

Effects Of Naproxen On The Nitrification Rates In A Laboratory Scale Biological Wastewater Treatment Reactor

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Abstract—The effects of salinity and the presence of Pharmaceutical active Compounds (PhACs) on the biological treatment efficiency of a lab scale bioreactor with aeration were investigated. The combined effect of salinity and Presence of a pharmaceutical compound Naproxen on the nitrification process was investigated. Naproxen was observed to cause significant inhibition of the ammonia oxidation process with a consequent decrease in nitrification activity and efficiency. An initial Nitrification rate of $4.5 \text{ mg NH}_4\text{-N L}^{-1} \text{ h}^{-1}$ was estimated. Decreased Nitrification rates were observed with the introduction of naproxen into the reactor system. Decrease in Nitrification rates from $4.5 \text{ mg NH}_4\text{-N/l-h}$ to $2.5 \text{ mg NH}_4\text{-N/l-h}$ at 1ml, $0.5 \text{ mg NH}_4\text{-N/l-h}$ at 5ml and $0.5 \text{ mg NH}_4\text{-N/l-h}$ at 100ml naproxen solution respectively. Though inhibition was pronounced the system was observed to have recovered and oxidized ammonia to nitrates.

Keywords—Salinity, PhACs, Naproxen, Bioreactor, Aeration, Nitrification, Denitrification.

1. INTRODUCTION

Biological wastewater treatment process is essential for the treatment of municipal wastewater streams for environmental pollution prevention and control. Conventional systems utilize bacteria cultures for the transformation and oxidation of dissolved and suspended organic and inorganic compounds in solution into biomass with the evolution of gases.

The increasing use of seawater for toilet flushing in arid areas due to water shortages, effluent wastewater discharged from industries- fish processing and packaging, vegetable pickling, road deicing, and the inflow of highly saline sea water into sewer systems in coastal areas increases the salt contents of water treatment systems. (Panswad and Anan, 1999; woolard and Irvine ,1995). The effects of salinity on wastewater treatment systems for nutrient removal have reported by several researchers (Uygur, 2006; Sohair, et al, 2010; Dincer and Kargi, 2010, Kincannon and Gaudy, 1966).

Pharmaceutical active compounds and their metabolites have been identified in wastewater and are most often introduced into the environment through wastewaters from homes, hospitals,

(including veterinary clinics), pharmaceuticals producing industries and landfill leachates in significant concentrations (Bound et al, 2007, Gomez, et al, 2007).

Considered potentially harmful environmental contaminants, non-steroidal, anti-inflammatory (NSAID) (such as ibuprofen, diclofenac and naproxen), anticonvulsant/anti-epileptic (- carbamazepine, primidone) and antibiotics (lincomycin penicillin, tetracycline and sulfonamides), analgesics and anti-inflammatory (paracetamol, acetylsalicylic acid) have been detected in surface waters, ground water and wastewaters, (Tixier et al, 2003, Virkuyte et al, 2010, Heberer, 2002). The toxicity and inhibitory effect of the presence of pharmaceuticals on the activity of nitrifying bacteria in WWTP have been reported by researchers (Halling-Sorrensen; 2000 Carrucci et al, (2006).

Wang and Gunsch (2011) reported inhibition of nitrite production by PhACs at concentrations of 1 and $10 \mu\text{m}$ at 3 and 4hrs time periods. Naproxen was observed as having the highest nitrification inhibition percentage of 29% at the end of a 4h period. It was also observed that at concentration of $0.1 \mu\text{m}$ no inhibition occurred. However at the maximum concentration of pharmaceutical tested significant inhibition of ammonia oxidizing ability of the bacteria *Nitrosomonas Europeae* was observed, (Wang and Gunsch, 2011).

The objective was to study the effects of seawater salinity and the presence of pharmaceutically active compounds on the biological treatment of municipal wastewater. Special focus was given to the toxic effects of Naproxen on the nitrification activity of the treatment process.

2. MATERIALS AND METHOD

2.1 EXPERIMENTAL SET-UP

Batch degradation studies were carried out in a batch reactor of a 2000ml capacity. The reactor was filled sea water and wastewater from the Godalming wastewater plants to a volume of 13000ml. Air was introduced to circulate and aerate the reacting mixtures throughout the study period. Before experimental start up for wastewater degradation, wastewater was continuously aerated for 2 days to reactivate bacteria incubated during the period of

refrigeration. Pre-aerated wastewater was fed into the reactor containing sea water with the aid of a feed pump (Watson Marlow, 505DU). Volume of wastewater in the reactor was replenished after treated effluent extraction. Effluent was extracted manually using a suction tube and analyzed.

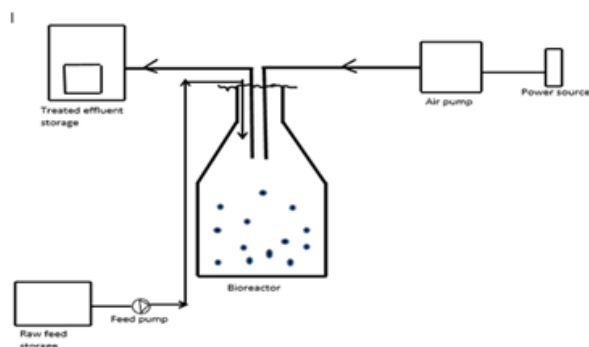


Fig 1: Schematic Representation of Experimental Set-up

The wastewater for batch degradation studies was obtained from the Godalming wastewater treatment. Sampling was done at the effluent point of the primary sedimentation tank. Saline environment needed was achieved by use of raw sea water for the wastewater treatment. Sea water was obtained from the English sea side town of little Hampton in west Sussex. Table 1 presents the raw wastewater characteristics.

Reactor was operated at an initial feed rate of 17mg NH₄-N/l and organic loading rate of 164mg COD/l with Influent sea water salinity of 35g/l. The Reactor was operated with aerobic/anaerobic cycle maintained all through the study period. Treated effluent water was extracted at intervals and analyzed.

2.2 ANALYSIS

Settled effluents water samples were extracted and filtered using the Del-Agua filtration device connected to a vacuum pump before analysis. Ammonia-nitrogen and Nitrates were performed after sample filtration using the Hach DR 890 spectrophotometer according to standard methods (APHA, 1995).

2.3 BATCH ASSAYS

Nitrification/Denitrification toxicity assays tests were carried out in the reactor to determine the effects of salts and the naproxen on the ammonia oxidation and nitrates denitrifying process. The activity test closely represents the nitrification and denitrification processes in wastewater treatment plants. Nitrifying activity was measured in order to determine ammonia oxidation activity of *Nitrosomonas* in the presence of oxygen. Denitrification activity was measured in the absence of oxygen using methanol as an external source of carbon.

Naproxen toxicity assays were performed using 500mg/l solution of naproxen fed 1ml, 5ml and 100ml into the reactor and inhibition activity investigated.

3. RESULTS AND DISCUSSIONS

Reactor feed wastewater was fed at an organic loading rate of 71mg BOD/l and ALR of 17 mg NH₄-N/l. Seawater salinity was 35g NaCl/l.

Table 1: Raw feed Wastewater and Seawater Characteristics.

Parameters	Values
Ammonia nitrogen	17 mg/l
Total nitrogen	8 mg/l
Phosphorus	15.7 mg/l
COD	164 mg/l
BOD	71 mg/l
TSS	7.2 x 10 ⁻³ mg SS /l
P ^H	6.95

3.1 NAPROXEN TOXICITY TEST- Nitrification inhibition assays were performed in activated sludge process to monitor the disappearance of ammonium containing compounds and the appearance of nitrites and nitrates, results obtained used to assess nitrification inhibition rates of Naproxen in wastewater treatment process. Plots of toxicity assays are presented below:

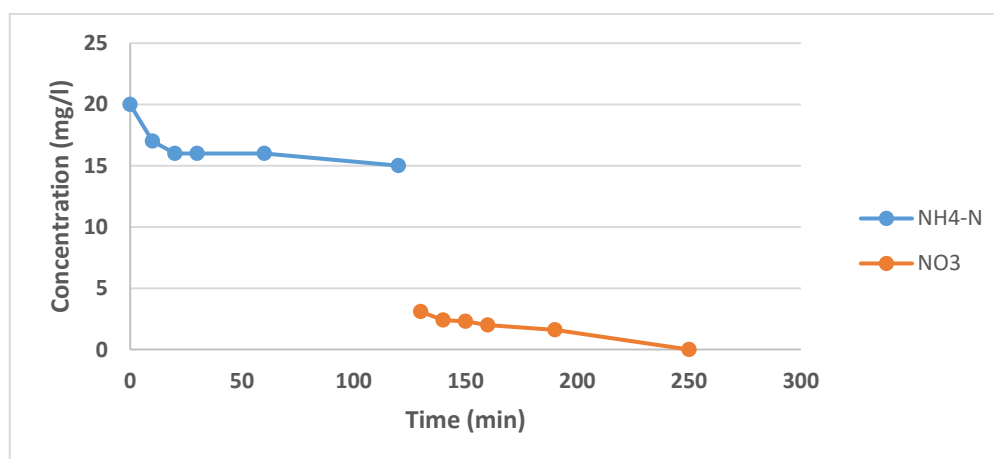


Fig 2a: Nitrification toxicity test using 1ml Naproxen solution

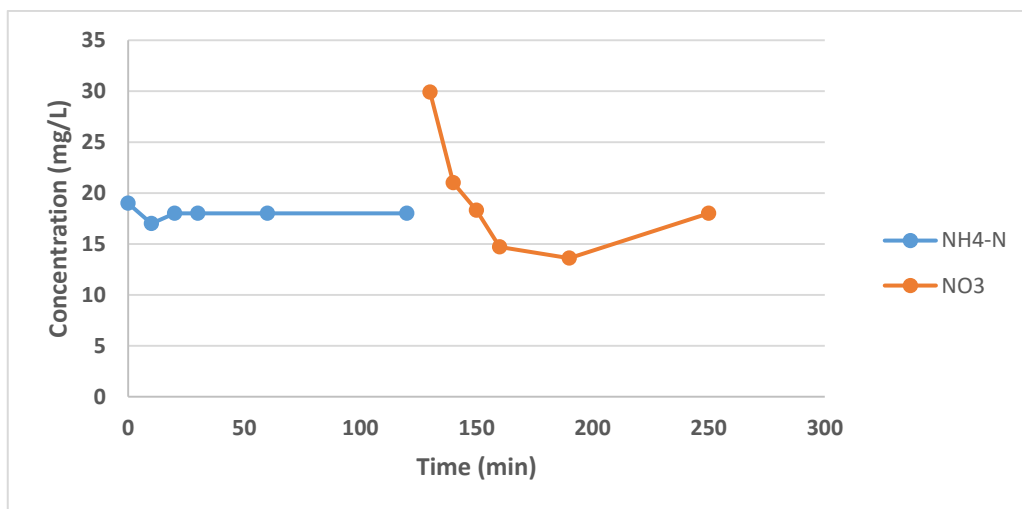


Figure 2b: Nitrification inhibition test using 5ml Naproxen.

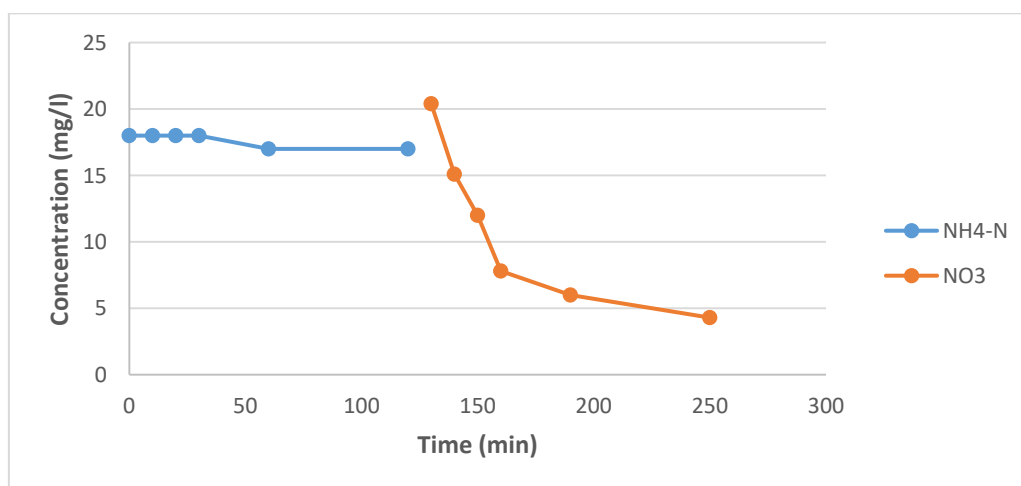


Figure 2c: Nitrification inhibition test using Naproxen at 100ml.

The effect of naproxen on nitrification inhibition was monitored using 1ml, 5ml and 100ml volumes of 500mg/l Naproxen solution. All concentration as shown above caused significant inhibition of the ammonia oxidation in the reactor system. Percentage inhibition was observed to be 95%, 75% and 94.4% for 1ml, 5ml and 100ml respectively. Though inhibition was pronounced, the system was observed to have recovered in less than 4 days period. Nitrification rates were observed to have decreased from 4.5 mg NH₄-N/l.h. to 2.5mg NH₄-N/l.h at 1ml, 0.5 NH₄-N/l.h at 5ml and 0.5 mg NH₄-N/l.h at 100ml respectively.

Though inhibition was pronounced the system was observed to have recovered and oxidized ammonia to nitrate this is in agreement of observations made by Metcalfe et al, (2003) in which analysis of sewage effluents in STP showed 100% removal of Naproxen. A study by Wang and Gunsch (2011) on the effects of PhaCs commonly found in wastewater on the

ammonia oxidizing bacteria *N.europaea* observed a maximum naproxen inhibition of nitrification of 29% the highest of all the PhaCs studied. The high inhibition observed in this study as compared to others in literature reported could be due to the combined effects of the naproxen inhibitor and salinity of the reactor environment.

It was postulated that the inhibitory mechanism of PhaCs in wastewater treatment could be as a result of changes in AMO by changing the membrane permeability. It is believed that cellular leakages as a result of toxicity and interference of PhaCs with the AOB, compromise cellular integrity with possibility of death of the ammonia oxidizing bacteria *Nitrosomonas*. It was thus suggested that inhibition was a result of membrane damage and not competitive inhibition of AMO as inhibition was observed to continue after removal of PhaCs (Wang and Gunsch, 2011).

4. CONCLUSION

- Nitrification rates was estimated to be $4.5 \text{ mg NH}_4\text{-N L}^{-1} \text{ h}^{-1}$ and specific nitrification rate was estimated at $18.18 \text{ g NH}_4\text{-N/g VSS}$. The denitrification rate were observed to be almost twice nitrification rate at $10 \text{ mg NO}_3\text{-N L}^{-1} \text{ h}^{-1}$ and specific denitrification rates of $40.40 \text{ g NO}_3\text{-N/ g VSS}$.

- Naproxen was observed to cause significant inhibition of the ammonia oxidation process with consequent decrease in nitrification activity and efficiency.

- Nitrification rates were observed to have decreased from $4.5 \text{ mg NH}_4\text{-N/l-h}$ to $2.5 \text{ mg NH}_4\text{-N/l-h}$ at 1ml, $0.5 \text{ mg NH}_4\text{-N/l-h}$ at 5ml and $0.5 \text{ mg NH}_4\text{-N/l-h}$ at 100ml respectively. Though significant nitrification inhibition was observed, inhibitory effect was reversed and ammonia oxidation efficiency recovered to conditions before the introduction of the naproxen in the system.

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