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Trace metal speciation and bioavailability in anaerobic digestion: A review

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ABSTRACT

Trace metals are essential for the growth of anaerobic microorganisms, however, in practice they are often added to anaerobic digesters in excessive amounts, which can lead to inhibition. The concept of bioavailability of metals in anaerobic digestion has been poorly understood in the past, and a lack of deep understanding of the relationship between trace metal speciation and bioavailability can result in ineffective metal dosing strategies for anaerobic digesters. Sequential extraction schemes are useful for fractionating trace metals into their different forms, and metal sulfides can serve as a store and source for trace metals during anaerobic digestion, while natural/synthetic chelating agents (soluble microbial products-SMPs, extracellular polysaccharides-EPS, and EDTA/NTA) are capable of controlling trace metal bioavailability. Nevertheless, more work is needed to: investigate the speciation and bioavailability of Ca, Mg, Mn, W, and Se; compare the bioavailability of different forms of trace metals e.g. carbonates, sulfides, phosphates to different anaerobic trophic groups; determine what factors influence metal sulfide dissolution; investigate whether chelating agents can increase trace metal bioavailability; develop and adapt specialized analytical techniques, and; determine how trace metal dynamics change in an anaerobic membrane bioreactor (AnMBR).

Contents

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1. Introduction

Trace metals are essential components of cofactors and enzymes, and their roles in anaerobic processes have been studied extensively (Oleszkiewicz and Sharma, 1990; Fermoso et al., 2009; Demirel and Scherer, 2011). However, the supplementation of trace metals for enhanced metabolism has not been as well understood as the toxicity of metals to anaerobic microorganisms. In practice, to fulfill these nutrient requirements trace metals are often supplemented in sufficient quantities to support microbial growth, and hence ensure the optimal performance of the treatment processes. On the other hand, trace metals should only be dosed below the inhibitory or toxic level as an excessive metal content in the sludge will cause harm to the environment, and minimize the quality and applicability of anaerobic products in agriculture, e.g. digestate used as fertilizer. However, the supplemented trace metals are not always necessarily bioavailable for the microorganisms to take up (Zitomer et al., 2008).

The concept of bioavailability of metals in anaerobic digestion has been poorly understood even though it has been widely used in the literature. Total metal concentration is generally used to evaluate the effects of metal stimulation and toxicity in anaerobic digestion. However, it has been demonstrated that the measurement of total metal concentration is not sufficient to determine its bioavailability (Hsu and Lo, 2001; Amir et al., 2005). As a matter of fact, trace metal bioavailability depends on their speciation, which is controlled by the operating conditions of anaerobic reactors (Oleszkiewicz and Sharma, 1990; He et al., 2009).

This review will examine the basics of the most essential trace metals in anaerobic digestion, including their limitations, stimulation, requirements, and dosing strategies. The main focus will be on trace metal speciation and bioavailability in anaerobic digestion including the current state of art for analytical techniques, building on the comprehensive reviews carried out by Zandvoort et al. (2006a) and Worms et al. (2006). Finally, future research needs will be identified in order to further understand the relationship between trace metal speciation and bioavailability in anaerobic digestion.

2. Importance of trace metals in anaerobic digestion

Biological treatment of wastewaters, including anaerobic treatment, requires not only organic matter, but also essential nutrients for the growth of microorganisms. Some types of wastewater contain a sufficient amount of these nutrients, eg. swine wastewater (Cestonaro do Amaral et al., 2014). However, other types of wastewater might require metal supplementation in order to avoid nutrient deficiency, eg. methanol wastewater (Fermoso et al., 2008a), maize silage (Evranos and Demirel, 2014), and wheat stillage (Schmidt et al., 2014).

The metal nutrients can be classified based on their concentration in the cells into major cations (K, Mg, Ca), and micronutrients (Mn, Fe, Co, Cu, Mo, Ni, Se, W) (Merchant and Helmann, 2012). Metal concentration in the cells range from 10^{-7} to 10^{-3} M for the major cations, and from 10^{-6} to 10^{-15} M for the micronutrients (Williams and Fraústo da Silva, 2000). The essential micronutrients known as trace metals are constituents of cofactors in enzyme systems, and the function of these trace metals and their associated enzymes in anaerobic reactions were summarized by a number of researchers (Jarrell and Kalmokoff, 1988; Oleszkiewicz and Sharma, 1990; Schattauer et al., 2011).

Trace metals considered the most essential in anaerobic digestion are transition metals i.e. Fe, Ni, and Co (Oleszkiewicz and Sharma, 1990), and their effects on anaerobic digestion have been studied extensively in the literature (Hoban and Van Den Berg, 1979; Sharma and Singh, 2001; Pobeheim et al., 2011; Qiang et al., 2012; Shakeri Yekta et al., 2012; Gustavsson et al., 2013a). The importance of Fe depends on its redox properties, and its engagement in energy metabolism (Takashima and Speece, 1989). Fe is utilized in the transport system of the methanogenic bacteria for the conversion of CO_2 to CH_4, and functions both as an electron acceptor and donor (Vintiloiu et al., 2013). Fe also acts as a binding component in sulfide precipitation as it is often supplemented into anaerobic reactors, not only to precipitate the formed sulfide, but also to control the level of hydrogen sulfide in the biogas (Gustavsson et al., 2013a). A corrinoid such as vitamin B_{12}, containing the Co ion, can bind to the coenzyme methylase which catalyzes methane formation in both acetoclastic methanogens and hydrogenotrophic bacteria (Schonheit et al., 1979; Kida et al., 2001). Although Ni was initially considered as not being essential for bacterial growth (Diekert et al., 1981), a low molecular weight coenzyme, F_{430}, was discovered in extracts from *Methanobacterium thermoautotrophicum*; however, which was shown to contain substantial amounts of Ni (Speece et al., 1983; Thauer, 1998; Kida et al., 2001). This coenzyme (F_{430}) is contained within the Methyl-coenzyme M reductase enzyme, which reduces methyl coenzyme M to methane in all methanogenic pathways (Friedmann et al., 1990).

Mn acts as an electron acceptor in anaerobic respiration processes (Langenhoff et al., 1997), while Zn takes part in the functioning of enzymes involved in methanogenesis such as coenzyme M methyltransferase (Sauer and Thauer, 2000), and Zn, Cu, and Ni have all been found in a single hydrogenase (Jarrell and Kalmokoff, 1988). There is limited information available in the literature on the positive effects of Zn and Cu on methanogens, but Zn was found in remarkably high concentrations (50–630 ppm) in 10 methanogenic bacteria, whereas Cu was only present in some species (Scherer et al., 1983).

Other trace metals such as W and Mo are also found in enzymes, such as formate dehydrogenase (FDH), which catalyzes formate production by propionate oxidizers (Dong et al., 1994; Fermoso et al., 2009; Banks et al., 2012), and some methanogenic bacteria contain W and Mo-containing enzymes for the same purpose (Nies, 1999). *Methanobacterium thermoautotrophicum* contains two formylmethanofuran dehydrogenase iso-enzymes, a W containing form and a Mo containing form; the Mo enzyme is synthesized only when Mo is present in the growth medium, while the W enzyme is synthesized when either W or Mo is available. If the growth medium contains Mo, the W enzyme will contain Mo rather than W