



Sulfur K-edge XANES and acid volatile sulfide analyses of changes in chemical speciation of S and Fe during sequential extraction of trace metals in anoxic sludge from biogas reactors

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ABSTRACT

The effect of sequential extraction of trace metals on sulfur (S) speciation in anoxic sludge samples from two lab-scale biogas reactors augmented with Fe was investigated. Analyses of sulfur K-edge X-ray absorption near edge structure (S XANES) spectroscopy and acid volatile sulfide (AVS) were conducted on the residues from each step of the sequential extraction. The S speciation in sludge samples after AVS analysis was also determined by S XANES. Sulfur was mainly present as FeS (~60% of total S) and reduced organic S (~30% of total S), such as organic sulfide and thiol groups, in the anoxic solid phase. Sulfur XANES and AVS analyses showed that during first step of the extraction procedure (the removal of exchangeable cations), a part of the FeS fraction corresponding to 20% of total S was transformed to zero-valent S, whereas Fe was not released into the solution during this transformation. After the last extraction step (organic/sulfide fraction) a secondary Fe phase was formed. The change in chemical speciation of S and Fe occurring during sequential extraction procedure suggests indirect effects on trace metals associated to the FeS fraction that may lead to incorrect results. Furthermore, by S XANES it was verified that the AVS analysis effectively removed the FeS fraction. The present results identified critical limitations for the application of sequential extraction for trace metal speciation analysis outside the framework for which the methods were developed.

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1. Introduction

Sequential extraction methods are widely used for characterization of chemical forms or fractions of metals in samples from soil, sediment, and sludge. Reagents, such as solutions of neutral salts, weak and strong acids as well as reducing and oxidizing compounds, are selected to be as specific as possible toward solubilization of metal binding fractions. Thus, it is assumed that the reagents extract specific forms of metals in a mixture of metal species [1,2]. The reagents are applied in a successive manner with increasing degree of reactivity. Accordingly, metals released after the extraction steps are attributed to operationally defined fractions ranging from loosely bound to strongly bound forms [1–4]. Attribution of the specified fractions to certain chemical forms or

phases of metals has uncertainties associated with selectivity of the reagents and additive effects caused by reactions occurring in a mixture of metal forms and sequentially added reagents [5].

Trace metals are important micronutrients for growth and activity of microorganisms in biogas reactors in which organic content of the influent material is biologically converted to methane and carbon dioxide under anaerobic conditions [6–10]. Processes regulating the chemical speciation and bioavailability of trace metals are complex involving dynamic interaction of microorganisms with organic and inorganic compounds [11,12]. Laboratory and practical evidences have demonstrated that speciation and bioavailability of trace metals essential for the anaerobic digestion process are highly influenced by the chemistry of sulfur (S) [11–15]. The precipitation of metal sulfide phases and/or adsorption of trace metals to iron sulfide particles are considered to be the most important processes contributing to trace metal dynamics in biogas reactors. The sequential extraction methods are widely used for analysis of trace metal fractionations in sludge from biogas reactors e.g. [16–19], but possible changes in the S chemistry during sequential extractions, and how they may affect operationally defined trace metal fractions, have not been investigated previously for sludge samples from biogas reactors. In a parallel study, we observed that Co

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(but not Ni) was encountered in the residual fraction (after extraction of organic/sulfide bonded trace metals) of a biogas sludge together with Fe (Gustavsson et al., unpublished). The question arose whether or not this was due to an artifactual formation of an Fe-phase during the extraction procedure, to which Co was associated.

The objective of the present study was to determine the chemical speciation of S in sludge from biogas reactors, and to investigate possible changes in the chemical speciation of S and Fe during a sequential extraction procedure used for trace metal speciation. The feasibility of three different sequential extraction procedures used for analysis of trace metal fractionation in anaerobic granular sludge was compared by Hullebusch et al. [17]. They suggested that a modified version of the method developed by Tessier et al. [1] as described by Osuna et al. [4], has a better reproducibility and reagent selectivity compared to other sequential extraction methods. We used sulfur K-edge X-ray absorption near edge structure (S XANES) spectroscopy and acid volatile sulfide (AVS) extraction as analytical tools to quantify changes in S speciation during sequential extraction scheme of the modified Tessier method [1,4].

Sulfur K-edge XANES is a suitable method for identification and quantification of various S compounds, their oxidation states and binding forms in a sample [20,21], which allow us to follow the fate of S species during sequential extraction. Acid volatile sulfide analysis is a classical approach for measurement of the sulfide fraction reactive toward metals in anoxic samples, based on volatilization of reduced S bonded in mineral fractions, mainly FeS [12,22,23]. The method has in principal similar disadvantages as sequential extraction regarding the uncertainty in selectivity of the applied reagent for volatilization of reduced S compounds and simultaneously extracted metals [22]. To analyze possible changes in S forms during AVS extraction, we used S XANES to compare the S speciation before and after AVS analysis. To our knowledge, this is the first study quantifying changes in the S chemistry using S XANES, during sequential extraction of metals and before and after AVS extraction. Thus, this study will contribute to a better understanding of the accuracy of sequential extraction of trace metals, as well as AVS analysis, in general and their indirect effects on trace metal speciation in sludge samples from biogas reactors in particular.

2. Material and methods

2.1. Sample sources

Samples were taken from two lab-scale biogas reactors semi-continuously fed with grain stillage. The reactors, designated as J2 and J4, were operated at 37 °C with a hydraulic retention time (HRT) of 20 days and organic loading rates (OLR) of 2.5 and 4.0 g L⁻¹ d⁻¹ volatile solid (VS), respectively. The only difference between J2 and J4 is their different OLRs. The reactors were supplemented with 0.5 mg Co L⁻¹ d⁻¹ (as CoCl₂), 0.2 mg Ni L⁻¹ d⁻¹ (as NiCl₂) and 0.5 g Fe L⁻¹ d⁻¹ (as a solution with Fe(III):Fe(II) ratio of 2:1). Trace metals were added in order to provide the microbial community with micronutrients. Iron was supplemented to precipitate inorganic sulfide and decrease the H₂S concentration in biogas. For a detailed description of the operational conditions and rationale for trace metal and Fe addition, the reader is referred to Gustavsson et al. [10].

2.2. Sequential extraction

Bulk sludge samples were transported to an anaerobic box (Vinyl Anaerobic Airlock Chamber type Coy, Coy Laboratories Inc., USA) containing gas composition of CO₂ (40%), N₂ (55%), and H₂ (5%). The CO₂ was introduced into the chamber in order to simulate

the headspace of biogas reactor and avoid degassing of dissolved CO₂ from sludge liquid when exposed to box atmosphere, which otherwise may result in a pH change of the sludge. The H₂ was used in order to remove traces of oxygen in contact with located palladium catalyst in the anaerobic box. Sub-samples were transferred into polypropylene tubes (Falcon, Sarstedt, Germany) and centrifuged at 10,000 rpm for 10 min. The supernatant was decanted and its Fe concentration was measured by atomic absorption spectroscopy (AAS, 1100 Atomic Absorption Spectrophotometer, Perkin Elmer, USA). Sub-samples corresponding to a dry mass of 0.18–0.30 g were used for sequential extraction of modified Tessier following the protocol by Osuna et al. [4]. Total solid (TS) content of the samples was measured according to Swedish Standard method (SS-028113) by drying the samples at 105 °C for 20 h.

A summary of the sequential extraction procedure is given in Table 1, beginning with a centrifugation of sludge and analysis of metals in the sludge liquid fraction. Results on trace metals such as Ni and Co will be reported in Gustavsson et al. [unpublished]. Here we only report Fe (as determined by AAS) after each sequential extraction step. The solid residue after each step was washed with deaerated Milli-Q water, centrifuged and the Fe concentration in the supernatant was measured in order to check possible Fe release from the solid phase during the washing step. After decanting the water, the reagent for extraction of the next fraction was added to the tubes. The same procedure was applied for all extraction steps. The two first fractions (i.e. exchangeable and carbonate) were extracted inside the anaerobic box to avoid exposure of the samples to air and oxidation of reduced S species. The residual fraction, i.e. last step of the sequential extraction, was extracted according to Swedish Standard method (SS-028311) for extraction of metals from sludge by 7 M nitric acid in an autoclave (at 120 °C for 30 min). The total S content of the samples was analyzed by Eurofins Environment Sweden AB (Lidköping, Sweden).

2.3. Acid volatile sulfide (AVS)

The AVS method presented by Hsieh and Yang [24] and modified by Brouwer and Murphy [25] and Leonard et al. [26] was applied in the present study. The AVS extraction was performed in the anaerobic box to avoid oxidation of sulfide due to exposure to air. In summary, 0.18–0.30 g TS of sludge was transferred into a 250 mL glass bottle with a vial attached to its inner wall. The vial was filled up with 10 mL of sulfide antioxidant buffer (SAOB) solution containing 2 M NaOH, 0.1 M ascorbic acid and 0.1 M EDTA. 25 ml of 1 M HCl acid was added to the glass bottles. The bottles were capped and the solid suspension was stirred by a magnetic stirrer for 1 h. The addition of HCl results in volatilization of reduced, inorganic S compounds of the solid phase which is trapped by the SAOB solution in the vial attached to the inner wall of the reaction bottle. After 1 h, the liquid fraction was centrifuged and its Fe concentration was measured using AAS. The concentration of sulfide in SAOB solution (AVS) was measured using a sulfide sensor (Ag/S 800 Wissenschaftlich-Technische Werkstätten, Germany). The sensor was calibrated with 0.1 M Na₂S·9H₂O diluted in SAOB solution to sulfide concentrations ranging from 10⁻⁵ to 10⁻² M, which covered all the measured AVS concentrations. For more information about the details of AVS experimental setup the reader is referred to Brouwer and Murphy [25] and Leonard et al. [26].

2.4. Quality control of extraction procedures

The extraction reagents were prepared using Milli-Q water purged with N₂ to degas dissolved oxygen. All the chemicals were of analytical reagent grade. Glassware was washed with acid (7 M nitric acid for sequential extraction and 10% hydrochloric acid for AVS analysis) for 48 h and rinsed with Milli-Q water at least three

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