Application of Ozonation and Bioremediation for Integrated Treatment and Valorization of Drilling Waste: Technology Development and Monitoring of Microbial Dynamics

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Drilling Waste: Need for Environmental Friendly Methods

- Drilling waste: $25 \times 10^6$ m$^3$ y$^{-1}$
- O&G wastewater discharges: $14.5 \times 10^9$ m$^3$ y$^{-1}$
- Drilling fluid: 11000-19000 m$^3$ per drill hole
- Toxic & persistent pollutants (TPH, PAH)

Drilling fluid:
- Free fluid removal
- High salinity oily water
  - Washing
  - Centrifugation
  - Wastewater treatment
    - Oily mud
- Solid drill cuttings
- Thermal treatment
Biodegradation & Valorisation of Drilling Waste

Circular Economy of Drilling Waste

Drilling waste detoxification
1) Microbial isolation
2) Culture conditions
3) Drilling wastewater and oily mud biotreatment

Bioprocess analysis
1) COD, TPH and PAH biodegradation
2) Biosurfactant and PHA quantification and properties
3) Gene expression by qPCR

Valorization of drilling waste
1) Biosurfactant production
2) PHA production

Gene transcription monitoring
1) Stimulation of TPH and PAH biodegradation pathways
2) Stimulation of biosurfactant and bioplastic bioproduction pathways
3) Insights into the metabolic basis of the bioprocess
Drilling WasteWater Biodegradation

- **Hydrocarbon contaminated hypersaline wastewater**
- 0.5-200 g L\(^{-1}\) NaCl, 1% (v/v) DF, 60 h incubation
- 79-93% COD removal for 0.5-30 g L\(^{-1}\) NaCl
- 3 g L\(^{-1}\) NaCl: 177 mg L\(^{-1}\) \(n\)-dodecane, 79 mg L\(^{-1}\) \(n\)-tetradecane & 333 mg L\(^{-1}\) naphthalene biodegradation
Oily Mud Biodegradation

- 28 °C, pH 7, 3 g L⁻¹ NaCl, 96 h incubation
- 71% COD removal using 1% (w/v) oily mud
- 51% COD removal using 50% (w/v) oily mud

- 14-15 mg L⁻¹ $n$-dodecane, 3-7 mg L⁻¹ $n$-tetradecane & 29-37 mg L⁻¹ naphthalene biodegradation
- 10% and 50% (w/v) oily mud is difficult to treat and requires optimisation
Medium-chain-length PHA

- 1% DF at different conditions
- 24% of DCW
- Low salinity levels
- SJTE-3 converts DF into similar quantities of the promising biodegradable thermoelastomer to other studies without additional strategy for hydrocarbons solubilisation (e.g. surfactants, solvent)

Biosurfactant

- 53% water surface tension reduction
- 43.3% emulsification index (E24)

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Methyl decanoate (% of DCW)</th>
<th>Methyl myristate (% of DCW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 °C, pH 7, 0.5 g L⁻¹ NaCl</td>
<td>17.9</td>
<td>6.1</td>
</tr>
<tr>
<td>30 °C, pH 7, 1 g L⁻¹ NaCl</td>
<td>13.9</td>
<td>3.9</td>
</tr>
<tr>
<td>30 °C, pH 7, 2 g L⁻¹ NaCl</td>
<td>11.9</td>
<td>2.8</td>
</tr>
<tr>
<td>30 °C, pH 7, 3 g L⁻¹ NaCl</td>
<td>11.8</td>
<td>4.1</td>
</tr>
<tr>
<td>30 °C, pH 7, 4 g L⁻¹ NaCl</td>
<td>5.6</td>
<td>5.2</td>
</tr>
<tr>
<td>30 °C, pH 7, 5 g L⁻¹ NaCl</td>
<td>5.3</td>
<td>4.9</td>
</tr>
<tr>
<td>30 °C, pH 7, 10 g L⁻¹ NaCl</td>
<td>4.2</td>
<td>3.9</td>
</tr>
<tr>
<td>30 °C, pH 7, 20 g L⁻¹ NaCl</td>
<td>5.0</td>
<td>4.6</td>
</tr>
<tr>
<td>28 °C, pH 7, 3 g L⁻¹ NaCl</td>
<td>12.8</td>
<td>7.4</td>
</tr>
<tr>
<td>37 °C, pH 7, 3 g L⁻¹ NaCl</td>
<td>8.0</td>
<td>4.3</td>
</tr>
<tr>
<td>28 °C, pH 6, 3 g L⁻¹ NaCl</td>
<td>7.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Expression from Biosynthetic & Biodegradation Routes

- Transcription of *Pseudomonas* spp metabolic pathways monitored at different time points during biodegradation of 1% (v/v) DF

- **phaG** gene, putatively involved in the biosynthesis of medium-chain-length PHA

- **arfB, amsY, psoA** and **rhlB** genes associated to arthrofactin, amphisin, putisolvin and rhamnolipid

- **ndoB** gene encodes for naphthalene dioxygenase driving naphthalene biodegradation

- **alkB** gene constitutes universal marker for oil biodegradation
Expression from Biosynthetic & Biodegradation Routes

- PHA synthesis triggered during exponential growth

- \textit{rhlB} mRNA was not detected

- \textit{arfB} and \textit{amsY} were not expressed

- \textit{psoA} transcription remained at high levels

- \textit{P. citronellolis} could potentially produce \textit{putisolvin}

- \textit{alkB1} and \textit{ndoB} highly induced at all times
Hybrid Ozone-Bioprocess for Drill Cuttings Valorisation

1. Drilling waste

2. Drilling fluid
   - Free fluid removal
   - Washing
   - Centrifugation
   - Oily mud
   - Wastewater treatment

3. High salinity oily water

4. Ozonation

5. Bioremediation
   - Solid drill cuttings
   - H₂O

6. Tree prunings
   - Activated sludge

7. Compost
Ozonation & Bioremediation as Single Drill Cuttings Treatments

- Untreated DC: pH 8.5 and 40% (w/w) moisture
- 150 Kg DC
- Faster kinetics in pH 12.5 (47.3% removal)
- 44.2% removal in pH 11.5
- Additional moisture inhibited the process

<table>
<thead>
<tr>
<th>Treatment</th>
<th>7 d</th>
<th>110 d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (Composting only)</td>
<td>2.27</td>
<td>0.35</td>
</tr>
<tr>
<td>Ozonation + Composting</td>
<td>1.65</td>
<td>0.36</td>
</tr>
<tr>
<td>Ozonation + Composting + Biostimulation</td>
<td>1.74</td>
<td>0.27</td>
</tr>
<tr>
<td>Ozonation + Composting + Biostimulation + Bioaugmentation</td>
<td>1.79</td>
<td>0.21</td>
</tr>
<tr>
<td>Ozonation + Composting + Biostimulation + Bioaugmentation + Biochar</td>
<td>1.97</td>
<td>0.23</td>
</tr>
</tbody>
</table>

150 Kg DC
+ 250 Kg Prunings
+ 50 Kg Activated Sludge
Hybrid Ozone-Bioremediation for Drill Cuttings Valorisation

- **Ozonation vs no ozonation**
- 33% DC + 55% Prunings +12 AS
- 55% DC + 44% Prunings +12 AS
- Ozonation + 33% DC fastest kinetics
- **0.3-0.6% oil following 21 d**

- **33% DC without ozonation:** 0.6% oil at **70 d**
- **55% DC:** reduced performance with ozonation
- **Ozonation + 55% DC** failed to reach 0.5% of oil
- **55% DC bioremediation** performed 0.5% oil at **70 d**
- **Increase of AS** reduced performance of both systems
Microbial Dynamics and Use of Compost as End Product

Phylum Taxonomy

Class Taxonomy

Lettuce cultivation

Number of Leaves

Crop Production [Kg ha⁻¹]

Treatment

5% DC-compost  20% DC-compost  100% Comm.-compost  100% Soil

5% DC-compost  20% DC-compost  100% Comm.-compost  100% Soil
### Profit and Loss for Each Treatment Approach

<table>
<thead>
<tr>
<th></th>
<th>Thermal - TCC (€)</th>
<th>Hybrid Ozone-Bioprocess (€)</th>
<th>Bioprocess Only (€)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SALES</strong></td>
<td>2,280,960</td>
<td>2,160,000</td>
<td>1,296,000</td>
</tr>
<tr>
<td><strong>COST OF SALES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Raw materials</td>
<td>703,296</td>
<td>1,312,000</td>
<td>491,520</td>
</tr>
<tr>
<td>Labour</td>
<td>265,200</td>
<td>89,700</td>
<td>119,600</td>
</tr>
<tr>
<td>Manufacturing overhead</td>
<td>1,258,790</td>
<td>740,000</td>
<td>1,122,702</td>
</tr>
<tr>
<td></td>
<td>2,227,286</td>
<td>2,141,700</td>
<td>1,733,822</td>
</tr>
<tr>
<td><strong>Net annual (loss)/profit</strong></td>
<td>53,674</td>
<td>18,300</td>
<td>(437,822)</td>
</tr>
</tbody>
</table>

- **47,520 t_{DC} \text{yr}^{-1}, 10\% oil and moisture, 24 \text{h d}^{-1} for 330 \text{d}**
- Thermal desorption (Thermomechanical Cuttings Cleaner – TCC)
- 21 d of Ozone + Biotreatment (33\% DC+55\% Prunings+12\% AS)
- 70 d Biotreatment Only (55\% DC+33\% Prunings+12\% AS)

- TCC and hybrid treatments **exhibit profit**
- Biotreatment only: prolonged process duration
- Hybrid process: prunings transportation was a key cost parameter
Conclusions

- **Holistic approach** for sustainable drilling waste treatment

- *P. citronellolis* SJTE-3 enabled enhanced removal of **TPH** and **PAH** from DF

- **In situ** production of **bioplastics** and **biosurfactants**

- Activation of **putisolvin** biosynthetic pathway

- 47.3% oil removal via ozonation

- Similar microbial community composition in all treatments

- **Hybrid ozonation-bioremediation** is cost-competitive
Thank you!

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