



Simultaneous fluoride and nitrate removal from drinking water using mixotrophic denitrification processes in a fixed bed column reactor

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ABSTRACT

Nitrate and fluoride are water contaminants found together in some regions where agricultural activities are widespread. The concentration of these contaminants is important since nitrate causes methemoglobinemia in infants and fluoride causes dental diseases. In this study, a fixed bed column reactor was used with sulfur and limestone media to remove these contaminants under simultaneously autotrophic and heterotrophic (mixotrophic) conditions at 30°C. The reactor was operated under these conditions for 125 d and 49.7 mg/L of NO₃-N and 5.3 ± 0.4 mg/L of F⁻ were removed at 95.0 and 90.0% efficiency, respectively. Effluent pH was 7.8 and alkalinity was not exceeded 200 mg/L. Removal mechanisms of nitrate and fluoride were biological denitrification and physicochemical (adsorption and precipitation), respectively, since batch experiments agreed that the removal mechanism of fluoride was not biological. This study showed that both NO₃⁻ and F⁻ can be removed in one reactor under mixotrophic conditions, simultaneously.

Keywords: Nitrate; Fluoride; Removal; Mixotrophic; Denitrification; Fixed bed column reactor

1. Introduction

Fluorine exists in the form of fluoride in minerals such as fluorspar, cryolite and fluorapatite [1]. Fluoride is known to have both beneficial and adverse effects on humans, depending on the total intake [2]. The WHO health-based guideline value for drinking water, which is also the basis of the value in the EC Drinking Water Directive transposed into Turkish Drinking Water Standards [3] is 1.5 mg/L. 1.5–4.0 mg/L of fluoride ions concentration range that includes the consumption of drinking water for a long time, leads to dental fluorosis disease. Fluoride concentration of 4.0–10.0 mg/L cause dental fluorosis or skeletal fluorosis [4]. There are more than 20 developed and developing nations as Argentina, U.S.A., Morocco, Algeria, Libya, Egypt, Jordan, Turkey, Iran, Iraq, Kenya, Tanzania, China, Australia, New Zealand, Japan, Thailand, Canada, Saudi Arabia, Persian Gulf, Sri Lanka, Syria,

India, etc. that are endemic for fluorosis [5]. Fluoride is a major groundwater contaminant of worldwide concern that is difficult to remove [6].

The nitrate (NO₃⁻) is also a surface and ground water pollutant. Consumption of water contaminated with excess amount of nitrate can cause carcinoma, malformation and mutations when transformed into nitrosoamines. The United States Environmental Protection Agency has set the maximum contaminant level of 10.0 mg NO₃⁻-N/L for drinking water [7].

Presence of various hazardous contaminants like fluoride and nitrate in ground water is reported from Turkey [8,9]. In groundwater, the natural concentration of fluoride and nitrate depends on the geological, chemical and physical characteristics of the aquifer, the porosity and acidity of the soil and rocks, temperature, the action of other chemicals and the depth of wells. However, in many countries worldwide, high fluoride and nitrate concentrations

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originated from the discharges of fluoride and nitrate polluted wastewater. Such wastewater are usually produced by fertilizer industry, glass, ceramic manufacturing processes [10] for fluoride polluted waters and excessive fertilizer usage in agricultural facilities for nitrate pollution [11]. In drinking water resources, nitrate and fluoride can be present together as a common co-contaminant in surface and ground waters. For these reasons, the removal of the excess fluoride and nitrate from water sources is important in terms of protection of public health and environment.

Several treatment technologies are adopted to remove fluoride and nitrate from drinking water under both laboratory and field conditions. Defluoridation of drinking water using several chemical methods including separation process, ion exchange, electro dialysis, adsorption and reverse osmosis, are developed [5]. The physico-chemical methods are adopted to remove nitrate from drinking waters like reverse osmosis, electro dialysis and ion exchange. However, the shortcomings of most of these methods have high operational and maintenance costs, secondary pollution, high sludge generation and high capital investment. Out of these, biological processes like denitrification are also studied for the removal of excess amounts of nitrate from drinking water [12]. The advantages of biological processes are functional simplicity, cost-effectiveness and less sludge production [13]. Sulfur and limestone are used for the removal of excess amount of nitrate in many studies for auto trophic, heterotrophic and mixotrophic denitrification processes [7,8,14–16]. Sulfur is used as electron donor when the nitrate is electron acceptor, while limestone is used as alkalinity supplementation in a fixed bed column reactor [8]. The removal mechanism of fluoride in a fixed bed denitrifying column reactor should be studied to investigate the possible biological or physical treatment mechanism.

The aim of this study is to examine the remediation of contaminated drinking water pollutants, both nitrate and fluoride. It is a challenge to develop an effective and cheap method for these co-contaminants from drinking water resources. However, based on the review of literature, fluoride and nitrate removal from drinking water in one reactor is not investigated previously for their treatment potential simultaneously. Therefore, in this research, the feasibility of an integrated biological denitrification and physiochemical (defluoridation through precipitation and adsorption) treatment process for nitrate and fluoride removal using a fixed-bed column reactor (FBCR) is evaluated.

2. Materials and methods

2.1. Fixed-bed column reactor

The test solutions of different initial fluoride and nitrate concentrations were prepared by adding the appropriate amounts of stock solutions of sodium fluoride and potassium nitrate to tap water. The biological denitrifying reactor had one entry port for influent and four exit ports for clarified water, sample collection, sludge discharge, and release of nitrogen. It was sealed and connected to a water displacement gas collector. A

laboratory-scale fixed-bed column reactor used in this study was made of glass with an empty bed volume of 400 mL (Fig. 1). The column reactor was filled with sulfur (0.5–1.0 mm):limestone (0.5–1.0 mm) particles in volume ratio of 1:3. The reactor was covered with aluminum foil to prevent the growth of photo trophic bacteria. A denitrifying sludge obtained from the anoxic tank of Bardenpho process was used as inoculum. The column reactor was operated in continuous up-flow mode at 28–30°C in a temperature controlled room.

Biomass was acclimatized to develop denitrifying microorganisms and to stabilize the microbial activity during the first seven days. During the first seven days, the reactor was fed with tap water containing 50 mg/L NO_3^- -N as KNO_3 and 50 mg/L K_2HPO_4 solution for adaptation of denitrifiers. The feed solution was deoxygenated by passing through the N_2 gas for 5 min. Then, the feed was kept under anaerobic conditions in a collapsible feed container and stored 4°C in refrigerator during all periods. A peristaltic pump (Cole Parmer, IL, US) was used to deliver the feed solution to the column reactor. In order to stimulate simultaneous autotrophic and heterotrophic denitrification (mixotrophic denitrification), methanol was added as an external organic carbon at through the study (Table 1).

The nitrogen gas production was measured by liquid displacement method (Fig. 1) and the volume of gas was compared to the theoretical value (mL/d) using the following equation [20].

$$\text{Th.value} \left(\frac{\text{mL}}{\text{d}} \right) = \text{Rem. NO}_3^- - \text{N} \left(\frac{\text{mg}}{\text{L}} \right) \times \frac{22.4 \text{ mL}}{28 \text{ mg}} \times \frac{\text{Temp} (^{\circ}\text{K})}{273.15 (^{\circ}\text{K})} \times Q \left(\frac{\text{L}}{\text{d}} \right) \quad (1)$$

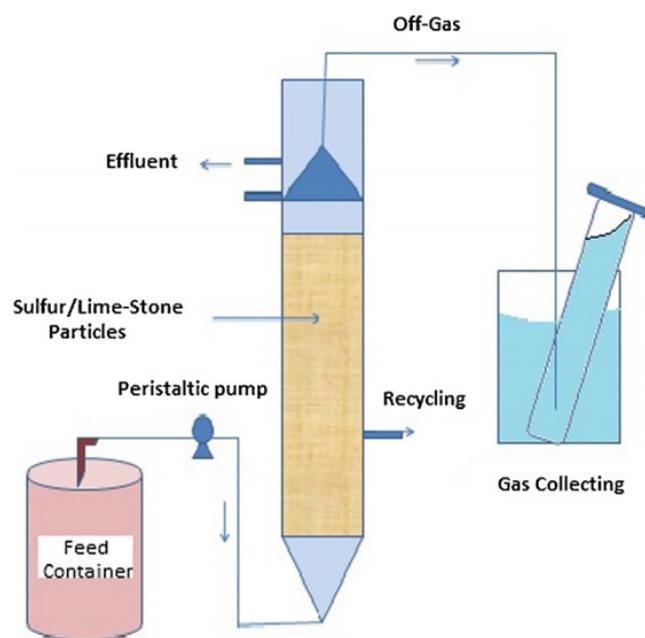


Fig. 1. Schematic representation of the lab-scale fixed-bed column reactor.

Table 1
Operational conditions used in the reactor

Stages	Auto trophic	Mixotrophic
Periods	1	2
Days	0–30	30–100
Fluoride feed (mg/L) ^a	5.0	5.0
NO ₃ -N feed (mg/L)	50.0	50.0
HRT (h)	12	12
Methanol feed (mg/L)*	–	75.0 (29.5)

*Values in parenthesis represents the methanol concentration as DOC

Batch experiments were also done for investigating the removal mechanism of the fluoride whether it is biological or physical. For this reason, 100 mL of glass reactors were used for the feed; i) without limestone, ii) with limestone after inoculating them with the seed. For this reason, 100 mL of glass reactors were used for the feed; i) without sulphur and limestone, ii) with sulphur and limestone after inoculating them with the seed. Each reactor was purged with N₂ gas. In this stage, NaHCO₃ was used instead of limestone as a source of alkalinity for denitrification.

2.2. Sampling and analytical techniques

In addition to fluoride and nitrate, other related water quality parameters i.e. nitrite, sulfate, sulfide, alkalinity and pH were analyzed in the denitrified and defluoridated effluents. All parameters were analyzed in accordance with the procedures outlined in Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

Samples for analysis were collected from the reactor effluent at least three times a week for the measurement of NO₃⁻, NO₂⁻, sulfate, pH, and alkalinity. The feed solution was sampled once a week for the determination of F⁻, NO₃⁻, NO₂⁻, sulfate, pH, and alkalinity. All samples were filtered over a 0.45 µm-pore-size sterile filter and stored at 4°C until analysis. NO₃⁻, NO₂⁻ and SO₄²⁻ concentrations were determined by ion chromatography (Schimadzu, Prominence HIC-NS). Alkalinity was also measured according to Standard Methods. All chemicals were of analytical grade (Merck) except for sulfur and limestone that was technical grade.

3. Results and discussion

The reactor was operated under autotrophic conditions for the first 30 days. Nitrate was feeded as 50 mg/L concentration throughout the study and it was almost completely removed after a couple of days as shown in Fig. 2 except for a few days. After 38 days of operation, nitrite concentration was fluctuated unexpectedly reaching as high as 30 mg/L. Thus, the results from Fig. 2 might be due to oxygen leakage to the reactor during changing the feed solution or limited growth of a very small inoculum

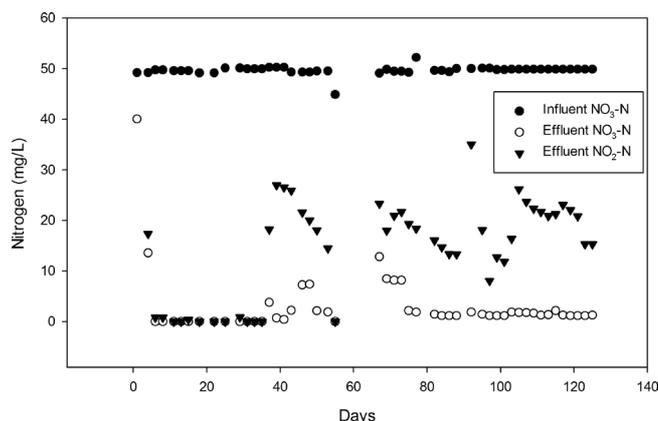


Fig. 2. Influent and effluent nitrogen concentrations as NO₃-N and NO₂-N.

of microorganisms in the highly inhibitory environment of fluoride and sulfate.

In the previous autotrophic denitrification studies this situation was not seen since nitrite was directly used by easily oxidizable compounds or converted to nitrogen gas if the biological conditions is appropriate [8,14,17,18]. Nitrite was known to accumulate in over loading conditions of sulfur-based denitrification process [12]. The reasons for the nitrite accumulation may be i) the high sulphur to nitrogen (S/N) ratio [19], ii) excess supply of organic matter [12], iii) other operational factors (pH, dissolved oxygen level, and sludge retention time) [15] or iv) fluoride toxicity on biomass activity [20]. S/N ratio was not the factor affecting the nitrite accumulation because sulfur was known to dissolve slowly and also its volume in the reactor was similar to other studies [8,14]. Alkalinity and pH levels were not different than the expected since it was around 8 at the effluent for pH and it increased as high as 200.0 mg/L for alkalinity as shown in Fig. 3. It was found that the concentration of nitrite increased as the pH increased from 7.0 to 8.0. Another study also reported that accumulation of nitrite may enhance during denitrification when the pH was not at its optimum [16]. However, pH was not different than

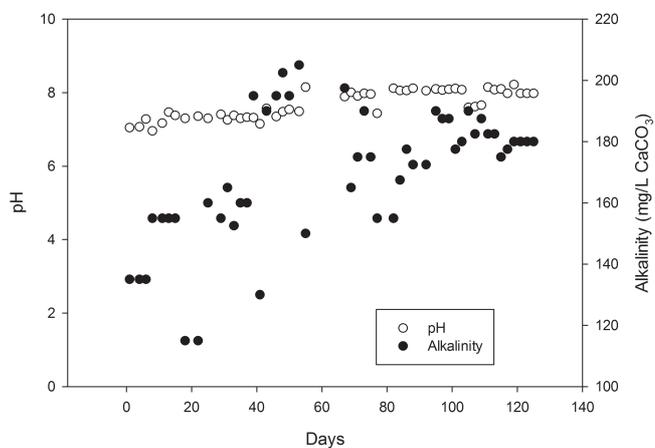
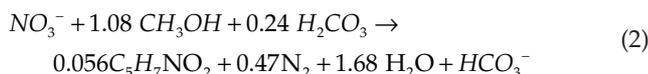


Fig. 3. pH and alkalinity levels in FBCR.

the similar studies conducted, like perchlorate removal [21], and nitrate removal [7,8,22]. Fluoride toxicity could not be the reason of nitrite accumulation in this very low concentration (about 5 mg/L) compared to highly concentrated coke wastewater treatment that is around 100 mg/L [23]. Therefore oxygen level in the reactor or organic loading rate may be the reasons of accumulation of nitrite.

According to Reaction (2), 2.47 g of methanol is required per g of NO_3^- -N reduction [7]. Therefore, the fraction of nitrate reduced was calculated as 60.72 % by heterotrophic denitrifiers under mixotrophic conditions.



Measured sulfate production was given in Fig. 4. Addition of methanol at day 38 decreased the level of sulfate production that was calculated from the mixotrophic denitrification reaction [8]. Increase in sulfate concentration between 70–90 days may arise from the fluoride toxicity on heterotrophic denitrifiers. The decrease in NO_2^- -N concentration from 20 mg/L to 10 mg/L was in consistency with this finding. The presence of fluoride in the denitrification system might affect biomass activity and the performance of the process, especially heterotrophic denitrifiers. Some studies demonstrated that fluoride damages microorganisms such as nitrifier, methanogenium and propionate degradation bacteria in biological wastewater treatment systems [24,25]. For this reasons, it was concluded that the concentration of sulfate and nitrite is increased in mixotrophic conditions.

Based on the review of literature, it was seen that the number of simultaneous removal of nitrate and fluoride studies is very limited due to fluoride toxicity on microorganisms. Additionally, unlike organic pollutants, the fluoride ion cannot be mineralized or converted to any other form by microorganisms due to its atomic structure [26]. On the other hand, when the analysis results were examined, it was seen that nitrate and fluoride removal were performed in this study simultaneously (Fig. 2 and

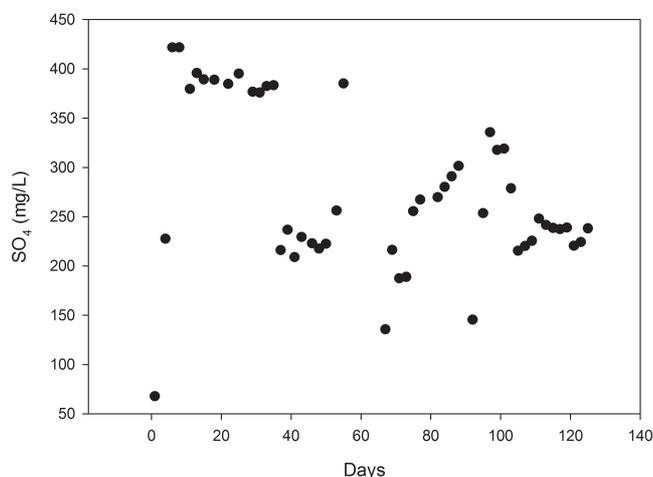


Fig. 4. Measured sulfate production

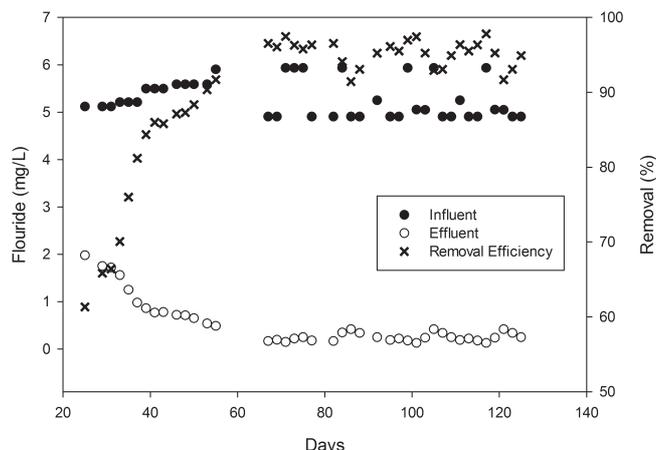


Fig. 5. Fluoride concentrations and removal efficiency

Fig. 5). It was observed that there is a steady decrease in effluent fluoride levels in Fig. 5. The reason for this is that as precipitated fluorite particles accumulated in the column, they provide more nucleation sites for F^- ions to crystallize on and the overall fluoride removal rate improves [27].

Batch experiments were also carried out to see if the removal of fluoride was taken place via biological pathways. In the batch reactors, no fluoride removal was observed (Fig. 6). The difference between FBCR and batch reactors were the absence of limestone. Flow of this carbonated water through the FBCR of crushed limestone causes calcite (CaCO_3) to dissolve and calcium fluoride (CaF_2) to become supersaturated and precipitate [28]. Therefore, it was thought that the removal of fluoride occurred physico-chemically by limestone in the FBCR. It was then concluded that the limestone removed fluoride by both the adsorption and the precipitation process. All nitrate was converted firstly to nitrite and then to nitrogen gas as the nitrate completely removed in batch reactors. Sulfate concentration increased to almost 1,000 mg/L as there was no external carbon source to provide mixotrophic conditions in these reactors. There is no connection between the removal mechanisms of nitrate and fluoride according to these experimental conditions.

4. Conclusion

In this study, simultaneous nitrate and fluoride removal was achieved using sulfur-limestone medium fixed bed column reactor. The removal mechanism of nitrate was biological mixotrophic denitrification providing the effluent sulfate concentration below 250 mg/L. Influent nitrate concentration was 50.0 mg/L and it was almost completely removed however nitrite accumulation was observed due to high organic loading rate. Fluoride was removed by limestone particles since batch experiments indicated that the biological degradation of fluoride is not possible with anoxic biological seed. This study revealed that nitrate and fluoride rich groundwater could be efficiently treated with sulfur and limestone packed bed column reactor with mixotrophic conditions by both biological and physical treatment mechanisms.

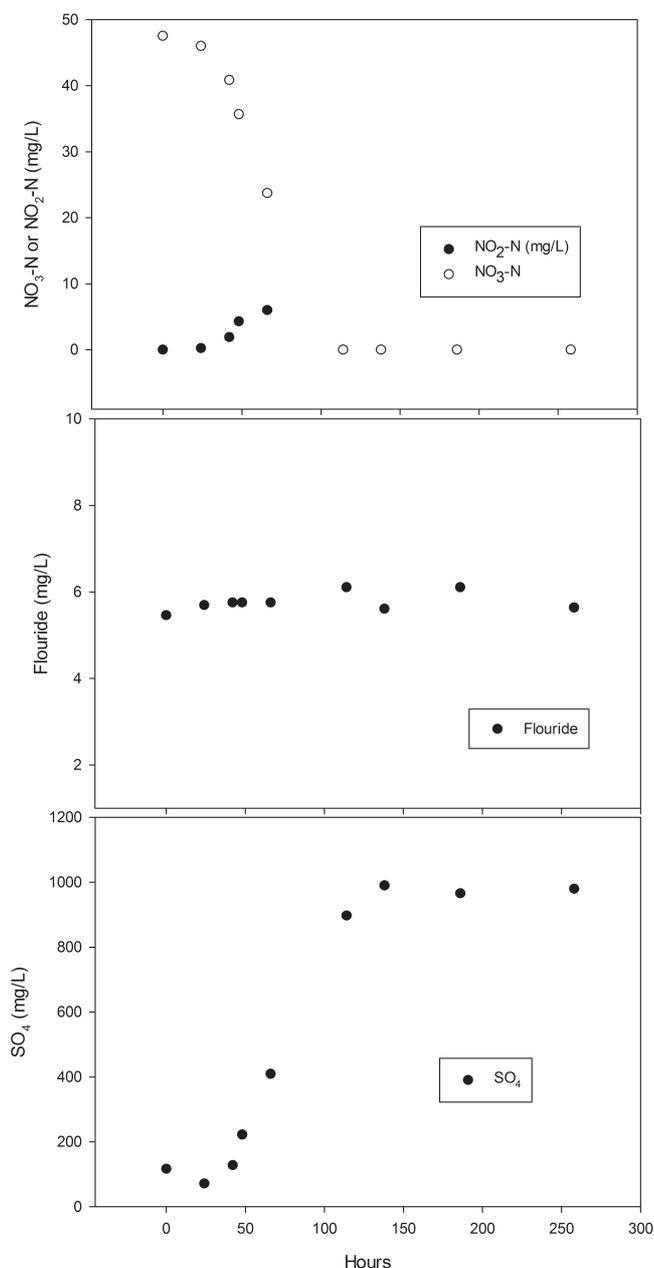


Fig. 6. Fate of monitored parameters in batch reactor

On the other hand, additional work is needed to prevent sulfate formation and nitrite accumulation during this process.

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