Nitrate concentrations were measured by PU 8700 UV/Visible spectrophotometer in wavelengths of 220nm and 275nm. All samples were measured as dilutions series and directly injected into the cell of spectrophotometer.

Zn concentrations were measured by Varian Techtron AA-5 atomic absorption unit. The unit was operated at a wavelength of 2146 Å, a slit width of 150 μm, and a constant current of 5 milliamps. An air-acetylene fuel mixture was used and was adjusted to produce an oxidizing flame. A spike and recovery analysis was performed on samples collected from effluent to check for interferences. This was accomplished by taking 300 ml samples of known concentrations and adding a 20% spike (Zn concentration) prior to reanalysis. These results typically showed excellent agreement between expected and measured values (less than 5% deviation), suggesting no significant interferences were present. Water samples were collected from each of the two separate compartments. A schematic drawing of the pilot plant includes chemical denitrification (ChemDen reactor) and electrolytic recovery reactors which was developed for testing is shown in Fig. 1. The pilot consisted of a two plexiglas rectangular container with effective volume of 4.5 liters. ChemDen reactor contained one stainless steel mixer and one outlet valve. In electrolytic recovery reactor stainless steel plate as anode and graphite as cathode were utilized as electrodes because it was believed that this type of material would be readily available to the typical plates, increasing the ease at which this configuration could be set up by the platter in their own facility. The electrodes plates

were hung from an electrically insulated rack above the reactor and extended vertically downward into the water. Alternate plates were connected in parallel to a 2 amps direct current rectifier and voltage had changed from 0-5 v.

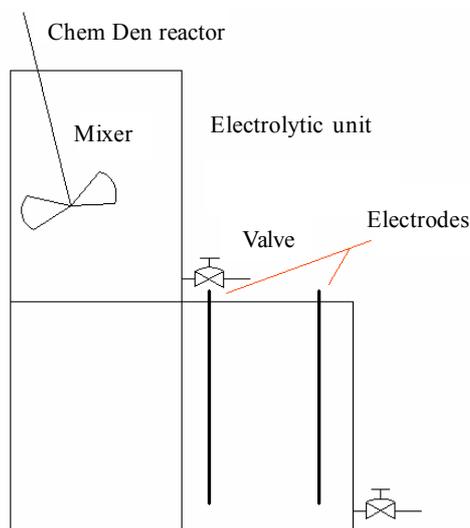


Fig. 1: The schematic drawing of the pilot plant

ChemDen reaction was carried out in duplicate and in a batch mode. This experiment had done in two phase. In first phase KNO_3 was added directly into 4.5 lit of distilled water containing sulfamic acid and Zn powder. In second phase a composite sample was prepared from groundwater wells located in Firouzkooh-Tehran.

In the first experiment, 6 samples were prepared with different sulfamic acid concentrations (50, 100, 156, 200, 250 and 300 mg/L in distilled water medium). Nitrate and Zn concentrations were 100 and 105 mg/L as stoichiometry equations. Afterwards 5 samples were prepared with different Zn concentrations (25, 50, 105, 150 and 200 mg/L in distilled water medium). Nitrate and sulfamic acid concentrations were 100 and 156 mg/L as stoichiometry equations. After 15 min the residual nitrate concentrations were measured at the end of the stages. Afterwards in optimum ratio of “nitrate: sulfamic acid: Zn”, the best hydraulic retention time and pH were analyzed. The Zn removal efficiencies were measured in electrolytic unit at optimum ratios. The Zn concentrations in influents were changed from 25 to 200 mg/L (25, 50, 100, 150 and 200 mg/L in distilled water

medium). Manual line was obtained by collecting 500 mL samples at 30 min intervals for 2 hours. Three 300 mL aliquots of the composite were taken for analysis. In optimum ratio of reactants, the concentration of sulfate and chloride were measured in various nitrate concentrations. All samples in first experiments had prepared via distilled water. In second experiment prepared sample from Firouzkooh wells was used in order to evaluate the effects of other anions and cations in groundwater. The water quality parameters in prepared sample have been shown in Table 1. The Zn powder and sulfamic acid were added into water as obtained optimum ratio of reactants.

Table 1: Water quality parameters in groundwater sample from Firouzkooh

Parameter	Unit	Concentration (mg/L)
Nitrate	mg/L	130
Sulfate	mg/L	75
Chloride	mg/L	45
Alkalinity	mg/L as CaCO_3	315
pH	-	7.6
T.H	mg/L as CaCO_3	420

RESULTS

In Figs. 2 and 3, the effects of sulfamic acid and Zn concentrations on the nitrate removal efficiency have been shown. The changes in pH value in ChemDen reactor and treated effluent from electrolytic unit have been shown in Table 2. The optimum pH value was in the range of 3-4, In addition, in all of the cases, the pH of treated solution increased to 7.

As shown in Figs. 2 and 3, if the sulfamic acid and Zn concentration increased, then the efficiency of nitrate removal increased. Maximum removal of >99% was attained at following mass ratios:

Nitrate: Zn = 100:105

Zn: Sulfamic acid = 100:200

As shown in Fig. 4 more than 90% of nitrate was removed primary in 15 minutes and then the nitrate removal rate remained constant. Fig. 5. shows the changes in Zn concentration in effluent as a function of Zn concentration in influent (Zn removal efficiency in electrolytic unit). The residual concentration of Zn in the treated effluent was about 1 mg/L at Zn influent concentration of 200 mg/L. Based on a total water volume in reactor a

Table 2: Changes in pH value in ChemDen reactor and treated effluent from electrolytic unit

pH (Influent water)	Sulfamic acid concentration (mg/L)	pH (In ChemDen reactor)	pH (Treated effluent)
7.6	50	4.5	7.2
7.6	100	4.2	7.2
7.6	156	4	6.9
7.6	200	3.7	6.7
7.6	250	3.5	6.6
7.6	300	3.3	6.3

Zn concentration in treated water of 1.2 mg/L has been calculated. Performance data for Firouzkooh sample are shown in Table 3. As shown in this table nitrate removal efficiency was greater than 99%. In Fig. 6, the changes in concentrations of sulfate and chloride ions in treated effluent as function of influent nitrate concentrations at optimum ratio of reactants have been shown. As shown in this figure, if 400 mg/L nitrate was removed from water by ChemDen process, then the concentrations of sulfate and chloride ions increased 131 and 45 mg/L, respectively.

Table 3: Nitrate conversion performance data by ChemDen at Firouzkooh –Tehran

parameter	Influent	Effluent
Nitrate (mg/L)	130	<1
Sulfate(mg/L)	75	123
Chloride(mg/L)	45	64
Alkalinity(mg/L as CaCO ₃)	315	-
pH	7.6	7.1
T.H(mg/L as CaCO ₃)	420	-

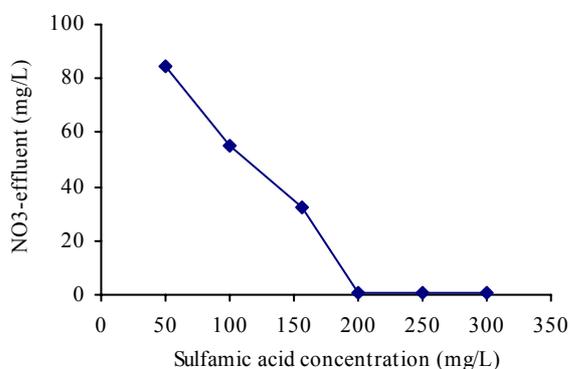


Fig. 2: The changes in effluent nitrate concentration with change in sulfamic acid concentrations.

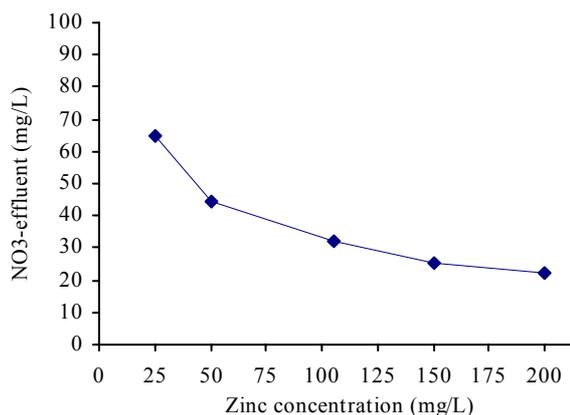


Fig. 3: The changes in effluent nitrate concentration with change in zn concentrations.

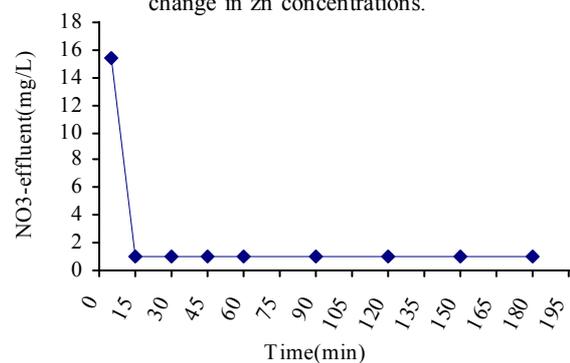


Fig. 4: The changes in effluent nitrate concentration as function of reaction times.

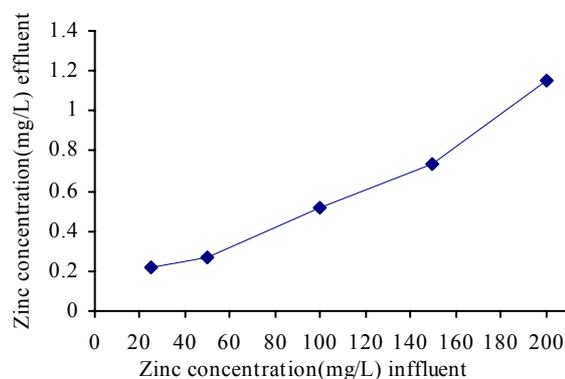


Fig. 5: The changes in effluent Zn concentration with change in Zn concentration in electrolytic unit.

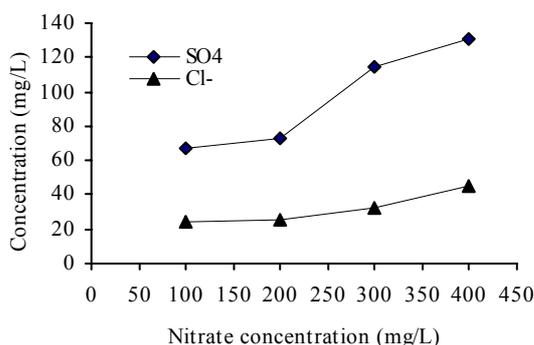
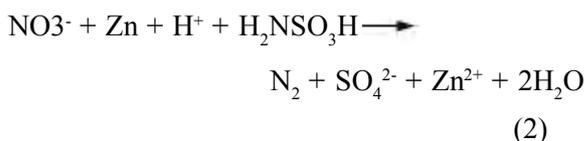


Fig. 6: Sulfate and chloride concentration variations

DISCUSSION

In ChemDen process, when sulfamic acid was added to the solution containing nitrate and Zn metal, these two reagents reduce the nitrate to gaseous nitrogen according to the following overall reaction (Dziewinski and Barber, 1999):



As shown in Fig. 2 sulfamic acid concentration was a limiting parameter of ChemDen process. On the other hand, Zn metal ion concentration had a low effect on nitrate removal efficiency. In all experiments a small amount of Zn metal precipitated in the ChemDen reactor (Fig. 3).

Regarding to sulfamic acid concentration factor (Fig. 2) and following mass ratios, maximum nitrate removal rate (approximately 100%) was obtained :

Nitrate: Zn: Sulfamic acid = 100:105:200

pH is an important element in ChemDen reaction. In all conditions, pH of water dropped immediately within 30s after the addition of sulfamic acid and after the reaction time, pH of treated water increased to 6.3-7.3. It is believed that the pH increasing in this condition was because of electrochemical reactions in electrolytic cell. It is obvious that shaking could be (with mixer or compressed air) one of the important stages in ChemDen process. Since the reactants did not mix completely, nitrate removal efficiency decreased when agitation reduced. Dziewinski (1999) reported that ChemDen process on the simultaneous reaction of nitrate

with a metal and sulfamic acid progressed at pH 1-4. The acid which added into reactor could also be recovered using a membrane cell.

Results showed that nitrate removal efficiency was about 100% and so the remained nitrate concentration was <1 mg/L. On the other hand, performance data by ChemDen at Los Alamos for March-September 1999 showed that nitrate removal efficiency was near to 100% (Dziewinski and Barber, 1999).

As shown in Fig.4, more than 90% of nitrate concentration was removed in the first 15 minutes of the process and then the nitrate removal rate remained constant.

Results of the electrolytic recovery tests were shown in Fig.5. The produced Zn cations were electrolytically reduced back to the metallic state in a subsequent way. Thus Zn powder is not a consumed reagent; it may be considered a mediator or catalyst. Zn is oxidized to form Zn⁺⁺ ion and then reduced back to Zn metal by electrolysis unit. The Zn ion concentration in effluent is depended on electrolysis efficiency.

During the periods of 3 hour testing, Zn removal efficiency depended upon specific operating conditions. However, in general more than 90% of Zn removal rate was obtained in all tests during this period, which this efficiency can easily met the Zn limit standard (d' 5 mg/L) in drinking water (USEPA, 1996). Total daily Intake for nitrate must be less than 13 mg/d. High concentrations of nitrate in water sources cause irritability muscle stiffness and pain, loss of appetite and nausea. In all conditions of doing experiments with different nitrate concentrations, Zn concentration in effluent were less than 1.2 mg/L (which was less than the standard of 5 mg/L).

In electrolytic recovery process the reactor configuration was effective for Zn removal. The most important factor for achieving high efficiency of Zn precipitation appeared to be agitation. Mechanical mixing and nitrogen gas aeration were both effective for agitation (Walters and Vitagliano, 2000). In this experiment agitation had done by manual mixing. Sulfate and chloride ions concentrations in the process effluent were increased in comparison with the concentrations in the influent. Regarding to this matter that the

concentrations of these ions in some underground water resources are high naturally; so the application of this process for the underground water resources with high sulfate and chloride ion concentrations is limited. As shown in Fig.6, for every 100 mg/L nitrate which removed from water by ChemDen process, 30 mg/L of sulfate ions and 11 mg/L of chloride ions were produced. The main sources of produced sulfate and chloride ions in effluent were sulfamic acid and electrolysis process.

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