# Valorization of industrial wastes with complementary properties for producing organic amendments

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## 1. Introduction

Wastewater treatment plants (WWTP) generates large quantities of sewage sludge (SS) that require efficient and consciously management. Nowadays, towards a circular economy framework, waste should be seen as a resource and landfill disposal is the last option. In this scope, land application of SS (directly or after composting) is a feasible option in several countries for its valorization. Indeed, SS can replace commercial fertilizers due to its high nutrient content (mainly P and N) and organic matter (Alketbi et al., 2019). However, it is necessary to be aware of the risks, mainly the presence of pathogenic microorganisms, potentially toxic metals (e.g., Pb, Zn, Cr, etc.), and other organic pollutants (e.g., PAH). Furthermore, the large moisture content of this waste (even after mechanical dehydration mechanisms) and unstable organic matter difficult the transport and storage and causes bad odors. Worldwide, thermal processes (drying) are emerging as an alternative to alleviate these problems. Besides drying reduces the volume (removal of water), also the content of pathogens can be decreased (or eliminated). However, energy consumption is the most significant disadvantage of thermal drying. Thus, it is essential to find a strategy to reduce energy requirements. In this context, industrial wastes (e.g., coal fly ash and green liquor dregs) have been used as drying adjuvants (Gomes et al., 2020). Lime mud (LM) from pulp and paper mills was not studied yet for this purpose. LM is an inorganic by-product generated during the causticizing reaction in kraft processes for recovery chemicals in the pulp mills. This by-product is mainly composed of $CaCO_3$, and thus it can be valorized as neutralizing agent or in liming applications. According to industrial information, about 25 kg of LM per ton of pulp air-dried are commonly produced and currently, landfill disposal is the main management route. However, LM may not only assist the water diffusion from SS in the thermal drying process but also the final product can own liming capacity for soil applications. Thus, this study aims to valorize LM as a SS drying adjuvant to produce an organic-rich product, containing macronutrients and without pathogen contamination for agricultural applications.

## 2. Materials and Methods

Two types of SS from Portuguese WWTP were tested: urban mixed sludge from an activated sludge system plant (UM) and digestate from an anaerobic digestion process (AD). The samples were collected after mechanical dehydration by filtration and centrifugation. Both samples UM and AD were kept at 4 ºC until analysis. LM sample (about 5 kg) was collected from a Portuguese pulp and paper mill. Moisture (H) and organic matter (OM) were determined based on EPA Method 1684. The pH and electrical conductivity (EC) were measured in an extract obtained at a liquid:solid ratio 10:1 L/kg. Potentially toxic metals (PTM) such as Pb, Cd, Zn, Cr, Cu and Cd, and major elements (Ca, Na, K, and Mg) were determined by flame atomic absorption spectrometry after acid digestion with aqua regia. Total phosphorus and nitrogen were measured by colorimetric analysis (EPA Method 365.3) and Kjeldahl method, respectively. Microbiological contamination was assessed according to ISO 16649-2:2001. All parameters were measured in duplicate for each sample. The drying process was investigated in plate geometry (2.5 mm thickness, 70 mm in diameter), and different proportions of SS with LM were prepared (0.05, 0.10, 0.15, 0.20, and 0.25 g LM/g $SS_{wet\ basis}$), ensuring homogenous composition. The feedstocks were dried at 100 ºC in a Moisture Analyzer, *Precisa XM50.* The weight loss was recorded once per minute until no variation was detected. The drying rate (DR) was determined according to the methodology described in our previous study (Gomes et al., 2020).

## 3. Results and discussion

Table 1 summarizes the physical and chemical properties of sewage sludge (UM and AD) and lime mud samples. Both UM and AD samples have pH close to neutrality, while LM is alkaline. Besides that, due to the $CaCO_3$ content in LM, it is expected that the final product can be used as a liming agent in acid soils (Portuguese case). Mixing SS with 0.15 g of LM, the products reach pH 8 for both types of samples (UM and AD). The content of organic matter, phosphorus, and nitrogen in UM and AD are of interest for soil fertilization, while the same does not happen with LM. However, the calcium concentration in LM can have a positive effect on soil conditions. Indeed, acidic soils tend to have lower calcium concentration, which hinders plant growth. All samples presented PTM concentrations (results not shown) below the limits established by Portuguese legislation (*Decreto Lei* n.º 276/2009).

Table 1. Properties of the wastes used in this work.

| | UM | AD | LM |
|---|---|---|---|
| pH | 6.53 | 6.71 | 10.4 |
| EC (mS/cm) | 2.17 | 1.72 | 1.20 |
| H (%) | 86.3 | 71.0 | - |
| OM (%) | 67.1 | 63.7 | 14.4 |
| $P_2O_5$ (%) | 2.15 | 3.83 | 0.96 |
| $N_{Kjeldahl}$ (%) | 5.68 | 3.89 | - |
| $K_2O$ (%) | 0.42 | 0.22 | 0.06 |
| CaO (%) | 0.54 | 5.50 | 54.1 |
| MgO (%) | 0.89 | 0.38 | 0.86 |
| $Na_2O$ (%) | 0.19 | nd | 0.91 |

Note: except for moisture, percentages were calculated on dry basis; nd – not detected.

Through the drying curves and assuming that the drying rate (g/min.kg $SS_{wet\ basis}$) was constant until reach a moisture ratio of 0.30 (moisture near to 50%) (Gomes et al., 2020), it was possible to determine the experimental values presented in Table 2. However, this methodology is currently being validated for plate geometry by measuring the temperature profiles inside the solid. This first approach revealed that it is easier to dry the UM samples comparing to AD, as less drying time is required to achieve the same level of dryness (43 min versus 48 min for AD). This result is due to the significantly higher drying rate for UM, indicating that the water vapor diffusion process is facilitate in this case. The LM revealed the potential to improve and accelerate the drying process of SS for both UM and AD samples. The optimal proportion of SS/LM was not the same in both cases. However, in-depth studies according to a design of experiments are being conducted to determine the best drying conditions in terms of plate thickness, drying temperature, and adjuvant addition. Regarding the final product properties, microbiological studies revealed that drying at 100 ºC allowed the reduction of pathogens in these samples (Santos et al., 2020). In addition, further drying studies with and without LM are ongoing to assess the extent of the reduction in the pathogenic contamination.

Table 2. Drying parameters obtained for both SS samples.

| g LM/g SS $_{wet\ basis}$ | UM sample | | AD sample | |
|---|---|---|---|---|
| | DR (g/min.kg $SS_{wet\ basis}$) | t (min) | DR (g/min.kg $SS_{wet\ basis}$) | t (min) |
| 0 | 12.21 | 43 | 9.88 | 48 |
| 0.05 | 12.80 | 41 | 11.42 | 41 |
| 0.10 | 13.57 | 39 | 11.20 | 44 |
| 0.15 | 14.70 | 36 | 11.62 | 43 |
| 0.20 | 14.32 | 36 | 11.31 | 45 |
| 0.25 | 13.47 | 40 | 12.81 | 39 |

Note: DR (drying rate) and t values obtained until a moisture ratio of 0.30.

## 4. Conclusions

According to the chemical and physical characterization, both SS types are of interest to substitute the commercial fertilizers in terms of organic matter and macronutrient content (P and N). The structure of UM may facilitate the diffusion process comparing to AD sample. Also, the lime mud showed a positive potential to act as drying adjuvant (drying rates have been increased), and then the final products can act as liming agents.


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