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Respirometric characterization of aerobic sulfide, thiosulfate and elemental sulfur oxidation by S-oxidizing biomass

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ABSTRACT

Respirometry was used to reveal the mechanisms involved in aerobic biological sulfide oxidation and to characterize the kinetics and stoichiometry of a microbial culture obtained from a desulfurizing biotrickling filter. Physical–chemical processes such as stripping and chemical oxidation of hydrogen sulfide were characterized since they contributed significantly to the conversions observed in respirometric tests. Mass transfer coefficient for hydrogen sulfide and the kinetic parameters for chemical oxidation of sulfide with oxygen were estimated. The stoichiometry of the process was determined and the different steps in the sulfide oxidation process were identified. The conversion scheme proposed includes intermediate production of elemental sulfur and thiosulfate and the subsequent oxidation of both compounds to sulfate. A kinetic model describing each of the reactions observed during sulfide oxidation was calibrated and validated. The product selectivity was found to be independent of the dissolved oxygen to hydrogen sulfide concentration ratio in the medium at sulfide concentrations ranging from 3 to 30 mg S L^{-1}. Sulfide was preferentially consumed ($SOUR_{max}$ = 49.2 mg DO g^{-1} VSS min^{-1}) and oxidized to elemental sulfur at dissolved oxygen concentrations above 0.8 mg DO L^{-1}. Substrate inhibition of sulfide oxidation was observed ($K_{i,S^{2-}}$ = 42.4 mg S L^{-1}). Intracellular sulfur accumulation also affected negatively the sulfide oxidation rate. The maximum fraction of elemental sulfur accumulated inside cells was estimated (25.6% w/w) and a shrinking particle equation was included in the kinetic model to describe elemental sulfur oxidation. The microbial diversity obtained through pyrosequencing analysis revealed that *Thiothrix* sp. was the main species present in the culture (>95%).

1. Introduction

Desulfurization of biogas under aerobic conditions using biotrickling filters (BTFs) has been demonstrated as an efficient and environmentally friendly process to upgrade biogas (Fortuny et al., 2008). In aerobic BTFs, air blown directly to the liquid phase is the most efficient way to supply oxygen as electron acceptor to oxidize sulfide to sulfate. However, excess air is passed through the packed bed to avoid products from partial sulfide oxidation, as elemental sulfur. Thus, air supply is limited since it lowers the methane content of biogas with the additional risk of reaching flammability limits when too much air is supplied. At high sulfide loading rates, elemental sulfur is produced instead of sulfate and accumulates inside the BTF packed bed as a consequence of oxygen transfer limitation (Fortuny et al., 2008; Rodriguez et al., 2014) (Eqs. (1)–(3)). Elemental sulfur accumulation imposes operational problems such as a pressure drop increase and it may eventually result in bioreactor clogging.

$$H_2S + 0.5\ O_2 \rightarrow S^0 + H_2O \quad (1)$$

$$S^0 + 1.5\ O_2 + H_2O \rightarrow SO_4^{2-} + 2H^+ \quad (2)$$

$$H_2S + 2\ O_2 \rightarrow SO_4^{2-} + 2H^+ \quad (3)$$

In order to gain insight in the factors that determine which products are formed during sulfide oxidation enabling process

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Nomenclature

a	chemical reaction order (dimensionless)
b	chemical reaction order (dimensionless)
β	chemical reaction order (dimensionless)
DO	dissolved oxygen concentration (mg O_2 L^{-1})
DO*	equilibrium oxygen concentration (mg O_2 L^{-1})
f_{max}	maximum ratio of intracellular sulfur stored to biomass (mg S mg^{-1} VSS)
f_{S0}	ratio of intracellular sulfur stored to biomass (mg S mg^{-1} VSS)
$K_{i,S^{2-}}$	sulfide inhibition constant (mg S L^{-1})
k_La_{O2}	mass transfer coefficient for oxygen (min^{-1})
K_O	affinity constant for oxygen (mg O_2 L^{-1})
$K_{S^{2-}}$	affinity constant for sulfide (mg S L^{-1})
k_{S^0}	shrinking kinetic constant for elemental sulfur oxidation ($mg^{2/3}$ VSS $mg^{-2/3}$ S)
K_{switch}	substrate switch constant (mg S L^{-1})
K_{TS}	affinity constant for thiosulfate (mg S L^{-1})
k_{TS_ab}	rate constant for thiosulfate production under abiotic conditions
k_{TS_p}	kinetic constant for thiosulfate production under biotic conditions
μ_{max}	maximum specific growth rate (h^{-1} or min^{-1})
η_{TS}	energetic correction factor to describe growth on thiosulfate
OUR_{end}	endogenous oxygen uptake rate (mg O_2 L^{-1} min^{-1})
OUR_{ex}	exogenous oxygen uptake rate (mg O_2 L^{-1} min^{-1})
PHB	Polyhydroxy-butyrate
r_{S2-}	biological sulfide oxidation rate (mg S L^{-1} min^{-1})
r_{S0}	biological sulfur oxidation rate (mg S L^{-1} min^{-1})
r_{TS}	biological thiosulfate oxidation rate ($mgS_2O_3^{2-}$–$SL^{-1}min^{-1}$)
r_{TS_ab}	thiosulfate production rate under abiotic conditions ($mgS_2O_3^{2-}$–$SL^{-1}min^{-1}$)
r_{TS_p}	thiosulfate production rate under biotic conditions ($mgS_2O_3^{2-}$–$SL^{-1}min^{-1}$)
S^{2-}	sulfide concentration (mg S L^{-1})
SO	sulfate concentration (mg S L^{-1})
SO_{in}	sulfate concentration in the outlet flow of the CSTR (mg S L^{-1})
SO_{out}	sulfate concentration in the inlet flow of the CSTR (mg S L^{-1})
θ	model parameter to be estimated through minimization
TDS	Total dissolved sulfide concentration (mg S^{2-} L^{-1})
TS	thiosulfate concentration (mg S L^{-1})
VSS_{out}	biomass concentration in the outlet flow of the CSTR (mg VSS L^{-1})
VSS_{in}	biomass concentration in the inlet flow of the CSTR (mg VSS L^{-1})
w_i	weighting coefficient
X	biomass concentration (mg VSS L^{-1})
$Y_{X/S^{2-}}$	biomass growth yield using sulfide as substrate (mg VSS mg^{-1} S)
Y_{X/S^0}	biomass growth yield using elemental sulfur as substrate (mg VSS mg^{-1} S)
$Y_{X/TS}$	biomass growth yield using thiosulfate as substrate (mg VSS mg^{-1} S)

optimization, a rigorous mathematical model describing desulfurization in a BTF is needed. The model can be applied to optimize the operational conditions of a desulfurizing BTF by avoiding elemental sulfur accumulation (Almenglo et al., 2013; López et al., 2015). To develop such process models, detailed kinetic characterization of sulfide-oxidizing biomass (SOB) is required. A validated and calibrated mathematical model can be used for proper prediction of bioreactor performance as a function of the operational conditions imposed.

Kinetic and stoichiometric characterization of SOB have been successfully conducted by Flowing gas-Static liquid respirometry (LFS), which is based on monitoring the dissolved oxygen (DO) concentration when a pulse of substrate is added to the respirometric vessel while air is continuously supplied to the liquid phase. At the end of the test, the initial dissolved oxygen concentration is recovered, once the substrate is completely depleted. The successful application of the LFS method is largely due to the high sensitivity associated with DO monitoring (Spanjers et al., 1996; Jubany et al., 2005 among many others). In an LFS respirometer, DO is measured in an aerated, suspended microbial culture. In desulfurizing BTFs, SOB are not suspended in the liquid phase but immobilized over the packing material surface. Immobilized biomass makes identification of kinetic and stoichiometric parameters more complicate due to steep substrate and product gradients. To overcome these limitations, Gonzalez-Sanchez et al. (2009) used the LFS respirometry to characterize SOB obtained from a BTF biofilm although the stoichiometry and oxidation mechanisms were not studied. Delhomenie et al. (2008) proposed a respirometric technique using directly the packing material with immobilized biomass. The problem with this method was that the conditions were not perfectly controlled (pH, homogeneity, active fraction of biomass and nutrients recirculation among others). Bonilla-Blancas et al. (2015) also proposed a novel respirometric methodology for SOB characterization using direct measurements in biotrickling beds, namely heterogeneous respirometry. However, the configuration of the respirometer did not allow sampling the liquid phase of the system, which hindered the validation of any kinetic model proposed to characterize SOB. LFS respirometry overcomes such limitations associated with direct measurement on a biofilm system. The main uncertainty to be considered when applying the kinetic data obtained using LFS in a biofiltration model is the correction needed for the fraction of active biomass and the actual biomass concentration in the biofilm.

Many authors have characterized suspended SOB but there is no clear agreement about the processes occurring or the kinetic equation to describe sulfide oxidation and elemental sulfur production and consumption rates. Most authors consider simple Monod or Haldane equations to describe limitation or substrate inhibition by sulfide, respectively (Roosta et al., 2011; Mora et al., 2014a). More complex kinetic models related to the physiology of SOB have also been reported (Klok et al., 2013). With regards to biological oxidation of elemental sulfur, kinetic models considering Monod equation or half or zero-order equations have also been reported (Koenig and Liu, 2001; Munz et al., 2009; Roosta et al., 2011; Mora et al., 2014a). The main objective of this work was to develop, calibrate and validate a complete kinetic model to characterize the aerobic biological sulfide oxidation process since no widely accepted mathematical framework to describe this process has been established so far. The model was developed taking into account the most relevant mechanisms involved in the process in order to be subsequently used in