An Investigation of Waste Material Parameters during Pretreatment

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Abstract Pretreatment of biomass and waste is important for its efficient utilization as biofuels and/or biochemicals. In this study, two different pretreatment techniques are discussed: physico-chemical (thermal, at elevated temperature) and biological (fermentation) with the addition of rumen fluid. Analyses were performed on sewage sludge, riverbank grass (Typha latifolia) and their combination (ratio 1:1). Various parameters were measured in the liquid phase, such as chemical oxygen demand (COD), amounts of nitrogen, phosphorus and potassium (NPK analysis), total organic carbon (TOC), conductivity and pH value, and composition of CH4, O2, CO2 and H2S in the gas phase. The values of parameters in the liquid phase were analyzed before and after pretreatment, while in the gas phase parameters were measured only after pretreatment.

Keywords: Waste materials, sewage sludge, riverbank grass, pretreatment of waste, determination of parameters.

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1 Introduction

Lignocellulosic biomass is an abundantly available renewable resource and includes agricultural and forest residues, energy crops and some components of municipal, agricultural, forestry and various industrial waste (Soccol *et al.*, 2019). Because of its wide availability, its conversion in biorefineries into biofuels, biochemicals and biopolymers has attracted much attention. Lignocellulosic materials are mainly composed of cellulose, hemicellulose and lignin and form complex cell walls which are resistant to degradation (Oh *et al.*, 2015). Pretreatment can help in delignification of biomass while making biomass more susceptible to saccharification by improving its digestibility (Hendriks *et al.*, 2009). Various pretreatment techniques exist, such as chemical, physico-chemical, physical and biological and integrated processes combining different techniques (Kumar *et al.*, 2017).

The goal of this study is to explore the effects of different pretreatment methods on the values of analyzed parameters. Two different pretreatment techniques were applied: biological treatment using rumen fluid (38.6 °C, duration of 8 days) and physico-chemical treatment with elevated temperature (80 °C, duration of 5 days). Various parameters were tested in the liquid (chemical oxygen demand – COD, amounts of nitrogen, phosphorus and potassium – NPK, total organic carbon – TOC, conductivity and pH value) and gas phases (composition of CH_4, O_2, CO_2 and H_2S). Cuvette tests were used for measuring the values of most parameters (COD, NPK, NH_3, and TOC) before and after pretreatment, sensors were used for measurements of conductivity and the pH value, and gas analyzers were used for measuring concentrations of gases.

2 Materials and methods

The following materials were used:

- Riverbank grass *Typha latifolia*;
- Sewage sludge;
- Rumen fluid.

Samples were prepared in triplicate with all samples containing 6 wt.% of solids based on average dry matter (DM) content. The following set of samples were analyzed:

– Untreated samples (denoted as "Before" in Figures);
– Riverbank grass (denoted as "T");
– Sewage sludge (denoted as "B");
– Grass and sewage sludge in a ratio of 1:1 (denoted as "T+B");
– Sewage sludge and 50 ml of rumen fluid (denoted as "B+V");
– Riverbank grass and 50 ml of rumen fluid (denoted "T+V");
– Grass and sewage sludge in a 1:1 ratio with 50 ml of rumen fluid (denoted as "T+B+V").

Two pretreatment methods were tested, pretreatment with the addition of rumen fluid and thermal pretreatment. All batch assays were maintained at mesophilic conditions in a heated bath filled with deionized water. Temperature was set at rumen temperature of 38.6 °C (Turbill *et al.*, 2011) by using a Thermo Scientific™ SC100 immersion circulator. Biological pretreatment was performed for 8 days, while thermal pretreatment was performed for 5 days at 80 °C.

Several parameters were tested in the liquid phase, such as chemical oxygen demand – COD, nitrogen, phosphorus and potassium – NPK, ammonia content, total organic carbon – TOC, conductivity and pH value. For the determination of most parameter values before and after pretreatment, samples were firstly diluted and measured with QUANTOFIX® test strips, and further analyses were performed using a PF-12^{Plus} photometer and NANOCOLOR® tube tests (COD, NPK, NH_3 and TOC). Pasco sensors were used for measurements of conductivity and the pH value, and an Optima7 Biogas gas analyzer for measuring concentrations of gases in the gas phase (CH_4, CO_2, O_2 in %, and H_2S in ppm). Dry solids were determined by drying a certain mass of material to constant weight. C/N ratio was determined according to Eq. (1):

$$C/N = \frac{TOC}{TN} \tag{1}$$

3 Results and discussion

Figure 1 shows the results of measurement of NPK concentration. The highest NPK values were obtained for the combination of grass and sludge. This sample has the highest value of potassium, as well as high values of nitrogen and phosphorus. The smallest values were obtained for untreated samples and grass samples. It is notable that NPK content decreased with the addition of rumen fluid. With thermal pretreatment (80 °C), concentrations of P and K decreased, while the concentration of N increased. Similar results in terms of N concentration were obtained previously (Risberg *et al.*, 2013). For the purpose of further digestate use as fertilizer, a combination of grass and sludge is suggested because of its higher NPK values. However, an important consideration for digestate's further use are the heavy metals, pathogens and persistent organic pollutants (POPs) contained in sludge (Zhang *et al.*, 2017).

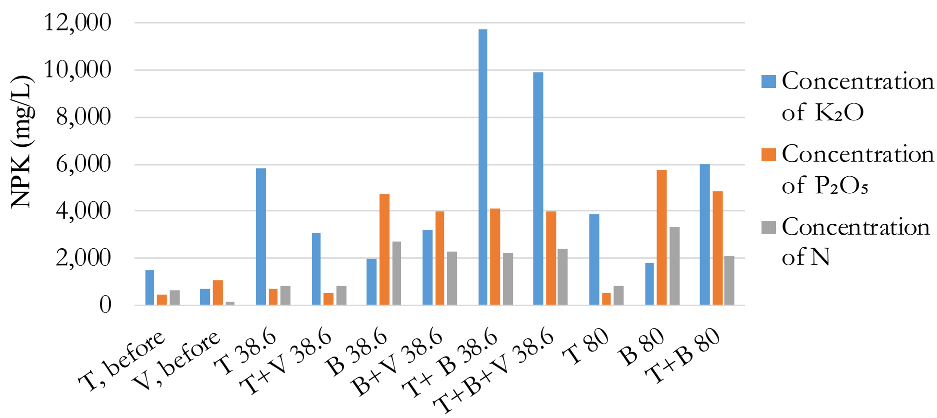

Figure 1: NPK concentrations.

Figure 2 further shows the C/N ratio, which is important for optimal growth of microorganisms (Bedoić *et al.*, 2019). The highest value is exhibited by rumen fluid and grass before pretreatment. The C/N ratio for all pretreated samples is between 4 and 7. For optimal growth of microorganisms, the C/N ratio of feedstocks should be between 20 and 30; otherwise, inhibition could occur (Wang *et al.*, 2019). C/N ratios considerably different than those suggested have been reported previously (Risberg *et al.*, 2013).

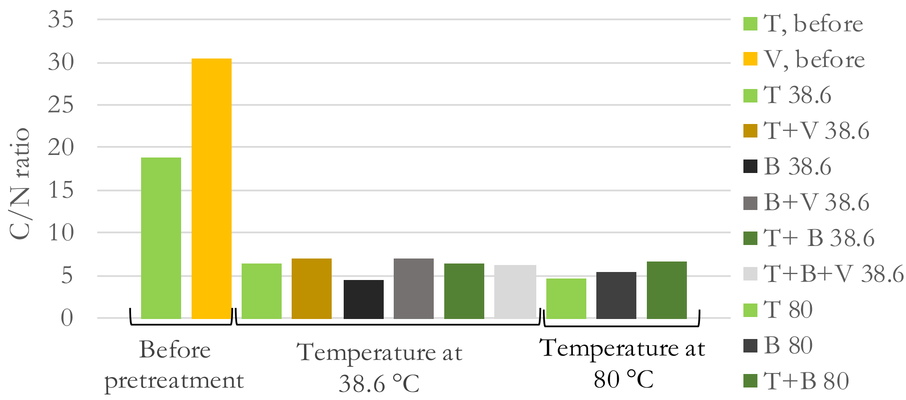

Figure 2: C/N ratio.

Figure 3 shows the composition of CH_4, CO_2, O_2 (in %) and H_2S (in 1/100 ppm) in the gas phase. CH_4 increased most significantly when rumen fluid was added to the samples. The highest CH_4 value was obtained in B+V samples as a result of fermentation, and thus the growth rate of methanogenic bacteria increased (Budiyono *et al.*, 2014). At higher temperatures (80 °C) no CH_4 was observed, as fermentation typically occurs up to 65 °C (Sunny & Joseph, 2018). Further, it could be seen that the most H_2S was produced in grass samples with the addition of rumen fluid. Higher H_2S concentrations are mainly the results of bacterial degradation under anaerobic conditions (Long *et al.*, 2016).

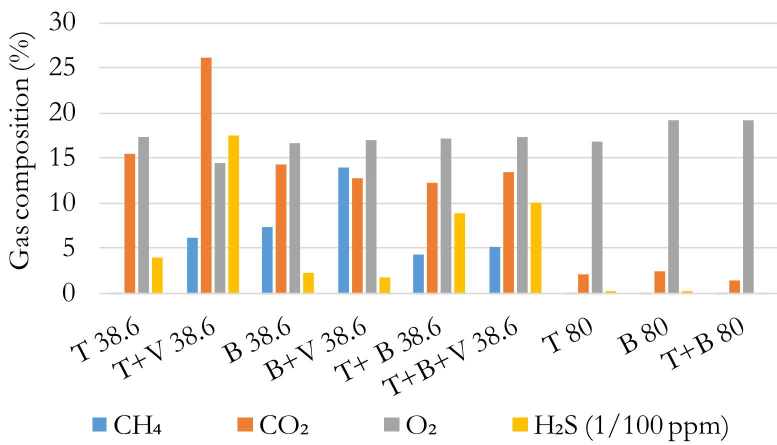

Figure 3: Gas composition.

4 Conclusions

The aim of this study was to test different pretreatment methods and to analyze how pretreatment influences the values of parameters. Two pretreatment methods were applied, biological and thermal pretreatment; sewage sludge and riverbank grass (*Typha latifolia*) were used as raw materials.

The results show that COD values increased during pretreatment, with the riverbank grass showing the highest increase. The highest NPK values were observed in samples of combined sewage sludge and riverbank grass. With the addition of rumen fluid, the concentration of K increased significantly, while samples containing sewage sludge showed higher values of P and N when compared to grass samples. Also, the concentration of ammonia was especially high in samples which contained sewage sludge; however, at higher temperatures, the concentration of ammonia decreased in all samples. In the samples containing sewage sludge and/or rumen fluid pretreated at 38.6 °C, significant concentrations of CH_4 were observed in the gas phase. Also, concentrations of H_2S were significant, especially in samples which contained rumen fluid. On the other hand, when pretreatment was performed at 80 °C, no CH_4 and insignificant amounts of H_2S were produced. For all samples containing grass, a significantly acidic environment was established, and conductivity increased when pretreatment was performed at 38.6 °C. Most of the parameters changed during pretreatment; however, the advantage of specific pretreatment techniques should be further tested for production of bioproducts.

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