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Single and Combined Effects of Copper and Nickel on Nitrification Organisms in Batch Units

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Abstract

Nickel and copper are widely encountered in the industrial wastewaters. The purpose of this batch experimental study was to evaluate single and combined effects of copper and nickel on the nitrification organism activities. Trace amounts of Cu2+ stimulate the activity of nitrifiers and ARRs increased from 0.225 to about 0.5 mg NH4-N/mg MLSS.day on the first day by elevating Cu2+ concentrations from zero to 0.05 mg/L, respectively. Nitrification inhibition was not observed during the experimental studies for the studied Cu2+ concentrations. The ARRs of the nitrification organisms were also found to have decreased by about 16 to 21 fold upon addition of Ni2+. Additions of Ni2+ negatively affect the ammonium oxidation and reaction was not detected during the operations of third day. The ARR values for the studied initial Ni2+ concentrations were lower than the blank sample. The simultaneous presences of Ni2+–Cu2+ negatively affect the activity of nitrification organisms. In order to achieve the same ammonium oxidation level as compared with the blank sample, it needs more reaction times. The experimental results indicated that it is possible to treat industrial wastewater Ni2+ and Cu2+ with individually or together. The toxicity of heavy metal could be minimized by increasing the microorganisms in the biological reactor.

Key words

Copper, Nickel, Nitrification

1. INTRODUCTION

Nitrification involves a sequential conversion of ammonium–nitrogen (NH_4^+–N) to nitrite– nitrogen (NO_2–N) and nitrate–nitrogen (NO_3–N), and the process is carried out by ammonia-oxidizing bacteria (AOB) and nitrite-oxidizing bacteria (NOB), respectively. Because of low growth rate of nitrifying bacteria and their high sensitivity to external factor, nitrification is the controlling step in biological nitrogen removal process [1, 2]. Nitrification is the most sensitive process in the biological wastewater treatment plants, with the autotrophic nitrifying biomass being about 10 times more sensitive than its aerobic heterotrophic part [3]. It has been reported by many researchers that nitrification activity can easily be inhibited by heavy metals and organics [1].

Biological treatment of industrial wastewater presents some difficulties due to its composition. In practice, wastewater treatment plants may be impacted by a stream of shock loading of industrial wastewater containing high concentration of heavy metals and caused deterioration in the performance of biological wastewater treatment systems [1,4]. Metals exist in wastewater in a soluble and particulate form. Settleable fractions of metals and their interactions with various components of water are removed in a primary settling tank. While 40–70% of cadmium, chromium, copper and lead is typically removed, the removal of nickel and manganese is significantly lower (20–30%)[5]. The aquatic life in water bodies receiving treated water include heavy metals is harmed to a great extent. Also, biological waste sludge fertilizers containing heavy metals lead to accumulation of metals in soil and cause harmful effects on vegetation, animals and humans along the food chain [4,6,7].

The presence of heavy metals in the industrial wastewater affects the microorganism activities in the biological wastewater treatment plant. Deterioration of heavy metals on the microorganism are usually overcome by adopting microorganism [4,7–9], applying various reactor types [10], low pollutants loads, and physical-chemical units with an increase in treatment costs [11].

Experimental studies on heavy metals inhibition on the biofilm and suspended growth systems have shown different results. The biofilm system was found to be 2-600 times higher capacity to resist heavy metals stress than suspended growth process. Nitrification organisms in biofilm were more tolerance than organisms in suspended flocs when subjected to shock loads of heavy metals [12]. Lee et al. [12] reported that the biofilm system was able to tolerate a higher total copper concentration (about more than 1.6 times higher) than suspended growth system. Due to the conventional wastewater treatment methods may partially remove heavy metals, residue of heavy metals in the treated waters cause serious problem to the aquatic organisms.

Nickel and copper are widely encountered in the industrial wastewater. Although trace concentrations of copper and nickel have been identified as micronutrients for microorganisms and stimulate the microbial activity, they are both growth inhibitors at high concentrations. Most of the industrial wastewaters usually contain more than one heavy metal. However, most countries have set the maximum acceptable heavy metal concentrations in the water for each heavy metal alone [13]. Nitrifying bacteria are considered as more susceptible to heavy metals toxicity than heterotrophic microorganisms [14,15]. Compared with Zn, Ni, Cd and other kinds of metals, Cu is considered as more toxic due to it may induce rapid loss of membrane integrity, so longer time is required for natural recovery after inhibition [1]. The molar inhibitory effect of heavy metal toward ammonium oxidation was reported as Cu^{2+}>Zn^{2+}> Cd^{2+}> Ni^{2+} by Hu et al.[16].

The purpose of this experimental study was to determine single and mixture effects of copper and nickel on the nitrification organisms in a batch unit.

2. MATERIALS AND METHODS

2.1. Feed wastewater

The synthetic wastewater contained micro and macronutrients were used throughout the experimental studies. Microorganisms, which were drawn from the nitrification unit of domestic wastewater treatment plant, were acclimatized to NH_4-N with medium solution prepared daily in a tap water. The inoculation conducted in a 5 L mixing and aerated vessel. The inoculation lasted approximately one month for microbial growth with daily replenishment of medium solution.

Table 1. Synthetic wastewater constituents

chemicals	concentrations (mg/L)	chemicals	concentrations (mg/L)
NH_4Cl	50-70	$CoCI_2.6H_2O$	0.0119
Na_2EDTA	4.83	$Na_2MoO_4.2H_2O$	0.066
$CuSO_4$	0.0046	$MgSO_4.7H_2O$	36.97
$ZnSO_4.7H_2O$	0.023	$NaHCO_3$	226
$CaCI_2.2H_2O$	36.74	$FeCI_3.6H_2O$	0.316
H_3BO_3	1.0	KH_2PO_4	1920

2.2. Batch Experiments

In order to determine the effects of single and mixture of Ni^{2+} and Cu^{2+} concentrations on the nitrification bacteria, batch experiments were carried out in 500 mL glass bottles, containing medium solutions and NH_4-N. After adding acclimated microorganisms into synthetic wastewater, the pH of mixed liquor was adjusted to 7.5 using alkaline solution of 10 N NaOH and bicarbonate buffer was added into the batch unit. The total volume of liquor was 200 mL. The dissolved oxygen concentration was kept over 2.0 mg/L throughout the experimental periods. Experimental studies were performed by varying the concentrations of Cu^{2+} (0.005–2.0 mg/L) and Ni^{2+} (0.005–2.0 mg/L) in three batch units for each concentration. Combined effects of heavy metals were investigated at various initial concentration ratios of Ni^{2+}/ Cu^{2+} (I: 0.00/0.00– II:0.01/0.2–III: 1.0/1.0– IV: 0.5/1.5– V: 2.0/2.0, and VI: 3.0/3.0 mg/L).

In order to compare the results, three blank samples (without heavy metals) were used through all batch procedures. Acclimated nitrification microorganisms about 50 mg/L were included for each batch units.

Batch units were placed on a shaking incubator at 150 rpm and constant temperature of 35 ^{0}C. The samples were withdrawn daily from batch units and filtered using 0.45 μm filters. The pH and DO level of solutions were checked daily. Concentrations of NH_4-N, NO_3-N, and NO_2-N in the clear samples were analyses at least three times.

The batch experiment was completed when the concentrations of NH_4-N was lower than 0.5 mg/L for each heavy metal concentrations. Concentrations of NH_4-N, NO_3-N and NO_2-N in the clear samples were measured with the Merck photometer (Nova 60 Model) using analytical kits; NH_4-N (14752), NO_2-N (14776) and NO_3-N (14773).The mixed liquor suspended solids (MLSS) analysis was carried out according to APHA [17].

3. RESULTS AND DISCUSSION

When the pH of mixing solution decreased to 7.0±0.1 because of the conversion of NH_4-N to NO_2-N and NO_3-N, pH was increased to about 7.5±0.1 by using alkaline solution in a day. Batch experiments at various single and mixture of Ni^{2+} and Cu^{2+} concentrations were carried out to highlight the differences between nitrification rates with and without heavy metals.

3.1. Effects of Copper Concentration

Effects of copper concentrations on the ammonium removal rates (ARRs) are presented in Figure 1. Considerable ARR difference between 0.005 and 0.04 mg Cu^{2+}/L were not observed. Trace amounts of Cu^{2+} stimulate the activity of nitrifiers and ARRs increased from 0.225 to about 0.55 mg NH_4-N/mg MLSS.day on a first day by elevating Cu^{2+} concentrations from zero to 0.05 mg/L, respectively. Up to the initial concentration of 0.05 mg/L, nitrification reaction was complete in five days. Further increase the concentrations of Cu^{2+} from 0.05 mg/L to 2.0 mg/L, the ARR steadily decrease and NH_4-N oxidation was almost completed in seven days. Due to the residue NH_4-N concentration in the solution decreases, the ARRs value decreased. The lowest ARRs value was observed at the concentration of 2.0 mg Cu^{2+}/L.Nitrification inhibition was not observed during the experimental studies for the studied Cu^{2+} concentrations. The concentrations of NH_4-N were lower than 0.5 mg/L for each Cu^{2+} concentration at the end of the experimental study.

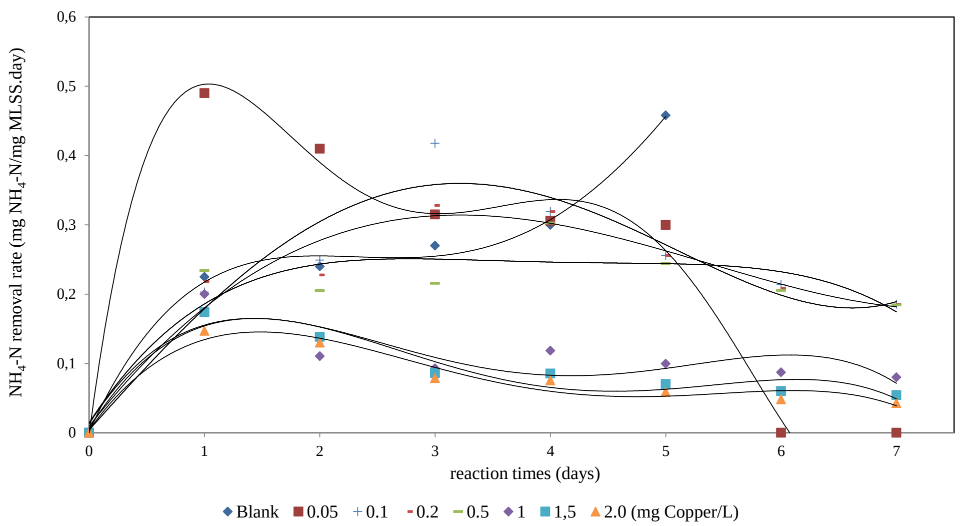

Figure 1.The ARRs variation at different Cu^{2+} concentrations.

3.2. Effects of Nickel Concentration

As can be seen in Figure 2 that, the NH_4-N oxidation steadily decreased significantly as the applied Ni^{2+} concentration to the nitrifying biomass increased. The AARs of the nitrification organisms was also found to have decreased by about 16 to 21 fold upon addition of Ni^{2+}. On the first day of operations, oxidation of NH_4-N was not detected for the studied concentrations of Ni^{2+} while ARR was 0.16 mg NH_4-N/mg MLSS.day for the blank sample. Additions of Ni^{2+} negatively affect the ammonium oxidation. The ARR values for the studied initial Ni^{2+} concentrations were lower than the blank sample. Until the third day of reaction, ammonium oxidation was not observed. The ARR values steadily decreased by increasing the initial Ni^{2+} concentrations in the solution.

The highest ARR of 0.45 mg NH_4-N/mg MLSS.day was observed when the nitrification culture was exposed with 0.05 mg Ni^{2+}/L.

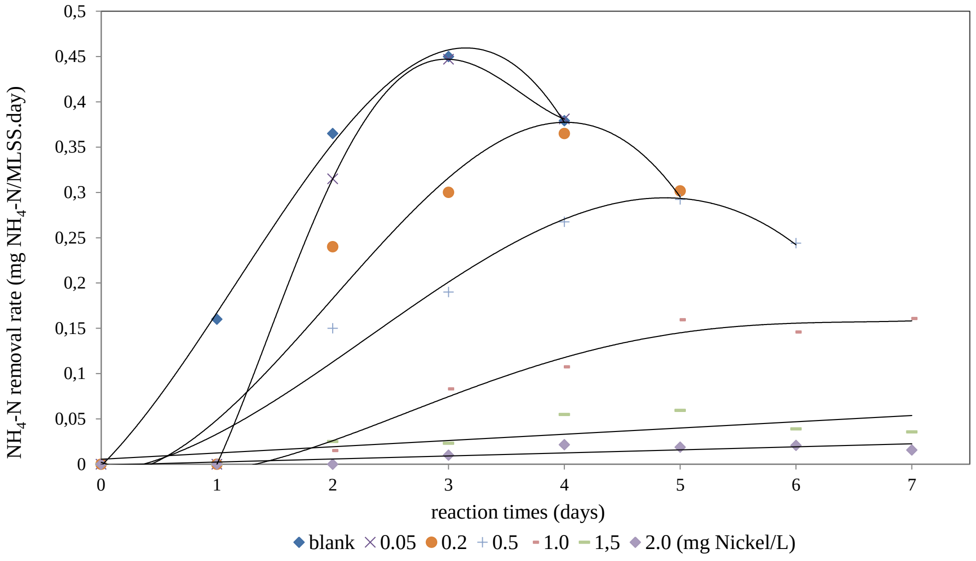

Figure 2.Effects of Ni^{2+} on the ARRs.

3.3. Effects of Cu^{2+} and Ni^{2+} mixture on the nitrification process

Batch experiments were carried out with various combinations of Ni^{2+}– Cu^{2+} for the initial MLSS concentrations of 100 and 200±10 mg/L. The effects of Ni^{2+} and Cu^{2+} mixture on the ammonium oxidations are depicted in Figure 3 and 4. The simultaneous presences of Ni^{2+}– Cu^{2+} negatively affect the activity of nitrification organisms. In order to achieve the same ammonium oxidation level as compared with the blank sample, it needs more reaction times. Although no significant difference was found between the removal efficiency of blank and 0.2–0.01 mg Ni^{2+}– Cu^{2+}/L mixtures, the NH_4-N removal efficiency was decreased with increasing of Ni^{2+}– Cu^{2+} concentrations. The ARRs decreased with increasing Ni^{2+}–Cu^{2+}concentrations from zero to 3.0–3.0 mg/L.

As shown in figures the inhibition level of heavy metal mixture was strongly dependent on the MLSS concentrations. Adding of Ni^{2+}– Cu^{2+} together resulted in decrease activity of nitrification organisms and NH_4-N oxidation rate was decreased. A decrease of 99.9% to 57% of NH_4-N oxidation was observed when the mixture concentrations were increased from zeroto 3.0 mg Ni^{2+}/ 3.0 mg Cu^{2+}/L. Removal efficiencies of NH_4-N increased about 10% with increasing MLSS concentration at all studied Ni^{2+}/Cu^{2+} combinations.

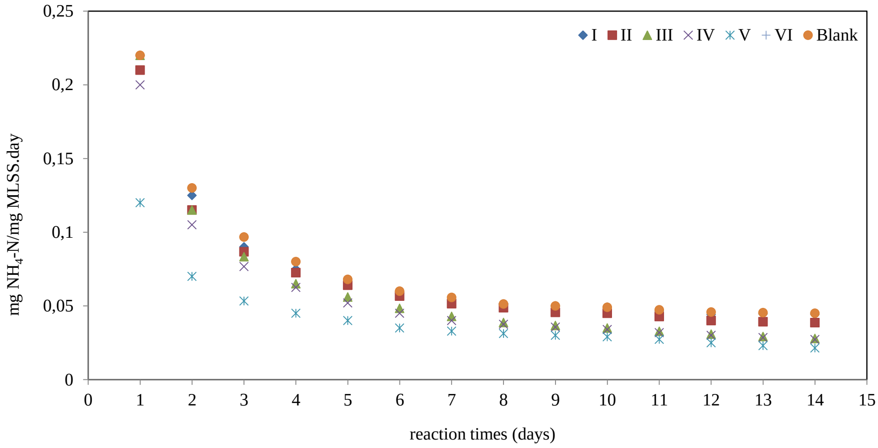

Figure 3. Combined effects of Cu^{+2} and Ni^{+2} on ARR_S

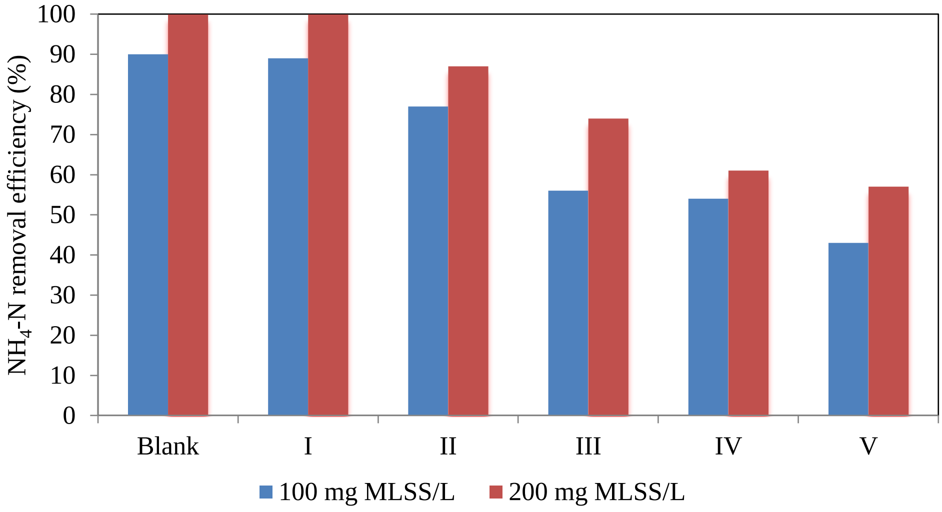

Figure 4. Combined effects of Cu^{+2} and Ni^{+2}at various MLSS concentrations

4. CONCLUSION

The effect of single and mixtures of Cu^{2+} and Ni^{2+} on the nitrification process were investigated. When the individual effect of nickel was studied, no nickel concentration causing any stimulation was observed, as happened with 0.05 mg/L of Cu^{2+}. The toxic inhibitory effect of nickel was found to be considerably higher than that of copper for the studied concentrations in the experiments. Combinations of Cu^{2+} and Ni^{2+} introduced to the wastewater might produce serious upsets in the nitrification process. Results showed that the toxicity of heavy metal could be minimized by increasing the microorganisms in the biological reactor

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