

Biodegradation of MCPA and Nitrate Removal in an Anoxic SBR

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Summary

This research achieved 98 % removal of the herbicide MCPA when it was fed at a concentration of 50 mg/L to an SBR operating under anoxic conditions.

Keywords: MCPA, nitrate, removal

Introduction

MCPA (2-methyl-4-chlorophenoxyacetic acid) is a selective, post-emergence herbicide frequently used to control broad leaf weeds in New Zealand (Costa et al., 2013). In 2013, approximately NZ \$7.5 million was invested to import MCPA from around the world (Statistics New Zealand, 2013). Unfortunately however, pollution of aqueous environments is caused by the discharge of MCPA originating from manufacturing plants, transportation and storage sites and/or accidental spills.

Some notable studies have shown that denitrifying microorganisms can acclimatize to industrial-strength concentrations of pesticides (e.g. 2,4-D) in a SBR regime (He and Wareham, 2009); however, there does not seem to be any studies that specifically focus on the ability of denitrifying microorganisms to degrade MCPA in an SBR. As such, the major aim of this work was to investigate the potential of MCPA biodegradation by activated sludge microorganisms under anoxic conditions. The research was divided into three phases; namely, Phase I (a proof-of-concept phase); Phase II (an initial “limit” exploration phase) and Phase III (effect of HRT phase).

Materials and Methods

A 20 L SBR bioreactor was constructed and inoculated with 10 L of activated sludge from a local wastewater treatment plant in Christchurch, New Zealand. To maintain a constant COD, a synthetic wastewater using acetate was prepared having approximately the same characteristics as municipal wastewater (i.e. 300 - 350 mg/L of COD). The target COD: NO₃-N ratio of 3.0 to 3.4 was achieved with NaNO₃ injected twice per cycle to provide an electron acceptor (NO₃-N). A long SRT of 40 – 60 days allowed for slow-growing biomass under anoxic conditions while a 24-hr HRT was initially selected. Filling, mixing/reacting, settling and decanting functions were controlled via a programmable controller. During Phase I, 20 mg/L of DMCPA (MCPA in the form of dimethylamine salt) was fed to the biomass; however once complete MCPA degradation was observed the herbicide concentration was increased to 50 mg/L (Phase II). A solid phase micro extraction (SPME) technique was used to extract the pesticide from wastewater samples, with herbicide analysis performed on a gas chromatograph HP 6890 series, equipped with a Ni-63 electron capture detector.

Results and Discussion

Baseline data collected prior to feeding MCPA into the bioreactor showed that TSS and VSS values stabilized at 4000 ± 400 mg/L and 2800 ± 300 mg/L respectively, with track studies revealing more than 98 % removal of the COD and NO₃-N within the first five hours' time period.

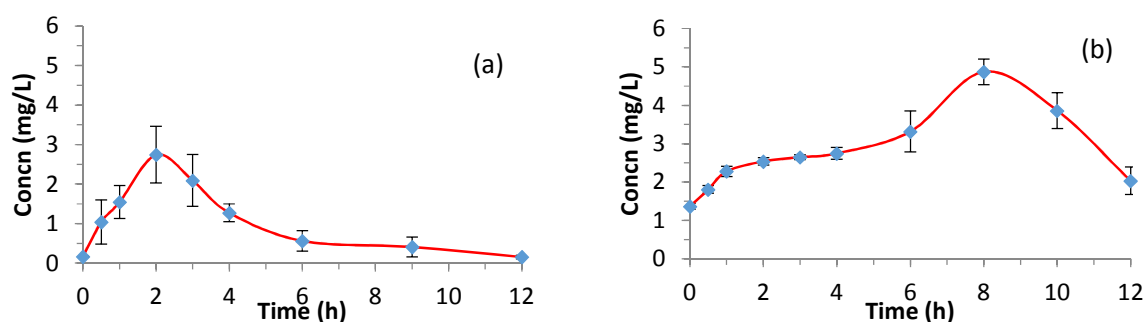


Figure 1. MCPA formation and degradation pattern with (a) 20 mg/L and (b) 50 mg/L of DMCPA and a 12 h cycle. Error bars show standard deviation (n=3).

Phase I: MCPA acclimatization period (proof of “degradation” concept):

As indicated, in Phase I, 20 mg/L of MCPA (in salt form) was continuously fed to the SBR with 25 days passing before MCPA removal was observed. Three track studies (Fig. 1a) revealed that MCPA conversion (from salt to acid form) and degradation occurred simultaneously. That is, the rising peak indicates the rate of acid formation was larger than its removal rate (in the first half of the cycle) while acid biodegradation was dominant in the second half of the cycle. More than 98 % removal of MCPA was achieved within 90 days.

Phase II: Effect of increased concentration of herbicide (“limit phase”):

The amount of DMCPA was increased to 50 mg/L and after steady effluent COD concentrations were obtained, track studies were conducted to observe the new MCPA formation and degradation pattern (Fig. 1b). Results indicate the microorganisms took much longer (i.e. 8-9 h) to convert 50 mg/L of MCPA salt to acid, with eventually incomplete biodegradation occurring.

Phase III: Effect of HRT on removal of herbicide:

Because incomplete removal of MCPA occurred in a 12 h cycle, the biodegradation response was investigated during a 48 h HRT (i.e. a 24 h cycle). Track studies revealed that 48 h HRT was sufficient to degrade 98 % of the concentration of 50 mg/L of MCPA.

Nitrate removal:

More than 98 % of the nitrate was removed in the first five hours of the cycle. In order to maintain the bioreactor in anoxic conditions, a second dose of nitrate was injected into the SBR after five hours of reaction time but in this particular instance only 50% of the nitrate was removed. Different levels of MCPA had no effect on denitrification activity.

Conclusion

Results show that an anoxic SBR can be designed to remove approximately 50 mg/L of MCPA in the presence of acetate while simultaneously removing nitrate.

References

- Costa, C., Maia, S., Silva, P., Garrido, J., Borges, F., & Garrido, E. M. (2013). Photostabilization of phenoxyacetic acid herbicides MCPA and Mecoprop by hydroxypropyl- β -cyclodextrin. *International Journal of Photoenergy*, 2013,8,doi: 10.1155/2013/542783.
- He, X., & Wareham, D. G. (2009). 2, 4-D removal via denitrification using volatile fatty acids. *Water Science & Technology*, 63(1), 178-183.
- Statistics New Zealand, 2013. (2013). Group harmonised trade- Imports: Acids; carboxylic acids, 2 methyl-4-chlorophenoxyacetic acid, (MCPA) and its salts and esters. Retrieved from <http://www.stats.govt.nz/infoshare/TradeVariables.aspx?DataType=TIM> , April 2015.