Sludge recovery from industrial wastewater treatment

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TOPICS

• Introduction – Industrial sludges
• Goals
• Materials and Methods
• Results and discussion
• Conclusions
• Future perspectives
Main Industries in Portugal

Food  Textiles  Chemicals  Paper  Wood and Cork

Industrial wastewater (IWW)

Composition – depends on the type of industrial activity.

Industrial sludges

With proper treatment are valuable material resources  sustainable circular economy
How to treat industrial wastewater?

Based on processes and operations units more suited to its characteristics.

- Industrial WWTP

  - Liquid Phase Treatment
    - Aeration tank
    - Sedimentation tank
    - Sludges
INTRODUCTION

How to treat industrial wastewater?

Solid Phase Treatment

Composting or Landfill

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How to treat or disposal industrial Sludges?

**co-composting with MSW** – problems due to the sludges composition.

700 ton/year industrial sludges – Composting 35€/ton e 395€/transport (31,800€/ year)

### Industrial Sludges Composition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Matter</td>
<td>%m/m</td>
<td>68.2</td>
</tr>
<tr>
<td>Organic matter</td>
<td>%m/m</td>
<td>56.2</td>
</tr>
<tr>
<td>pH</td>
<td>Escala de Sorensen</td>
<td>12.6</td>
</tr>
<tr>
<td>Calcium</td>
<td>g Ca/kg</td>
<td>210</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>g P/kg</td>
<td>0.22</td>
</tr>
<tr>
<td>Potassium</td>
<td>g K/kg</td>
<td>0.23</td>
</tr>
<tr>
<td>Magnesium</td>
<td>g Mg/kg</td>
<td>1.81</td>
</tr>
<tr>
<td>zinc</td>
<td>g Zn/kg</td>
<td>0.06</td>
</tr>
</tbody>
</table>
GOALS

- Identify and analyze treatment/valorization options for these wastes, giving priority to their recovery to the detriment of disposal.

Solutions hypotheses

- Anaerobic digestion
- Adsorption
- Mortar production
- Catalyst production
Materials and Methods

- Potential Metanogenic Assay (32 d)
- 2 substrate mixtures:
  - Reactors A - 80% MS + 20 % IS
  - Reactors B - 90% MS + 10% IS
- Inoculum – digested sludges from WWTP

### Composition of mixtures for reactors AD

<table>
<thead>
<tr>
<th>Item</th>
<th>Reactors A (g)</th>
<th>Reactors B (g)</th>
<th>Reactors I (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>4.85</td>
<td>5.45</td>
<td>-</td>
</tr>
<tr>
<td>IS</td>
<td>0.09</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>Inoculum</td>
<td>19.05</td>
<td>19.05</td>
<td>19.05</td>
</tr>
<tr>
<td>water</td>
<td>175.45</td>
<td>175.45</td>
<td>180.95</td>
</tr>
</tbody>
</table>

MS – Mixed sludge from Municipal WWTP
IS – Industrial sludge
Materials and Methods

- Quantitative and qualitative analysis of Biogas
- Specific methane production

Anaerobic digestion
Materials and Methods

- Adsorbent (75% ADS e 25 % IS)
- 4 Dyes:
  - Rhodamine-B - $\text{C}_{28}\text{H}_{31}\text{N}_{2}\text{O}_{3}\text{C}$
  - Mordant Orange 1 - $\text{C}_{13}\text{H}_{9}\text{N}_{3}\text{O}_{5}$
  - Methylene Blue - $\text{C}_{16}\text{H}_{18}\text{N}_{3}\text{SCl}$
  - Mordant Blue 9 - $\text{C}_{16}\text{H}_{9}\text{ClN}_{2}\text{Na}_{2}\text{O}_{8}\text{S}_{2}$
- 6 concentrations and Vuseful of 30 mL
- Adsorbent masses (0.5, 1, 1.5, 2 e 3 g)
- Tests of 1h30min with measurements of $\frac{1}{2}$ in $\frac{1}{2}$ h
Materials and Methods

- 5 mortar mixtures:
  - 1 reference (cement only)
  - 1%, 2.5%, 5% e 10% Sludge
- Test time 28 d

<table>
<thead>
<tr>
<th>Composition</th>
<th>Reference</th>
<th>Sludge (1%)</th>
<th>Sludge (2.5%)</th>
<th>Sludge (5%)</th>
<th>Sludge (10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement (g)</td>
<td>450.02</td>
<td>445.52</td>
<td>438.71</td>
<td>427.51</td>
<td>405.03</td>
</tr>
<tr>
<td>Sand (g)</td>
<td>1,350</td>
<td>1,350</td>
<td>1,350</td>
<td>1,350</td>
<td>1,350</td>
</tr>
<tr>
<td>Sludge (g)</td>
<td>-</td>
<td>4.51</td>
<td>11.32</td>
<td>22.51</td>
<td>45.02</td>
</tr>
<tr>
<td>Water (g)</td>
<td>225.02</td>
<td>225.01</td>
<td>225.03</td>
<td>225.03</td>
<td>225.02</td>
</tr>
</tbody>
</table>
Materials and Methods

- Bending strength tests
- Compressive strength tests

Mortar production
Biofuel production - heterogeneous catalysis

- Used food oils
- Pre-treatment drying - 70 °C
- Calcination pretreatment 850 °C
- Convert calcium (sludge) to calcium oxide.
Biofuel production - heterogeneous catalysis

- FTIR-ATR
- Acidity index
- Density
Results and Discussion

Anaerobic Digestion Assay

- Reactors A
  - 21% - SV removal
  - CH$_4$ - 55 to 60%

- Reactors B
  - 42% SV removal
  - CH$_4$ - 60 to 65%
Results and Discussion

- Methane production
  - Test Conditions – 1 atm and 35ºC
  - Conditions PTN – 1 atm and 0ºC

<table>
<thead>
<tr>
<th>Reactors</th>
<th>Prod. acumu. of biogas (mL)</th>
<th>Prod. acumu. of CH₄ (mL)</th>
<th>Prod. Espec. of CH₄ (mL CH₄ /gVS)</th>
<th>Prod espec. of CH₄ (N.mL CH₄ /gVS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>113</td>
<td>71</td>
<td>529</td>
<td>342</td>
</tr>
<tr>
<td>B</td>
<td>123</td>
<td>82</td>
<td>600</td>
<td>400</td>
</tr>
</tbody>
</table>
Results and Discussion

Adsorption tests

- It was obtained $R^2 \geq 0.989$
- Removal efficiency between 70 to 80%
 Isothermics of adsorption tests for each of the dyes

Linearized equation of Langmuir:

\[ \frac{C_e}{q_e} = \frac{1}{q_{\text{max}} k_L} + \frac{1}{q_{\text{max}}} C_e \]

Linearized equation of Freundlich:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \]

The isothermal that best fits – *Langmuir Isothermic*

- $q_{\text{max}} = 0,780 \text{ mg/g} - \text{Mordant Blue 9}$
- $q_{\text{max}} = 0,274 \text{ mg/g} - \text{Rhodamine-B}$
- $q_{\text{max}} = 0,494 \text{ mg/g} - \text{Mordante Oranje 1}$
- $q_{\text{max}} = 0,010 \text{ mg/g} - \text{Methylene Blue}$
## Results and Discussion

### Compressive Strength (MPa)

<table>
<thead>
<tr>
<th>Strength</th>
<th>Reference</th>
<th>Sludge (1%)</th>
<th>Sludge (2.5%)</th>
<th>Sludge (5%)</th>
<th>Sludge (10%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blending</td>
<td>5.13</td>
<td>4.46</td>
<td>3.89</td>
<td>2.73</td>
<td>-</td>
</tr>
<tr>
<td>Compressive</td>
<td>43.54</td>
<td>38.14</td>
<td>36.04</td>
<td>28.90</td>
<td>17.12</td>
</tr>
</tbody>
</table>

### Blending Strength (MPa)

<table>
<thead>
<tr>
<th>Blending Strength (MPa)</th>
<th>Referência</th>
<th>Lamas (1%)</th>
<th>Lamas (2.5%)</th>
<th>Lamas (5%)</th>
<th>Lamas (10%)</th>
</tr>
</thead>
</table>

**Graphs:**

- Compressive Strength (MPa) for different slurries.
- Blending Strength (MPa) for different slurries.
Catalyst production tests for biofuel production

- Conversion of 90%
- Acidity index: 0.17 e 0.18
Results and Discussion

- Functional groups (FTIR-ATR)

<table>
<thead>
<tr>
<th>Chemical bonding</th>
<th>Function</th>
<th>Wave Number (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>–O–H</td>
<td>Alcohol, phenol, enol, carboxylic acid</td>
<td>3650 – 3200</td>
</tr>
<tr>
<td>–R(_2)NH</td>
<td>Secondary Aminas</td>
<td>3400 – 3140</td>
</tr>
<tr>
<td>–NH(_2)</td>
<td>Primary amines</td>
<td>3400 – 3350</td>
</tr>
<tr>
<td>–C–H</td>
<td>Alkanes</td>
<td>2962 – 2853</td>
</tr>
<tr>
<td>–C–H</td>
<td>Alkenes</td>
<td>3095 – 3010</td>
</tr>
<tr>
<td>–CO–C–H</td>
<td>Aldehydes</td>
<td>2900 – 2800</td>
</tr>
<tr>
<td>–C≡C–, C≡N</td>
<td>Alcinos and Nitrites</td>
<td>2500 – 2000</td>
</tr>
<tr>
<td>R(_2)C=O</td>
<td>Carbonates</td>
<td>1630 – 1850</td>
</tr>
<tr>
<td>H(_2)C=CH(_2)</td>
<td>Alkenes</td>
<td>1680 – 1650</td>
</tr>
<tr>
<td>–C=C–</td>
<td>Aromatics</td>
<td>1450 – 1500</td>
</tr>
</tbody>
</table>

- Graph showing relative intensity vs wave number (cm\(^{-1}\)) with peaks indicating functional groups.

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Conclusions

- It is possible to apply anaerobic co-digestion with energy recovery. Specific methane production 0.400 L/gSV added, 4 kWh/kg SV corresponding to 2 kWh/kg industrial sludge.

- It is possible to produce adsorbents for removal of water dyes. With blue mordant 9, a maximum removal of 80% - qmax = 0.780 mg/g was obtained.

- The production of mortar - Visual analysis similar aspect between the specimens with the sludge and the reference. The bending and compression strengths are lower than the reference resistance but present acceptable values.

- Catalyst production - biofuel production was achieved 90% conversions and acidity indexes < 0.5.
Future Work

- **Cement production:**
  - Conduct pilot-scale trials

- **Anaerobic digestion:**
  - IS with fractions >20%
  - different substrates.

- **Adsorption:**
  - Apply the adsorbent – different pollutants.

- **Mortar production:**
  - Curing times less than 28 d
  - Replace the sand fraction.

- **Production of Heterogeneous Catalysts:**
  - Test the number of uses.
Acknowledgements:

We thank to the Chemical Industry for the sludge and data.

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Thank you for your attention

Questions ?