Pulp and Paper Mill Sludge Utilization by Biological Methods †

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Abstract: The aim of our contribution is to evaluate the possibilities for the biochemical utilization of paper wastes. We tested aerobic and anaerobic degradation of paper waste sludges from a plant that processes recycled paper. Testing included the assessment of phytotoxicity. We can conclude that the concentration of paper sludges did not have toxic effects on the bacterial consortium of the anaerobic or aerobic conditions. However, the leachate of paper sludges and water from sludge dewatering had a slightly negative effect on the germination of cress (Lepidium sativum L.) and lettuce (Lepidium sativum L.) seeds where the germination ranged from 83.3% to 100% but the mass yield was higher.

Keywords: pulp; paper; sludge; biogas; biodegradation; phytotoxicity

1. Introduction

The aim of our contribution is to evaluate the possibilities for the biochemical utilization of paper waste. The global production of waste from paper and paperboard was approximately 417.3 million metric tons in 2021 [1]. The production of paper and paperboard is resource-intensive, and the generation of pollutants is harmful to the environment [2]. The cellulose paper industry in Europe generates approximately 11 million tons of waste annually [3].

Waste materials or by-products generated in paper mills are typically categorized as follows [4]:
1. Residues (including coarse, heavy, and fine residues): These are generated during the use of recycled fiber pulp (RCF) and may contain fibrous pieces, plastics, metals, sand, and glass, respectively;
2. Deinking sludge: Produced during the removal of printing ink from RCF, typically comprising short fibers/fine particles, inorganic fillers, and ink particles;
3. Primary sludge: Generated in the mechanical water cleaning process, primarily consisting of short fibers/fine particles and fillers;
4. Secondary sludge: Formed during the treatment of process water using biological methods;
5. Process water (often referred to as wastewater): It is a significant component of paper production and is generally treated on-site to remove impurities [5].

Paper mill sludge generated from wastewater treatment constitutes the largest portion of waste in terms of volume. It contains the remnants of both organic and inorganic substances that were not utilized in the paper manufacturing process. These substances may include wood matter, sulfuric acid, hydrochloric acid, phosphoric acid, and various types of inorganic salts [6–8].

The disposal of paper waste has historically been addressed primarily through landfilling or incineration [9–11]. However, current preferences strongly favor recycling methods and the utilization of paper waste. Environmentally acceptable processes also include
biological treatment methods, which enable the transformation of waste into useful products such as compost or biogas [12]. Composting is a microbial process that breaks down organic material into a product that can enrich soil. Anaerobic digestion is a process in which organic waste is decomposed in the absence of oxygen, resulting in energetically useful methane and CO₂ [13].

2. Material and Methods

Samples were collected from a paper mill that processes recovered paper (recycling paper) and consisted of dewatered paper mill sludge with a dry matter content of 56.7% and water from the dewatering process. From the paper mill sludge, a water extract was prepared and used in the tests. For anaerobic degradation, sewage sludge from the anaerobic treatment of wastewater treatment plant were used as an inoculum. An inoculum obtained by leaching from the soil was used for the aerobic test. To evaluate the phytotoxic properties for the potential use of the sludge in soil or compost, modified tests on higher plant seeds were conducted.

2.1. Preparation of the Leachate

The preparation of the leachate followed the standard STN EN 12457-4, using a ratio of 1 L of distilled water per 100 g of sludge dry matter. The leaching process occurred for 24 h on an orbital shaker at laboratory temperature, and the extract was pre-filtered before testing [14].


The biodegradability tests were conducted using the OxiTop® OC 110 instrument (WTW, Weilheim, Germany), which operates based on the principle of respirometric measurement. The working volume of the instrument bottles was 510 cm³. The tests were conducted according to the following standards: OECD 311, OECD 301 D, ISO/DIS 14851:2016 E, and OECD 302 B. These standards were adapted to our specific requirements and conditions [15–18].

The anaerobic test was carried out with 3 different leachate concentrations A, B and C (Table 1).

Table 1. Content and volume of sample concentrations (anaerobic biodegradability).

<table>
<thead>
<tr>
<th>Ratio of Ingredients in Mixtures</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sludge (mL) *</td>
<td>1.0</td>
<td>1.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Leachate (mL)</td>
<td>50</td>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>Biomedium (mL) **</td>
<td>125</td>
<td>125</td>
<td>125</td>
</tr>
</tbody>
</table>

* Sludge from a wastewater treatment plant (anaerobic stage). ** Composition of the biomedium: K₂HPO₄, KCl, MgSO₄·7H₂O, NaNO₃, 1000 mL distilled water.

The aerobic test was also performed in 3 concentrations of leachate A, B and C (Table 2).

Table 2. Content and volume of sample concentrations (aerobic biodegradability).

<table>
<thead>
<tr>
<th>Ratio of Ingredients in Mixtures</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leachate (mL)</td>
<td>50</td>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>Inoculum (mL) *</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Biomedium (mL) **</td>
<td>125</td>
<td>125</td>
<td>125</td>
</tr>
</tbody>
</table>

* Inoculum obtained by leaching from soil. ** Composition of the biomedium: K₂HPO₄, KCl, MgSO₄·7H₂O, NaNO₃, 1000 mL distilled water.
We repeated all experiments three times, average values are shown in the tables and graphs.

2.3. Phytotoxicity Test with Lepidium sativum L.

The cress test, or phytotoxicity test with Lepidium sativum L., is a modified method for evaluating the intensity of the decomposition of organic materials and the maturity of the resulting compost for use in composting practices. It involves assessing the phytotoxicity of the sample extract using the germination index (GI) of a sensitive plant species, such as garden cress (Lepidium sativum L.) [19].

2.4. Phytotoxicity Test on Leaf Lettuce (Lactuca sativa L.)

To determine the toxic effects of pollutants on leaf lettuce (Lactuca sativa L.), we followed a modified ISO 18763:2016 procedure. We mixed the soil with different concentrations of the leachate (3 concentrations of leachate and water from sludge dewatering) of paper sludge to determine the optimum concentration for seed germination and growth [17].

2.5. Calculation of Biodegradation

\[
\text{Biodegradation (\%)} = 100 \times \frac{\text{BOD} - \text{BOD}_{\text{Blank}}}{\text{ThOD}}
\]

where:

- BOD is the biochemical oxygen demand of the test substance (mg/L),
- BOD blank is the biochemical oxygen demand of the biotic control (mg/L),
- ThOD is the theoretical oxygen demand required when the target compound is completely oxidized (mg/L) [20].

3. Results and Discussion

3.1. Anaerobic Biodegradability of Organic Substances in Paper Sludge

The test lasted 28 days, with three concentrations of the leachate. At regular intervals, the chemical oxygen demand (COD\text{Cr}), pH, and conductivity were determined in the samples.

The COD\text{Cr} value decreased during the test, indicating a gradual decrease in the organic pollution of the sample and an increased amount of organic pollution. The measured pressure (Figure 1), affected by the gas produced by the microorganisms, from the samples over the 28 days increased in direct proportion to the increasing amount of paper sludge leachate that was added, with approximately the same pattern of development. From these results, we can conclude that the increased concentration of sludge did not have toxic or inhibitory effects on the bacterial consortium of the anaerobic sewage sludge and supplied the necessary nutrients for the development and growth of the microorganisms. The positive effect of the addition of paper sludge during anaerobic fermentation has been demonstrated in the works of many authors, e.g., Chynoweth, 1993 [21], Zhu, 2021 [22].
3.2. Aerobic Biodegradability of Organic Substances in Paper Sludge

The test was performed in six repetitions and with three concentration levels. The pH values of all leachate concentrations were close to neutral pH, indicating the stability of the reaction and minimal contamination. The COD$_{Cr}$ values at each sample concentration decreased from the first to the last day, indicating that the samples were undergoing an oxidative process in which oxygen was consumed (Table 3).

As the leachate concentration of the paper sludge increased, the biological oxygen demand (BOD) increased in direct proportion (Figure 2). The conditions for the formation of the microbial consortium improved with the increasing concentration of the substances contained in the leachate; we assume enrichment with nutrients and trace elements. The percentage of biodegradation increased in direct proportion to the increasing concentration of the paper sludge leachate (Figure 3). This indicates that a greater amount of the test substance has been degraded and undergone biological transformation. A higher percentage of biodegradation indicates a higher capacity of the substance to be degraded by microorganisms.

Table 3. Sample properties for aerobic biodegradability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>COD$_{Cr}$ Day 1</th>
<th>COD$_{Cr}$ Day 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>847.80</td>
<td>561.90</td>
</tr>
<tr>
<td>B</td>
<td>960.84</td>
<td>481.11</td>
</tr>
<tr>
<td>C</td>
<td>1073.88</td>
<td>581.97</td>
</tr>
<tr>
<td>Blank</td>
<td>489.84</td>
<td>501.70</td>
</tr>
</tbody>
</table>

Figure 1. Pressure evolution during the test.
Figure 2. Evolution of average BOD values during the test (mg/L).

The percentage of biodegradation increased in direct proportion to the increasing concentration of the paper sludge leachate (Figure 3). This indicates that a greater amount of the test substance has been degraded and undergone biological transformation. A higher percentage of biodegradation indicates a higher capacity of the substance to be degraded by microorganisms.

Figure 3. Biodegradation of the samples.

3.3. Phytotoxicity Test with Lepidium sativum L.

The GI of Lepidium sativum L. shown in Table 4 indicates that the leachate and water from drainage had inhibitory effects. The samples contained substances that adversely affected seed germination. Some of these substances may be present in the callus due to the use of biocides, dyes, adhesives, and other chemicals in the papermaking process. Therefore, it is possible that the presence of these chemicals in the wastepaper sludge caused an inhibitory effect on the germination of Lepidium sativum L. seeds.

Table 4. Results of the phytotoxicity test with Lepidium sativum L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Germination (%)</th>
<th>Germination (%)</th>
<th>Average Root Length (mm)</th>
<th>(GI) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blind experiment</td>
<td>100</td>
<td>100</td>
<td>6.74</td>
<td>100</td>
</tr>
<tr>
<td>Water from sludge dewatering</td>
<td>92.50</td>
<td>92.50</td>
<td>4.09</td>
<td>56.12</td>
</tr>
<tr>
<td>Sludge leachate</td>
<td>88.89</td>
<td>88.89</td>
<td>4.81</td>
<td>63.40</td>
</tr>
</tbody>
</table>
3.4. *Leaf Lettuce* (*Lactuca sativa* L.) Growth Inhibition Test

As the concentration of the leachate from the paper sludge increased, the ability of the plants to germinate increased. From data shown in Table 5, it is clear that the optimum nutrient concentration for both growth and germination is at concentration C. This concentration of the sludge leachate did not have an inhibitory effect on the plants; we can assume that it had a more beneficial effect on the plants than the blind experiment since the plants had a greater dry weight compared with the blind experiment. Seeds watered with leachate concentration C had 100% germination. Their weight was higher than the weight of the plants in the blind experiment, the highest of the whole test. The dry matter percentage was one hundredth less than that of the blind. The concentration of the leachate from sludge C did not have an inhibitory effect on the plants, and it can be said that it had a better effect than the blind experiment, since these plants have a higher weight and dry matter percentage.

Table 5. Evaluation of inhibition test with *Lactuca sativa* L.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Germination (%)</th>
<th>Wet Weight (g)</th>
<th>Dry Weight (g)</th>
<th>Dry Matter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>100</td>
<td>0.29</td>
<td>0.27</td>
<td>4.88</td>
</tr>
<tr>
<td>A</td>
<td>83.3</td>
<td>0.26</td>
<td>0.25</td>
<td>5.30</td>
</tr>
<tr>
<td>B</td>
<td>86.6</td>
<td>0.26</td>
<td>0.25</td>
<td>4.82</td>
</tr>
<tr>
<td>C</td>
<td>100</td>
<td>0.33</td>
<td>0.31</td>
<td>5.03</td>
</tr>
<tr>
<td>Water from sludge dewatering</td>
<td>90</td>
<td>0.25</td>
<td>0.23</td>
<td>6.72</td>
</tr>
</tbody>
</table>

Paper sludge leachate contains nutrients that stimulate the biomass production of the test organism. However, the leachate tends to have an inhibitory effect on germination, but tends to stimulate the growth and biomass production of *Lactuca sativa* L.

4. Conclusions

The results of the anaerobic biodegradability tests showed that the paper sludge had no toxic or inhibitory effects on the bacterial consortium of the anaerobic sewage sludge and supplied the necessary nutrients for the development and growth of the microorganisms. Aerobic biodegradability tests showed that increasing the sludge concentration improved the decomposition of organic substances, with pH and COD$_{Cr}$ being positive indicators. The phytotoxicity test showed only a partial negative effect on the seed germination of *Lepidium sativum* L., indicating a possible limitation of seed growth in sludge. These results highlight the need for further tests before sludge is used in agriculture conditions. The results of *Lactuca sativa* L. growth inhibition showed that the leachate can possibly have a beneficial effect on plant growth, however, it can inhibit seed germination. It is important to take this factor into account when using sludge as a fertilizer. These findings suggest the need for further research to investigate the use of sludge as a fertilizer for different plant species and their response to this material.

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References
5. Casco, M.E.; Moreno, V.; Duarte, M.; Sapag, K.; Cuña, A. Valorization of Primary Sludge and Biosludge from the Pulp Mill Industry in Uruguay through Hydrothermal Carbonization. Waste Biomass Valorization 2023, 14, 3893–3907. [CrossRef]
20. Rosetti, I.; Conte, F.; Ramis, G. Kinetic Modelling of Biodegradability Data of Commercial Polymers Obtained under Aerobic Composting Conditions. Eng.—Adv. Eng. 2021, 2, 54–68. [CrossRef]