PRECHEMICAL OXIDATION AND MICROBIOLOGICAL PROCESSES FOR THE DEGRADATION OF BIODIESEL IN GROUNDWATER

Franciele Fedrizzi[1,2], Timothy M Vogel[1], Catherine Larose[1], Marilda Fernades[2], Henry X. Corseuil[2]

[1]EnvironmentalMicrobialGenomics, Laboratoire AMPERE, École Centrale de Lyon, Université de Lyon, 36 avenue Guy de Collongue, 69134 Ecully, France
[2] Núcleo Ressacada de Pesquisas em Meio Ambiente – REMA, Universidade Federal de Santa Catarina, Campus Sul da Ilha, Rua José Olímpio da Silva, 1326, Bairro Tapera, 88049-500 Florianópolis/SC

PRECHEMICAL OXIDATION AND MICROBIOLOGICAL PROCESSES FOR THE DEGRADATION OF BIODIESEL IN GROUNDWATER

Franciele Fedrizzi[1,2], Timothy M Vogel[1], Catherine Larose[1], Marilda Fernades[2], Henry X. Corseuil[2]

[1]EnvironmentalMicrobialGenomics, Laboratoire AMPERE, École Centrale de Lyon, Université de Lyon, 36 avenue Guy de Collongue, 69134 Ecully, France
[2] Núcleo Ressacada de Pesquisas em Meio Ambiente – REMA, Universidade Federal de Santa Catarina, Campus Sul da Ilha, Rua José Olímpio da Silva, 1326, Bairro Tapera, 88049-500 Florianópolis/SC

Abstract

Environmental and economic concerns associated with fossil fuels have encouraged the use of renewable transportation fuels, such as biodiesel. The demand for biodiesel could increase the probability of groundwater contamination. The applicability of existing groundwater biological treatment methods for biodiesel would depend partly on whether the indigenous microbial community can degrade these compounds or their chemically oxidized intermediates. A field experiment with a controlled biodiesel release (100 L of palm biodiesel) was conducted to assess the potential for bioremediation after prechemical oxidation by using magnesium peroxide (MgO_2) and iron oxide recovered from the treating acid mine drainage (OF DAM). Both chemical and microbial parameters were measured throughout the study. Our results show that the microbial community was stimulated by the contamination and subsequent peroxidation. Differences between different parts of the site and at different times indicated that the microbial community responded positively to the arrival of the biodiesel.

Keywords

Prechemical oxidation, Biodegradation, Palm Biodiesel, β-oxidation

INTRODUCTION

The use of fossil fuels throughout the world has resulted in considerable environmental problems. Efforts to alleviate dependence on imported oil and concern about increases in greenhouse gas emissions due to fossil fuel combustion have fostered new policies to incorporate renewable biofuels, such as biodiesel and ethanol, into the world's energy grid (CORSEUIL et al. 2011). This might increase the probability of groundwater contamination by biofuels as result of accidental and incidental spills during its production, transportation and storage. The subsurface contamination, configure itself as a widespread problem and constant threat to groundwater resources worldwide. Many remediation technologies and modifications of existing technologies are continuously being developed. This study is based on a two phase treatment consisting of chemical oxidation and microbiological degradation of biodiesel for the cleanup of the soil and groundwater.

MATERIALS AND METHODS

Controlled release field experiment

A controlled release field experiment at the Ressacada Experimental Farm in Florianópolis, SC, Brazil, is being developed to investigate whether chemical oxidation (MgO_2 + OF DAM) could enhance biodiesel biodegradation under anoxic conditions. The experimental area has 104 m^2 with a total of 30 multilevel sampling wells (SWs), each well contained a bundle of 3/16” ID polyethylene tubing to allow groundwater sampling at different depths [2, 3, 4, 5 and 6 m below ground surface (BGS)] (Figure 1). Briefly, a source zone was established by releasing 100 L of palm biodiesel into an area of 1 x 2 x 1.80 m deep down to the water table. For chemical oxidation, 88 kg of PERTOX (15.18% of MgO_2) and 8.8 kg of iron oxide recovered from the treating acid mine drainage (78.29% of Fe_2O_3) were added to the source zone. The field experiment began on the 26th of January, 2014. Samples were collected periodically (1.4, 3.4 and 6.5 months after the beginning of the experiment) from multilevel sampling wells for the monitoring of physical chemical and microbiological parameters of groundwater. A peristaltic pump and Teflon tubing were used to collect groundwater samples into capped sterile vials without headspace.

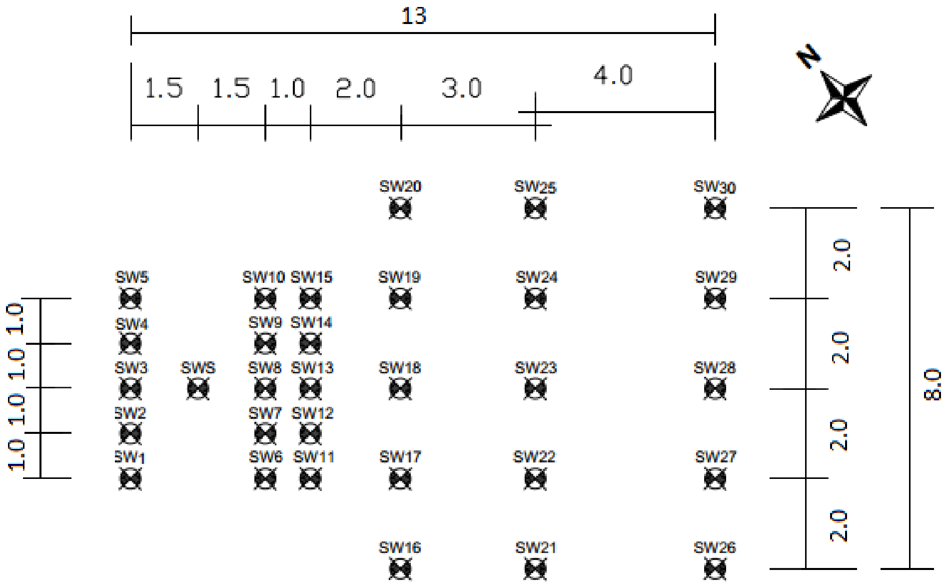

Figure 1. Ressacada Experimental Area sampling locations – plan view. All distances are given in meters.

Chemical analyses

Groundwater total organic carbon, redox potential, nitrite, nitrate, sulfide, sulfate, ferrous iron, acetate, methane and acetic acid were monitored over time. Micropurge Flow Cell (MP20) was used on site to measure redox potential. Nitrite, nitrate, sulfate and acetate analysis were performed by ion chromatography using a Dionex ICS-1000 equipped with a conductivity detector and an AS14A column. Iron (Fe^{2+}) and sulfide were analyzed using a spectrophotometer (DR/2500, HACH), according to the 1.10 phenanthroline and colorimetric methylene blue method, respectively (APHA, 2012). Methane was analyzed by gas chromatography using a GC HP model 6890 II equipped with a flame ionization detector (FID), HP 1 capillary column (30 cm 9 0.53 mm 9 2.65 mm) and HP 7694 headspace auto sampler. Acetic acid was analyzed in HP gas chromatograph (model 6890 - series II) equipped with a flame ionization detector (FID) and capillary column HP Innowax Polyethylene glycol 30m x 0.25 mm internal diameter and thickness of 0 film, 25 mm.

Microbial Analysis

Groundwater samples were filtered with Millipore membrane (polyethersulfone, hydrophilic), 0.22 lm pore size. DNA was extracted according to the MoBio Power SoilTM kit (Carlsbad, CA) protocol. The intergenic spacer between the small (16S) and large (23S) subunit rRNA genes were amplified using primers (RISA-fw: 5’-

TGCGGCTGGATCCCCTCCTT-γ', RISA-rv: 5'-CCGGGTTTCCCCATTCGG γ')(NORMAND, 1996). The amplified products then were loaded and migrated in gel using Agilent DNA 1000 Kit to analyze the bacterial community changes. Principal Component Analysis (PCA) was used to reveal the internal structure of data extracted from the gel by the software R.

RESULTS AND DISCUSSION

The main variations occurred in SWS (level 3 and 4 m BGS (below ground surface)) and SW8 (level 2 and 3 m BGS) wells, which were more affected by contaminants release in the experimental field (Figures 2 and 3).

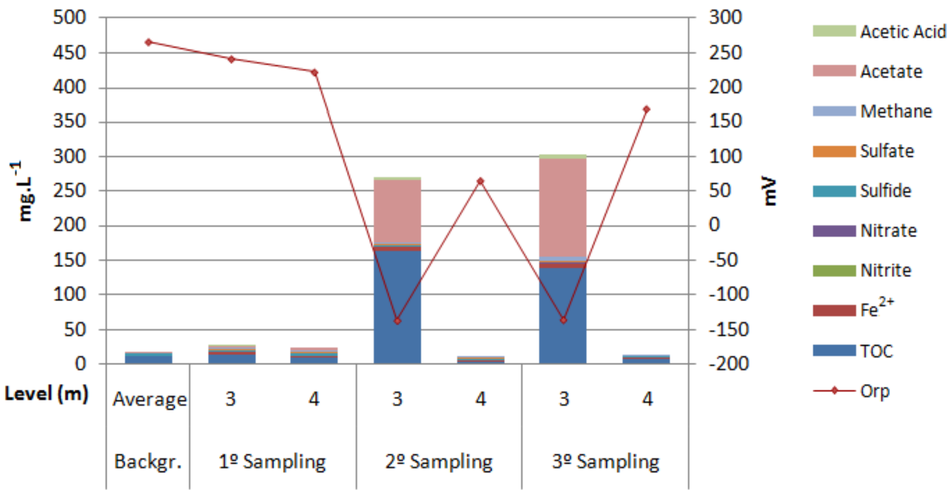

Figure 2. Result of physical-chemical monitoring – sampling well source.

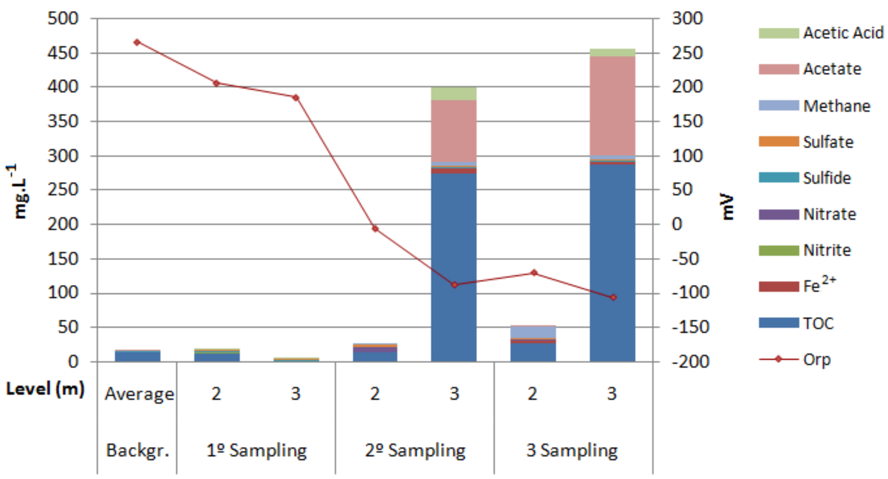

Figure 3. Result of physical-chemical monitoring – SW8.

The total organic carbon data indicates that the biodiesel or metabolites spread in the groundwater. The introduction of excess organic material contributed to the enhancement of anaerobic conditions in the system and reduced oxidation-reduction potential. As the acetate is a degradation metabolite of LCFA, its apparent production is an indication that the biofuel degradation process is occurring. The presence of methane indicated that the acetate produced is being consumed, leading to the complete degradation of biodiesel.

Based on microbiological analyses, a shift in microbial communities was observed (Figure 4). There were observed differences in microbial communities in SWS, SW7, SW8, SW9, SW11, SW12 and SW30 wells during the different sampling periods. The physico-chemical data for the same points indicate the occurrence of anaerobic degradation processes.

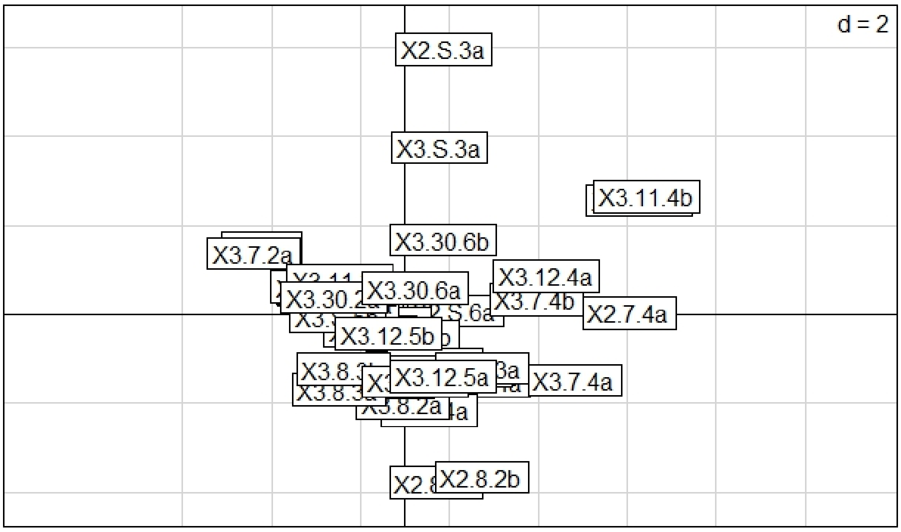

Figure 4. Principal component analysis (PCA) result for rRNA intergenic spacer analysis (RISA)[1].

Organic compounds degradation consists of a complex sequence of oxidation and reduction reactions. In theory, both saturated and unsaturated LCFA are degraded to acetate and hydrogen via β-oxidation (SOUSA et al., 2009). The results presented in this study suggest that the slightly oxidized metabolites resulting from chemical pretreatment can fit smoothly into existing biochemical pathways without novel functions required. However, more studies are needed to provide accurate information about the predominant processes in the system and metabolites generated in the palm biodiesel degradation.

CONCLUSIONS

The results suggest that palm biodiesel degradation is occurring, and the proposed remediation technology is responding positively. The differences between different parts of the site and different times indicated that the microbial community responded positively to the arrival of the biodiesel. More studies are needed for further the details of the processes occurring during the palm biodiesel bioremediation. Real-time quantitative polymerase chain reaction (qPCR) could be used to estimate the concentration of total bacteria to evaluate biomass growth. The 16S rRNA gene analyses will be conducted to identify, characterize and assess temporal changes in microbial community structure during anaerobic biodegradation of groundwater contaminated with palm biodiesel.

ACKNOWLEDGEMENTS

Authors thanks financial support from CNPq.

REFERENCES

- APHA – American Public Health Association (2012). Standard methods for the examination of water and wastewater. 22 ed. Washington, DC: *American Public Health Association*.
- CORSEUIL H.X., MONIER A.L., FERNANDES M., SCHNEIDER M.R., NUNES C.C., ROSARIO M., ALVAREZ P.J.J. (2011) BTEX plume dynamics following an ethanol blend release: geochemical footprint and thermodynamic constraints on natural attenuation. Environ Sci Technol 45(8):3422–3429.

[1] CODE LEGEND: axes.sampling.level.duplicate

- NORMAND P., P.C., NESME X. (1996). IT'S analysis of prokaryotes. Molecular Microbial Ecology Manual 3.
- SOUSA D.Z., SMIDT H., ALVES M.M., STAMS A.J.M. (2009) Ecophysiology of syntrophic communities that degrade saturated and unsaturated long-chain fatty acids. FEMS Microbiol Ecol 68(3):257–272.