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Research Article

MATHEMATICAL MODELLING AND DETERMINATION OF THE NICKEL INHIBITION CONSTANT FOR NITRIFICATION

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ABSTRACT

Conversion of ammonia into nitrate is sensitive to a number of inhibitors. There is limited information on the nitrification inhibition coefficient and mathematical models in the current literature. The nickel inhibition constant was found in nitrogen removal using an activated sludge system. In the first set of experiments, nickel-free wastewater was used to determine the optimum operating conditions. In the second set of experiments, the effect of the nickel concentration on the system performance was investigated. The ammonium removal efficiency was not affected by low Ni concentrations (< 7mg/L). When the Ni concentration was increased to 11 mg/L, the nitrification efficiency decreased by more than 45.53%.
Based on the experimental results, a mathematical model was developed, and the nickel inhibition constants (KNi) were found to be 8.75 mg/L.
Keywords: Nitrification, nickel, nitrification kinetics, inhibition.

1. INTRODUCTION

Nitrification and denitrification processes are widely used in nitrogen removal from wastewater. Nitrification involves conversion of nitrogenous compounds into nitrite and nitrate by Nitrosomonas and Nitrobacter respectively [1-3]. Biological nitrification is a known method to reduce high ammonium concentrations in wastewater down to acceptable levels in receiving bodies. The kinetics and performance of a nitrification system depend on the slow growth rate of nitrification bacteria and their sensitivity to metallic toxic substances [4]. Since nitrification bacteria are sensitive to chemicals, they are considered to be possible biological analysis organisms in evaluation of toxicity levels [5]. As nitrification bacteria grow slowly and are sensitive to physical, chemical and environmental conditions, this may lead to nitrification instability in purification systems [3]. Nitrification bacteria rapidly enrich even at low temperatures during a longer sludge retention time [6,7].

Ni and Zn concentrations are present on high levels in various industrial wastewaters. Nickel is found in batteries, roll coatings, copper forming, electrical and electronic components, electroplating, iron and steel waste. Nickel concentrations up to 2950 mg dm^{-3} may be seen in electroplating wastewaters [8,9]. Heavy metals have a toxic effect on bacteria at certain

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concentrations and a negative impact on biological treatment efficiency [10]. Discharge of industrial and urban wastewaters containing heavy metals to receiving bodies is a significant cause of pollution [11]. Sato et al. (1986) found that inhibition of the growth of *Nitrosomonas europaea* is highly associated with nickel amine compounds[12]. Many studies have examined the effects of heavy metals on nitrification bacteria, because these metals and their complexes can inhibit nitrification by passing through bacterial cell membranes and disrupting their protein structure [13-15]. The most common theory used to explain the effects of cations on microorganisms is that a cation damages or neutralizes the critical enzyme [16]. A study by Harper et al. (1996) showed that, in the nitrification - denitrification process in leachate treatment, chromium (Cr^{+3}) and nickel (Ni^{+2}) cause inhibitory effects in the system at soluble concentrations of approximately 0.30 and 0.70 mg/L, respectively[17]. At a 1.0 mg / l nickel concentration, nitrification was partially affected, and there was a decrease in the NO_3-N concentration and an increase in the NH_4-N concentration [18]. In a system, nitrification inhibition was investigated by emphasizing the effect of copper and nickel shock load. As a result of applying different copper and nickel concentrations, *Nitrosomonas* was found to be equal to or more sensitive than *Nitrobacter* [5]. According to Skinner et al. (1961), Ni^{+2} has an inhibition effect on *Nitrosomonas* bacteria at a concentration of 0.25 mg/L[19]. Low nickel concentrations increase growth rates, while high nickel concentrations can inhibit nitrification processes [20,21]. For ammonia oxidizing bacteria and nitrite oxidizing bacteria, based on the Ni / MLSS ratio at different temperatures, the nickel inhibition half-speed constants (KI, Ni) were found as 5.4 and 5.6 mg Ni/g MLSS [13].

In this study, a nickel inhibition constant was found on nitrification bacteria, and a mathematical model was developed. The nitrification kinetics in bioreactors were modeled according to the 3 following models: 1) 0^{th} order kinetics, 2) Michaelis-Menten (Monod) and 3) Haldane[22].

2. MATERIAL AND METHODS

Experimental setup

The laboratory-scale experimental setup is shown Figure 1. The volumes in the aeration and settling tanks were 8.0 L and 3.0 L, respectively. The sedimentation tank was separated from the aeration tank. The reactor was continuously aerated, and the dissolved oxygen concentration was kept above 4.0 mg/L. The temperature in the reactor was 25 ± 1 °C.

Synthetic Wastewater

The synthetic wastewater was composed of 150 mg/L NH_4-N, 800 mg/L alkalinity ($CaCO_3$), 45 mg/L KH_2PO_4. 0.5 molar $NaHCO_3$ was automatically added to the aeration tank to keep the reactor pH at 7.5 ± 0.5. The nickel concentration ranged from 0 to 0.017 g/L. $NiSO_4.6H_2O$ was used as the nickel source. Influent wastewater was prepared synthetically with pure water. The micronutrients contained 50 mg/L $MgSO_4.7H_2O$, 5 mg/L $MnSO_4$. H_2O, 10 mg/L $FeSO_4.7H_2O$, 8.1 mg/L K_2HPO_4, 0.0046 mg/L $CuSO_4$, 0.023 mg/L $ZnSO_4$7H2O, 0.0119 mg/L $CoCl_2$ 6H2O, 0.066 Na_2MoO_4 $2H_2O$ and 1.0 mg/L H_3BO_3 [18,23].

Experimental Procedure and Analysis

Before starting the experiments, the reactor was operated intermittently to create enough bacteria in the reactor. The sludge age was adjusted by removing sludge daily from the aeration tank. The experiments started after the system reached a steady state (E>90%). In this study, the experiments were carried out primarily using nickel-free synthetic wastewater. The experiments were conducted at different hydraulic retention times (Θ_H) and sludge ages (Θ_C). The hydraulic retention time was changed between 3 and 21 hours. The sludge age was adjusted between 4 and 30 days. In the second series of experiments, the nitrification efficiency at different nickel concentrations (optimum hydraulic retention time and sludge age) was studied. The nitrification bacteria were obtained from the Lüleburgaz Domestic wastewater treatment plant (from the nitrification section). The bacteria were reproduced in laboratory conditions under the optimum growth conditions and used in the experiments. Daily samples were taken from the reactor effluent and analyzed. The samples were centrifuged before analysis. Ammonium nitrogen (No:1.14559.001, NH_4-N =4-80 mg /L and No:114752, NH_4-N =0.010-3.0 mg/L), nitrate nitrogen (No:1.14773.0001,NO_3-N=0.2-20mg/L) and nitrite nitrogen (No:114776,NO_2-N=0.002-1.00 mg/L) measurements were made using Merck brand Spectroquant analytical kits. Dissolved oxygen concentration measurements were made with a Hanna DO analyzer.

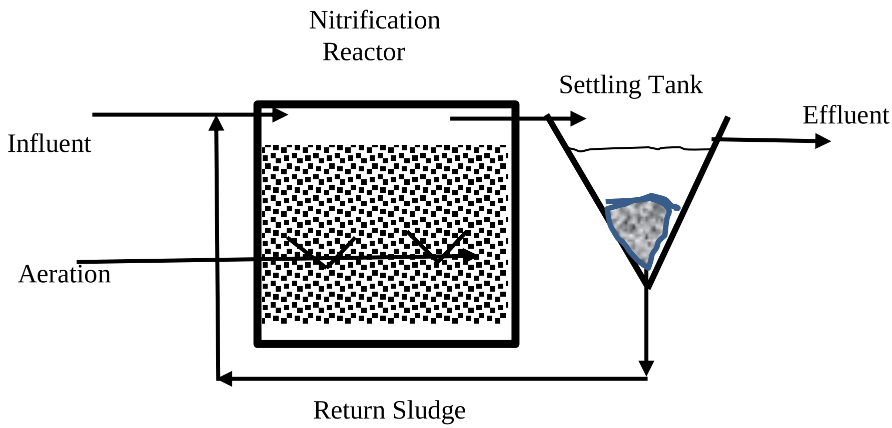

Figure 1. Laboratory-Scale Experimntal Setup

3. RESULTS AND DISCUSSIONS

The optimum sludge age and hydraulic retention time were studied in the first-phase experiments. Figure 2 shows the change in nitrate-nitrogen, nitrite-nitrogen and ammonium-nitrogen ions depending on the sludge age in a nitrification system. In this experiment, the optimum sludge age was determined in the system by using nickel-free wastewater. The hydraulic retention time was fixed for 30 hours. Each experiment was performed for a week after the system reached a steady state. The ammonium and nitrite concentrations decreased at the reactor effluent with increasing sludge age. It was determined that the nitrate concentration increased with increasing sludge age. The effluent ammonium nitrogen and nitrate nitrogen exchanges were found approximately the same in the sludge age range of 16-30 days. When the sludge age increased from 4 days to 20 days, the effluent nitrate nitrogen increased from 100.6 to 139.8 mg N/L. Contrary to the nitrate concentration, when the sludge age increased from 4 days to 20 days, the waste nitrite nitrogen decreased from 12.3 mg / L to 0.9 mg/L. When the sludge age was 4, 20 and 30 days, the effluent ammonium nitrogen concentration was found to be 32.1, 1.5 and 0.3 mg N / L, respectively. The optimum sludge age was found to be 20 days. Accumulation of nitrite in a short hydraulic retention time was due to the slow growth of Nitrobacter compared to Nitrosomonas bacteria. Hall et al. (1985) reported that more nitrate and biomass were formed during sludge retention times longer than 5 days[24]. The study conducted by Hocaoğlu et al. (2011) stated that nitrogen removal efficiency and kinetics changed significantly as a function of dissolved oxygen concentration and sludge age[25].

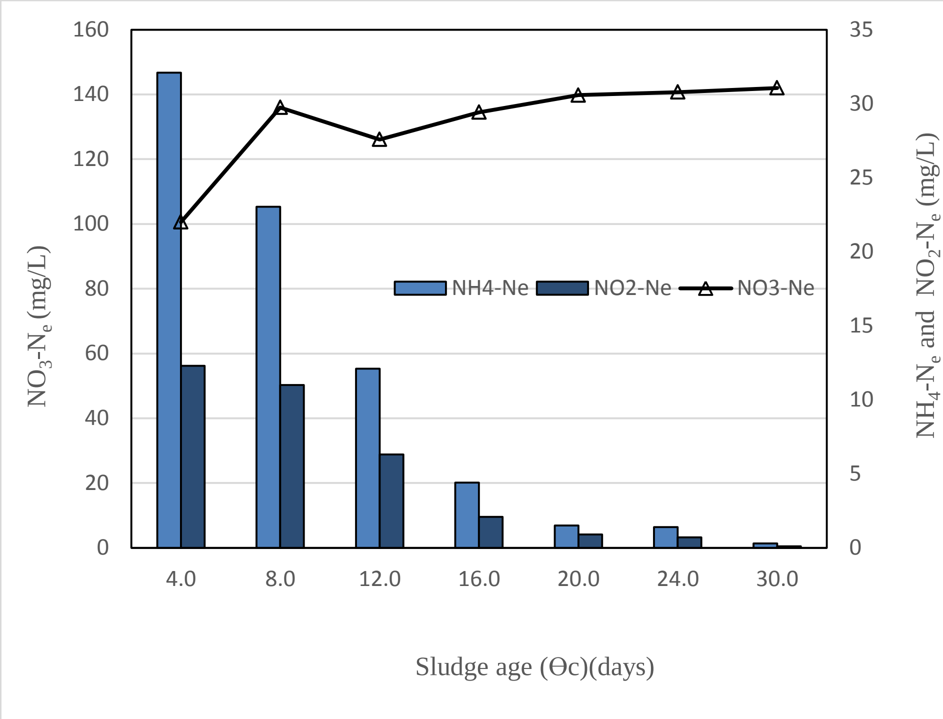

Figure 2. Variation of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen with sludge age (Θ_H=30 hours)

The change in NH_4^+-N, NO_2^--N and NO_3^--N with the hydraulic retention time for nickel-free wastewater is shown in Figure 3. The purpose of this experiment was to determine the optimum hydraulic retention time at a fixed sludge age (20 days). The effluent ammonium nitrogen concentration showed a decreasing trend with increasing hydraulic retention time. Similarly, the effluent nitrite concentration decreased with increasing hydraulic retention time. When the hydraulic retention time increased from 3 to 18 days, the effluent nitrate-nitrogen concentration increased from 55.7 to 141.2 mg N/L. Moreover, the nitrite nitrogen concentration decreased from 26.4 mg/L to 0.9 mg/L. In shorter hydraulic retention times, the nitrite buildup in the environment was due to the slow growth of Nitrobacter. The effluent ammonium nitrogen concentration decreased from 150 mg/L to 1.5 mg/L when the hydraulic retention time was 18 hours. The optimum hydraulic retention time was found to be 18 hours, resulting in almost complete nitrification (99%). Increases in the hydraulic retention time of more than 18 hours had little effect on the system's performance. In biological treatment, nitrification is limited to several genera, often called Nitrosomonas and Nitrobacter. The slow growth of these bacteria makes the nitrification process very sensitive to inhibition [26].

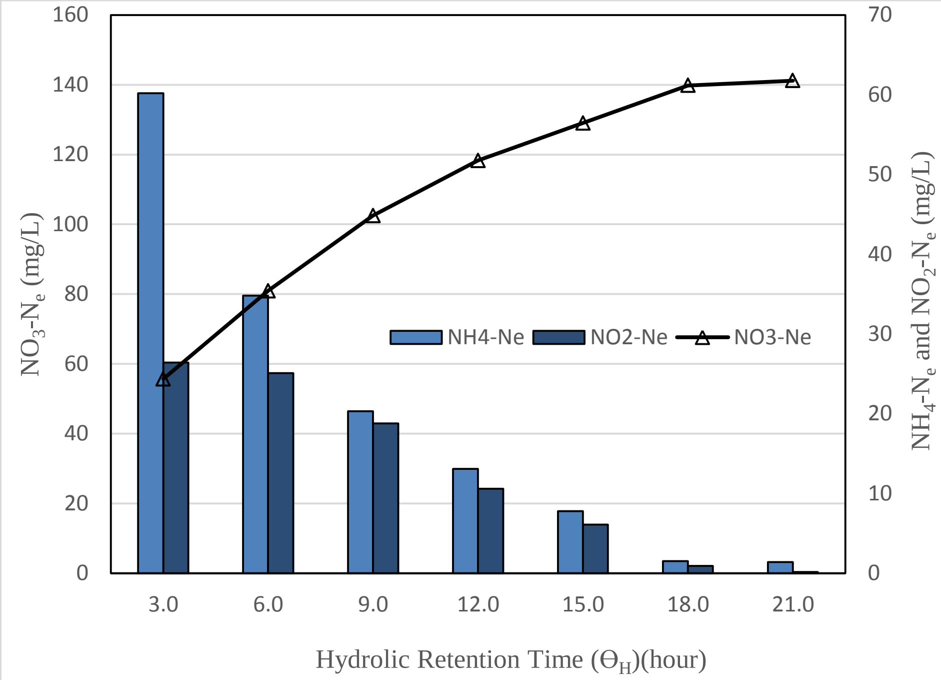

Figure 3. Variation of ammonia nitrogen, nitrate nitrogen and nitrite nitrogen with hydraulic retention time (Hours).

The effects of the nickel concentrations on the ammonium removal efficiency and conversion rate of ammonium to nitrite and nitrate are given in Figure 4. The conversion rates of nitrite and nitrate at 150 mg/L influent ammonium concentration were considered as the performance criteria at different nickel concentrations. The sludge age and hydraulic retention time were 20 days and 18 hours, respectively. Dinçer et al. (2000) found that nitrification efficiency increased with increasing sludge age (>12 days) and hydraulic retention time (>15 hours) [27].

The experiments were carried out with a nickel content of 3-17 mg/L to investigate the effects of nickel on nitrification. The nitrification efficiency was not affected by nickel concentrations below 3 mg/L. When the Ni concentration increased to 9 mg/L, the nitrification efficiency decreased by more than 30.5%. In a study by Lee et al. (1997), nickel concentration did not produce a significant inhibition of up to 100 mg/L[5]. A loss of 35% yield was detected at a 150 mg/L nickel concentration [5]. As seen in Figure 4, the system did not reach a state due to the inhibitory effects of nickel. The nitrate nitrogen concentrations in the wastewater decreased, and the nitrite nitrogen slowly increased with increasing nickel concentrations. A sharp increase in the effluent ammonium nitrogen concentration was found at nickel concentrations greater than 7 mg/L. In a study similar to this study, a 1.0 mg/L nickel concentration did not adversely affect nitrification, and little inhibition occurred at 5 and 10 mg/L nickel concentrations. It resulted in significant inhibition at a concentration of 50 mg/L of nickel [3]. The effect of heavy metals on nitrifying bacteria may potentially inhibit nitrification by disrupting proteins as metals and their complexes are transported across bacterial cell membranes [14,15].

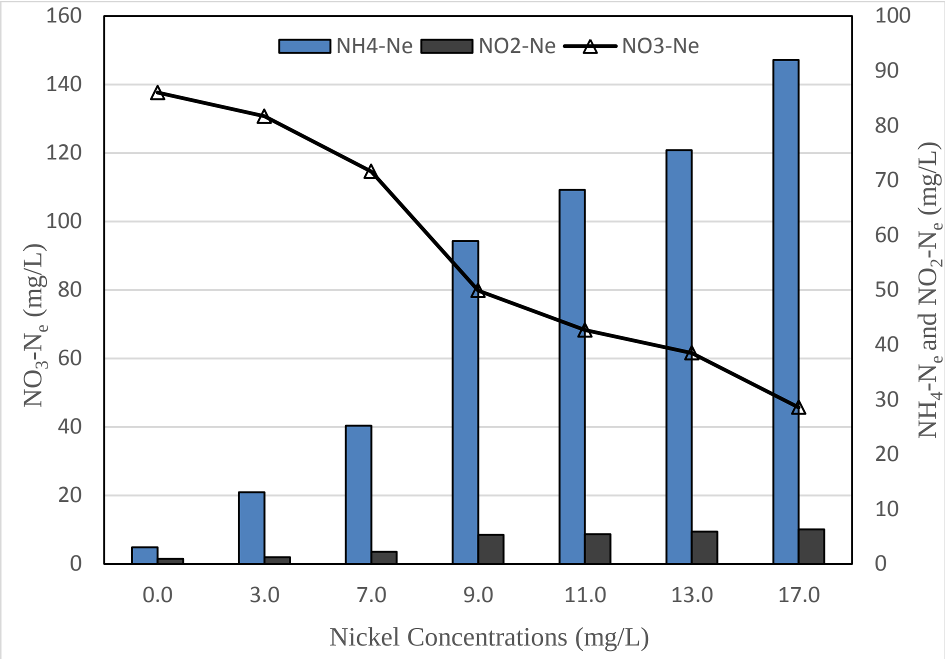

Figure 4. Effect of nickel concentrations effluent NO_3-N_e, NH_4-N_e and NO_2-N_e concentrations

Figure5 shows the variation of the nitrification rate with the nickel concentration. As the nickel concentration increased from 0 to 7 mg/L and 17 mg/L, the nitrification rate decreased from 8.17 mgN/L.h to 6.93 mgN/L.h and 3.22 mgN/L.h, respectively. When the nickel concentration increased from 3mg/L to 17 mg/L, the nitrification removal rate decreased by 60.59%. The reduction in the nitrification removal rate at 3mg/L nickel concentrations was around 6%. While 2 mg / L Ni (II) showed a slight increase in microbial nitrification rates and related enzyme activities, 5–30 mg / L Ni (II) was found to decrease basic enzymatic activity [28].

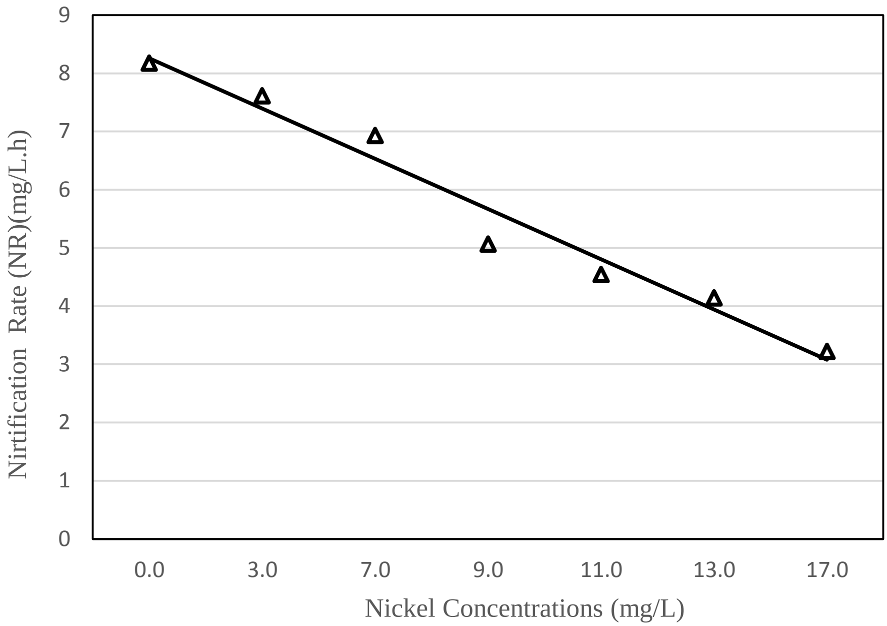

Figure 5. Variation of NH_4^+-N removal rate with nickel concentrations

In the current literature, there are many studies on heavy metals that inhibit nitrification [2-5,8,9,12-14,17-19]. There is no mathematical model for inhibition of nickel on nitrification. Using the experimental data with different nickel concentrations, a plot of 1/NR against Ni was created as shown in Figure 6. The following rate equation was used to determine the nickel inhibition constant [13,27,29,30].

$$\mathrm{NR} = \frac{\mathrm{Q(No-Ne)}}{\mathrm{V}} = \mathrm{NRo}\ \frac{\mathrm{KNi}}{\mathrm{KNi+Ni}} \tag{1}$$

Where KNi is the nickel inhibition constant (mg/L); Ni is the nickel concentration (mg/L); NR is the nitrification rate (mg/L.h); NRo is the nickel-free nitrification rate.

Equation 1 was converted to the following figure

$$\frac{1}{\mathrm{NR}} = \frac{1}{\mathrm{NRo}} + \frac{\mathrm{Ni}}{\mathrm{NRo*KNi}} \tag{2}$$

Figure 6 shows the 1/NR values against the Nickel concentrations. The following values were found from the slope and intersection of the line given in Figure 6.

NRo=10.13 mg/L.h and KNi=8.75 mg/L.

When the coefficients obtained from Figure 6 were replaced by equation 1, the following equation was obtained for nitrogen removal from nickel-containing wastewater.

$$\mathrm{NR} = 10.13\ \frac{8.75}{8.75+\mathrm{Ni}} \tag{3}$$

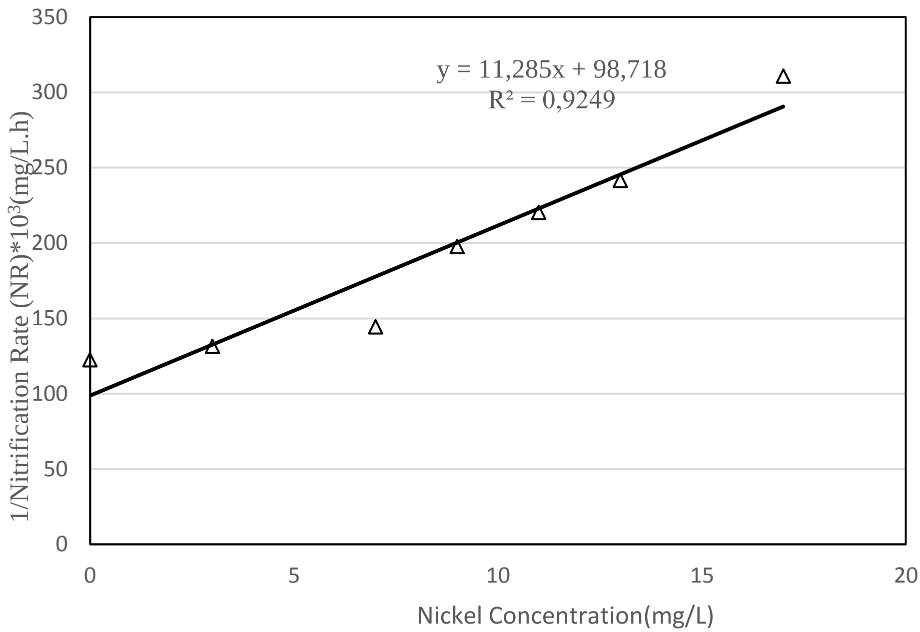

Figure 6. Variation of nitrification rate versus nickel concentration for determination of the nickel inhibition constant.

4. CONCLUSIONS

The yields of nitrification bacteria in a continuous flow reactor were investigated at different nickel concentrations. The ammonium removal efficiency decreased sharply at higher nickel concentrations in comparison to lower nickel concentrations. No sharp increase in the toxicity was observed until the nickel concentration increased to 7 mg/L. However, at 9 mg/L, there was a rapid increase in the ammonium in the effluent and a decrease in the nitrate concentration. The nitrite accumulation in the medium was limited against nickel inhibition. Increased nickel concentration had a greater impact on conversion of ammonium into nitrite. Based on the available data, the nickel inhibition constant KNi was determined to be 8.75. A mathematical model was developed in line with the available data.

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