Biological Reduction of Nitrate from Secondary Treated Wastewater Using Sulfur-Limestone Reactor

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Abstract: ***This study evaluates the efficiency of autotrophic denitrification using a sulfur-limestone biofilter in removing nitrates from synthetic wastewater. Four nitrate concentrations (10, 45, 75, and 100 mg/l) were treated to determine the optimal hydraulic retention time (HRT) for each. Results showed that lower nitrate concentrations required shorter HRTs (3-4 hours) to achieve over 90% removal, while higher concentrations required longer HRTs (6-8 hours) for around 80% efficiency. Sulfate levels in the effluent remained below the guideline value of 500 mg/l, and pH levels did not exceed 8.8 due to the buffering capacity of limestone. The method offers a cost-effective and sustainable alternative for nitrate removal without external carbon sources or excessive sludge production.***

Keywords: Autotrophic denitrification, Sulfur-limestone biofilter, nitrate removal, Wastewater treatment, hydraulic retention time

1. Introduction

Water pollution with nitrate was an important problem and very necessary to treat it, especially that which comes from municipal wastewater treatment plant with a low BOD/N. Sulfur limestone autotrophic denitrification SLAD has become an important method for nitrate removal from secondary treated wastewater and because the organic materials in this kind of water does not degradable (1) so the autotrophic denitrification is better than heterotrophic one, this is for two reasons (2-3-4).

1-No need to add organic carbon sources and this reduces the cost and reduce the risk of secondary contamination.
2-Less sludge and this is reflected in the post-treatment cost.

Autotrophic denitrification in the sulfur-limestone reactor uses sulfur as an electron donor and nitrate as an electron receiver when converting to nitrogen gas according to Eq1: (5-6)

$55S+50NO3^{-}+38H2O+ 20CO2+ 4NH^{+}\ 4\rightarrow 55SO^{-2}{}_{4}+25N2 \uparrow + 64H^{+} +4C5H7O2N$ Eq1

In this process hydrogen ions are produced, indicating that alkalinity is consumed by the reaction. Therefore, alkaline like limestone is usually added in sulfur based autotrophic denitrification reactors, limestone also supplies inorganic carbon to autotrophic denitrifiers according to Eq2 (7-8).

$Caco3+H^{-}\rightarrow Ca+2+HCO3$-Eq2

The sulfur/limestone technology has been generally evaluated in lab scale bioreactors especially for drinking water treatment (9) and ground water treatment (10) and it is not commonly used in wastewater treatment.

Therefore, this study aims to evaluate the efficiency of nitrate removal using sulfur-limestone autotrophic denitrification and to determine the optimal hydraulic retention time across varying nitrate concentrations.

This study is significant as it explores a sustainable and low-cost method for nitrate removal using readily available materials, which could benefit small-scale or resource-limited wastewater treatment facilities.

2. Materials and Methods

The SLAD biofilter was an anoxic upflow fixed-bed reactor with a height of 160 cm and an internal diameter of 10 cm (fig1).

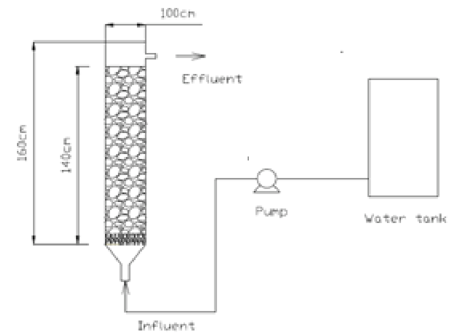


Figure 1: Schematic diagram of the SLAD biofilter

Sulfur and limestone were mixed homogeneously with a ratio of 1: 1 (v/v), and it was filled with sulfur and limestone particles (both 3-5 mm in diameter) and Pebbles (8-10mm in diameter) were packed at the reactor bottom as the supporting layer. (5)

The biofilter was seeded with 2L of anaerobic sludge taken from ALDOWER wastewater treatment plant. Homs. Syria.

And was fed with the culturing medium continuously, which was made from tap water containing: (5)

$Na_2S_2O_3.5H_2O$=0.5 g/l, KH_2PO_4=0.2g/l, KNO_3=0.2g/l, $NAHCO_3$=0.1g/l, NH_4CL=0.05g/l, $MgCL_2.6H_2O$=0.05g/l, $FeSO_4.7H_2O$=0.001g/l.

Sludge culture method as in research (5)

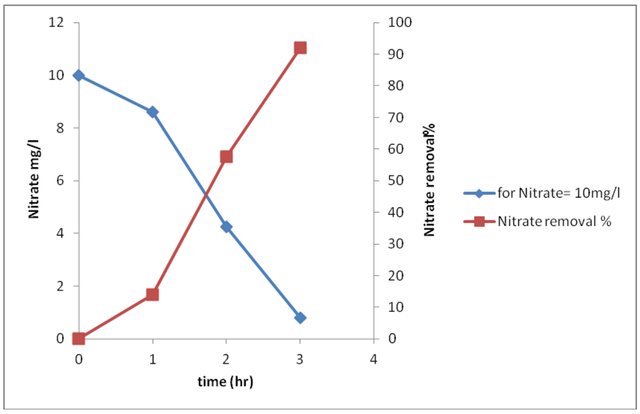
After the start-up stage, synthetic wastewater made from tap water containing KNO3 with different concentration of nitrate.

3. Results and Discussion

The following concentration (10-45-75-100) mg/l were studied during different hydraulic retention time (HRT):

The concentration 10mg/l:

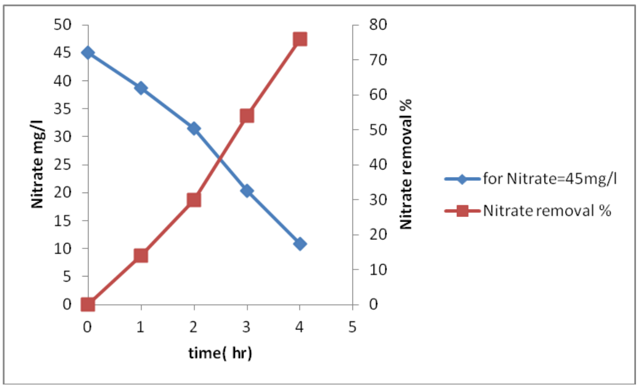
The fig (2) shows the changes during the time.



The figure (2) effluent concentrations, and corresponding removal efficiencies for influent concentration equal 10 mg/l

The concentration 45mg/l:

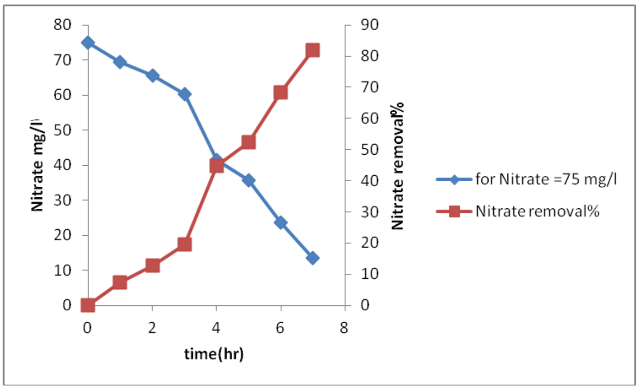
The fig (3) shows the changes during the time



The figure (3) effluent concentrations, and corresponding removal efficiencies for influent concentration equal 45 mg/l

The concentration 75mg/l:

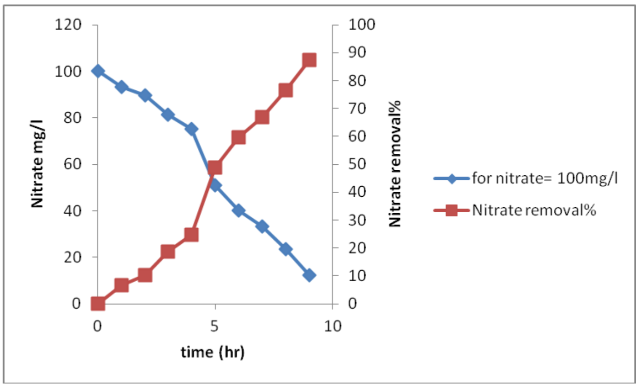
The fig (4) shows the changes during the time



The figure (4) effluent concentrations, and corresponding removal efficiencies for influent concentration equal 75 mg/l

The concentration 100mg/l:

The fig (5) shows the changes during the time



The figure (5) effluent concentrations, and corresponding removal efficiencies for influent concentration equal 100 mg/l

By observing the results fig (2-3-4-5) and taking into consideration that the allowed limits for nitrates about (10-15) mg/l (1-11), this study found that the influent concentration was a decisive factor by the required time for reducing nitrates, and low concentration of nitrate required short HRT to get a high removal rate, but high concentration required long HRT to get high removal rate, for example the 100mg/l as fig (5) most of the nitrate removal occurred after 8 hr, while 10 mg/l nitrate as fig (2) was removed by 90% in just 2.5hour.

Based on the data from this test, HRT of 3 hour was recommended for the nitrate concentration of less than or equal 10 mg/l as fig (2), 4hour for nitrate concentration until 45 mg/l as fig (3), 6hour or more was important to get good removal efficiency when the nitrate concentration is75mg/l or more as fig (4) and fig (5).

Sulfates

The effluent sulfate concentration about (80-400) mg/l as show at fig (6) and according to the influent concentration. in all cases this study found that, there was a direct correlation between the influent concentration (10-45-75-

100)mg/l and the effluent produced sulfate, and the level of sulfate was below 250 mg/l (which it is the guideline value in drinking water (12-13))for influent concentration equal 45 mg/l, and for bigger influent concentration, the level of sulfate was between (300-400)mg/l and this levels remain in lower than allowed limit wastewater that equal 500 mg/l according to guideline in treated waste water.

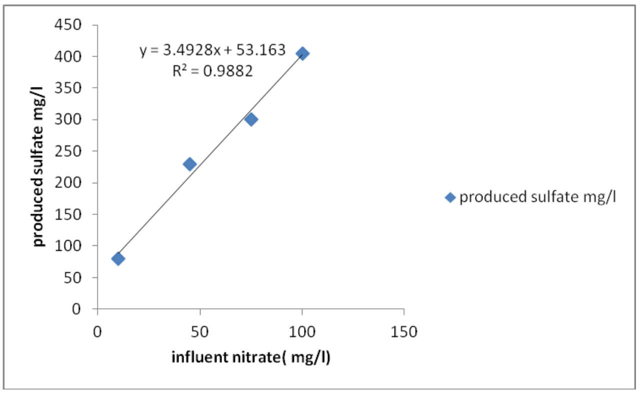


Figure 6 shows the relationship between influent nitrate (10-45-75-100) mg/l and effluent produced sulfate at end treating time.

pH:
Influent pH of the synthetic wastewater was adjusted to 7.2 (14), and although hydrogen ions are produced, and alkalinity is consumed in the SLAD reactor, and according to equation (1), the effluent pH was between (7.5-8.8) as shown in the fig7 this is because good ability of lime to modify the media without addition new alkaline materials when treating nitrate contaminated water.

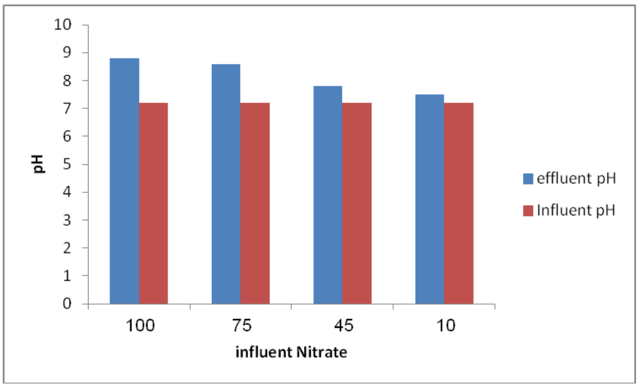


Figure (7) shows effluent PH according influent Nitrate concentration (10-45-75-100) mg/l at end treating time

4. Conclusions

- This study demonstrated that sulfur-limestone autotrophic denitrification is effective in removing nitrates from wastewater across a range of concentrations. shorter hydraulic retention times were sufficient for lower concentrations, while higher concentrations required extended durations.
- The resulting sulfate levels remained within acceptable limits, and pH values were stable, affirming the suitability of limestone for buffering.
- The reactor design offers a sustainable alternative to conventional methods, with minimal operational complexity and no need for organic carbon sources.
- Future research should explore bacterial community dynamics and optimize sulfur-limestone ratios for enhanced efficiency.

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