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Can bioavailability of trace nutrients be measured in anaerobic digestion?

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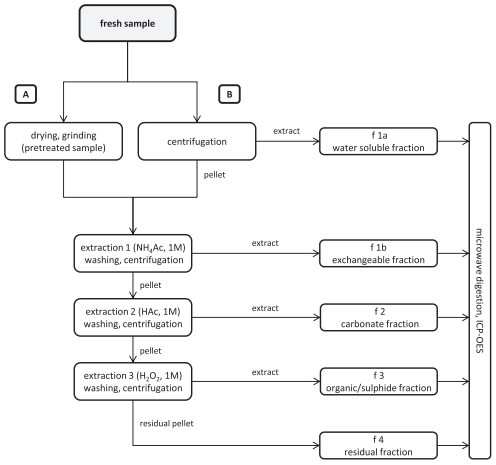
HIGHLIGHTS

- Sequential extraction technique was successfully applied to biogas slurries.
- Sample pretreatment caused major shifts in element speciation.
- Recovery rates of elements were between 90% and 110%.
- Adapted method provides more reliable information about bioavailable fractions.

GRAPHICAL ABSTRACT



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ABSTRACT

Trace nutrients significantly affect the microbial metabolic activity within anaerobic digestion processes but always imply the risk of overdosing of heavy metals. In this study the applicability of a sequential extraction scheme established for soil and sediment samples on biogas slurries with different compositions was tested and compared to an adapted version of this extraction method. The analytical results proved the successful applicability of the developed analytical technique for the speciation of trace nutrients in anaerobic digestion systems. The procedure fulfills the basic requirements of reproducible data, a time-saving analytical approach and economic feasibility. Recovery rates of 90–110% were obtained for the most important trace elements Fe, Co, Cu, Mo, Ni and Zn. However, it was demonstrated that the adapted method provides more reliable information about the bioavailable fractions and it is considered the more appropriate approach. Data on fractionation indicated that up to 76% of these essential trace nutrients might be present in an insoluble state. Depending on the specific trace element a significant fraction, from 30% to more than 70%, is not directly bioavailable. This important aspect should be

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considered to guarantee sufficient supply of the microbial consortium with trace elements and at the same time to avoid overdosage.

1. Introduction

The growing interest in biogas production by anaerobic digestion of biomass as a source of renewable energy leads to increasing research effort on optimization strategies of the bioconversion process within the anaerobic digesters [1–6]. Optimum supply of mineral nutrients needed for growth and enzyme activity in the digestion process, both in quantity and composition, is one of the key predominant strategies to increase the biomethanation rate. Microbial requirements for minerals often differ from their supply by the input material and consequently supplementation of those minerals is needed, which are not sufficiently provided.

To overcome nutrient deficits, a broad spectrum of commercial mineral supplementation products are available on the market, more or less addressing the specific needs for trace elements [7]. However, addition of trace nutrients also implies the risk of overdosing of heavy metals, in this way causing toxic effects on the microbial consortium of anaerobic digestion. Moreover, elevated heavy metal concentrations may limit the proper use of digestate as fertilizer and can cause environmental pollution.

Adequate supplementation requires not only substantial knowledge on trace nutrients content of the substrates but also bioavailability of the considered minerals. In particular about the latter aspect, bioavailability, little knowledge is available. Demirel and Scherer [8] reviewed the literature about requirements of macro- and micro-nutrients in anaerobic digestion of both agricultural substrates and the organic fraction of municipal waste (OFMSW). In this review chemical bonding state of the minerals was not considered, which may cause quite different degrees of bioavailability.

Some work has been done to investigate the effects of certain trace metal nutrients on methane production in anaerobic wastewater treatment including analysis of metal speciation. Most of them dealt with granular sludge in UASB-reactors [9–15]. Aquino and Stuckey [16] investigated the effect of copper complexation on bioavailability and toxicity in a laboratory CSTR.

Up to date there is no investigation on metal fractionation of digester slurry obtained from biogas plants utilizing agricultural substrates or organic wastes for renewable energy production. These kinds of processes differ from granular sludge processes by significantly higher concentrations of suspended solids in the digester. Therefore different patterns of metal fractionation can be expected, resulting in different bioavailabilities.

In soil bioremediation, bioavailability, has traditionally been an important issue been to provide information on potential transfer of sediment and soil bound potential toxic heavy metals to the ground water and the food chain [17]. Since many decades sequential extraction of soils is a very well established technique and numerous multi-step extraction schemes have been developed. Just recently such investigations have been applied to other materials such as sewage sludge and anaerobic sludge. However, in all cases the focus was to obtain information on the mobility of toxic metals in order to evaluate potential ecotoxicological risks [18].

The aim of this work was to examine the applicability of sequential extraction on anaerobic digestion slurries originating from different sources. The investigated biogas slurries were obtained from three biogas processes: an agricultural biogas plant utilizing a mixture of pig manure and maize silage as substrates, a plant using solely energy crops, and a plant processing animal byproducts.

For examination the modified Tessier scheme of sequential fractionation, a widely applied method in soil and sediment analyses was adapted [19]. This analytical procedure yields four fractions: an exchangeable fraction, a carbonate fraction, a fraction of organic matter and sulphides, and a residual fraction.

Moreover, an adapted procedure yielding an additional fraction was developed. Both, our adapted method and the original modified Tessier scheme were compared to see possible shifts in fractionation. Besides the evaluation of reproducibility of the analytical methods attention was given to the interpretability of the obtained results based on chemical characteristics of the samples and on thermodynamic considerations.

2. Materials and methods

2.1. Origin of the samples

Samples were taken from three different large scale industrial and agricultural AD plants. All of them used a single stage process with main and post fermenters with average hydraulic retention times (HRT) between 35 (plant III) and 50 days (plant I and II) for the main fermenter. AD plant I was an industrial biogas plant operated solely with slaughterhouse waste derived from the close-by pig abattoir. The biogas produced in the AD plant is purified by an external biological desulphurisation unit and combusted in a combined heat and power plant (CHP) with an electrical power of 525 kW. Plants II and III were agricultural AD plants using on the one hand grass and maize silage on the other hand a mixture of pig manure and maize silage. Again biogas was utilized in CHPs with an electrical power of 525 kW and 1050 kW, respectively.

Beside AD plant no. II, the two other plants received additional micro- and macronutrients (plant I trace element mixture, plant III ferrous chloride). All operating conditions (e.g. feeding, substrate composition stirring, organic loading rate) of all AD plants were kept relatively constant for at least 6 month before sampling. Samples were always taken from the main fermenter. General sample characteristics are provided in Table 1.

Immediately after sampling the pH was measured. All the other relevant parameters were analyzed in laboratory. Samples were stored at 4 °C for the time of 7 days maximum before further processing.

2.2. Analysis of standard parameter

TS (total solid content) and VSS (volatile suspended solid content) were analyzed by DIN methods [20,21], for NH_4-N (ammonium nitrogen) a slightly modified standard method [22] was used, where MgO was substituted by NaOH for pH adjustment.

2.3. Reagents and equipment

Double-distilled water was used for the preparation of all extracting agents and washing solutions. Glassware were rinsed with double-distilled water and dried at 105 °C.

All centrifugation steps were done with a Beckman GS-6 device at the rotation speed of 3000 rpm (1459 g) using polypropylene centrifuge tubes. The filtration steps were done with cellulose filters (Whatman 595½).