Stoichiometry of sulphide oxidation with nitrate as electron acceptor

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INTRODUCTION

The removal of nitrogen by using sulphide as electron donor is a potentially interesting solution when sulphate and nitrogen are abundant in an effluent (such as for tannery industry), that can be advantageously treated through anaerobic digestionAMPLIARE. This process was already investigated with reference both to liquid (Lu et al., 2009) and gaseous streams (Kleerebezem and Mendez, 2002; Mora et al. 2014); however, when biogas is treated in a biotrickling filter (BTF) at high volumetric load, biomass accumulation may lead to the clogging of the bed (Mannucci et al., 2012). Within the Biosur Life+ project we developed a moving bed biofilm reactor for gaseous effluent treatment, with the aim of allowing biomass removal and solids retention time control; in this context, however, it is still important to quantify the kinetics and the stoichiometry of the processes involved.

Most of previous work on the kinetics and stoichiometry of sulphur compounds oxidation, were carried out with thiosulphate as electron donor (inter alia Mora et al., 2014), while very few tests (Munz et al., 2009; Mora et al. 2014) have been carried out with sulphide due to the difficulty of using a strongly volatile and, at the same time inhibiting, substrate (ampliare in riferimento alla sorgente di solfuro, spegando il perchè delle scelte) . This work is aimed at investigating denitrification with sulphide, in the presence of typical S/N ratio that can derive from the anaerobic digestion of primary sludge of tannery wastewater and estimating those parameters that can affect the production of biomass in a BTF, that is mainly, the stoichiometric coefficients of sulphide oxidizing bacteria (SOB) growth and the decay kinetics.

MATERIALS AND METHODS

The experiment was carried out at CER[2]CO (Cuoiodepur tannery WWTP-Pisa, Italy). A sequencing batch reactor (SBR) (working volume of 3.2 L; HRT of 24 h; see Figure 1) was fed with liquid influent on the hypothesis that all the H_2S produced by the anaerobic digestion would be transferred to the liquid phase and that the ammonia from the digester would be completely oxidized to nitrate.
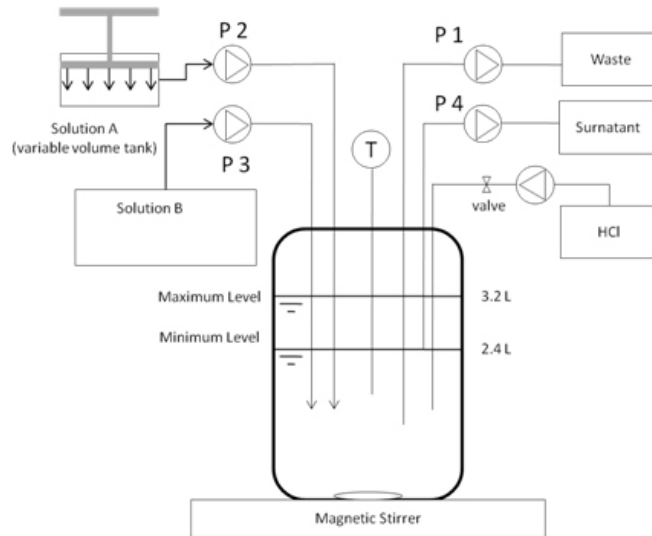
Figure 1 – Schematic of the used bench scale SBR

The reactor was fed for 160 d with two distinct peristaltic pumps with sulphide (Solution A) with a solution of micronutrients and nitrate (Solution B or C). The operating conditions are summarized in Table 1,.

Solution A was stored in the absence of headspace, that is, in a storage tank with a variable volume, and at pH =10 to minimize the desorption of hydrogen sulphide. For Solution A $NaHCO_3$ (1.24 g L^{-1}) and $Na_2S \cdot 3H_2O$ (0.41 g L^{-1}) diluted in demineralised water were used; for Solution B and C $Na_2HPO_4 \cdot 2H_2O$ (0.66 g L^{-1}); KH_2PO_4 (0.52 g L^{-1}); NH_4Cl (0.05 g L^{-1}); $MgSO_4 \cdot 7H_2O$ (0.063 g L^{-1}); KNO_3 (1.63 g L^{-1}; B only) and $NaNO_2$ (0.96 g L^{-1} C only) were diluted in tap water.

The cycle phases of the SBR were as follow: feeding (30 min); mixing (60 min); settling (240 min); decant (30 min). The excess biomass was removed during the last 2 min of the mixing phase. The reactors were maintained at pH between 7 and 8 through the dosage of an HCl solution and at room temperature (between 18 and 28 °C).

Samples were collected three times a week and the following parameters were monitored: COD, VSS, TSS, $N-NO_2^-$, $N-NO_3^-$, $S-SO_4^{2-}$, Sulphide, Total Sulphur, T, pH. Soluble and total COD, TSS and VSS were analyzed according to IRSA-CNR methods. $S-SO_4^{2-}$, Sulphide, Nitrite and Nitrate were measured through ionic chromatography (ICS1000, Dionex, U.S.A.) and total sulphur through plasma spectrophotometry (ICP-OES, Agilent Technology, U.S.A.). Thiosulphate and elemental sulphur, were estimated indirectly by using Eq. 1 and Eq. 2, (where MW is molecular weight where):

$$S_{thiosulphate} = \left(COD_S - N_{nitrite} \frac{gCOD}{gN_{nitrite}} \frac{gCOD}{gS_{thiosulphate}} \right) \frac{MW_{sulphur}}{MW_{thiosulphate}} \qquad \text{Eq. 1}$$

$$S_{elementalsulphur} = \left(COD_P - \frac{VSS}{TSS} \frac{gCOD}{gSSV} TSS \right) \frac{gCOD}{gS_{elemental\ sulphur}} \qquad \text{Eq. 2}$$

The stoichiometry of the process and the decay coefficient where estimated by using an activated sludge model that included a two-step denitrification and three steps sulphide oxidation (to elemental sulphur, thiosulphate and sulphate). The model was calibrated with the experimental data of two subperiods of phase I (SRT=5d) and phase II (SRT=20 d) during which the process was stable. The number of parameters to be calibrated was reduced with the following assumptions: 1) a single SOB population; 2) the yield coefficient of SOB growing with nitrite and nitrate was

identical; 3) the yield coefficient associate to the growth of SOB was proportional to the increase of the oxidation state of sulphur in the reaction and expressed as a fraction of a total yield coefficient referring to the oxidation of HS^- to SO_4^{2-} (Y_{SOB}), that is: $0.145 \cdot Y_{SOB}$ from HS^- to S^0; $0.145 \cdot Y_{SOB}$ from S^0 to $S_2O_3^{2-}$ and $0.29 \cdot Y_{SOB}$ from $S_2O_3^{2-}$ to SO_4^{2-}; 4) the decay process was represented with the death regeneration model and heterotrophic biomass was considered as growing on the SOB decay products.

RESULTS AND DISCUSSION

During the experiment sulphide removal efficiency (RE) in the SBR was always higher than 99%. Sulphide removal kinetics resulted extremely high and only few minutes were needed for sulphide concentration to decrease below 1 mg L^{-1} during each cycle. The analysis of the SBR effluent confirmed the presence of intermediate sulphur compounds (Table 1). Nitrate removal was not complete and nitrite accumulated in the reactor and was present in the effluent (Table 1).

Parameter	Units	Value		Sample
		Phase I	Phase II	
SRT	d	5	20	
S	mg S-HS$^-$ L^{-1}	375	340	Inflow
N	mg N-NO$_3^-$ L^{-1}	220	220	Inflow
S/N	g S (g N)$^{-1}$	1.70	1.55	Inflow
		Experimental phase	**Models estimation**	**Experimental phase**	**Models estimation**	
HS$^-$	mg S L^{-1}	0±0	0	0±0	0	Effluent
S^0	mg S L^{-1}	2	0	0	0	Effluent
S$_2$O$_3^-$	mg S L^{-1}	20.0	23	28.9	14	Effluent
SO$_4^{2-}$	mg S L^{-1}	180±25	164.1	175±17	156	Effluent
NO$_2^-$	mg N L^{-1}	12±4	8	17±6	9	Effluent
NO$_3^-$	mg N L^{-1}	10±3	7	13±6	10	Effluent

Table 1 – Sulphur mass balance in the SBR in quasi-steady state conditions during.

In Table 1, the results of model simulation and experimental data are reported. The hypotheses at the basis of the model where verified to be compatible with a representation of the phenomena related to biomass production at SRT=5 d and SRT=20 d. The estimated values for the decay coefficient was 0.06 d^{-1}, quite lower than the values previously estimated in aerobic conditions (Munz et al. 2009), while the yield factor resulted $Y_{SOB} = 0.62$ mgX$_{SOB(COD)}$ mgS^{-1}. A ratio between $\Delta S_{tot,\,measured}/\Delta S_{tot,theoretical}$ equal to 1.06 and 0.94 resulted in steady state conditions in phase I and II, respectively. From an application perspective, this imply that for the load expected at Cuoiodepur WWTP (0.95 gS gN^{-1} when anaerobic digestion of the primary sludge would be applied), the

process would allow to completely remove sulphide and a large fraction of nitrogen from the supernatant.

CONCLUSIONS
The results of this study indicate that denitrification with sulphide as electron donor is effective for the removal of sulphide in a wide range of operating conditions (SRT, T, S/N ratio). Sulphide removal efficiency was higher than 99% in all the tested conditions and nitrogen removal efficiencies higher than 80% were obtained. The loads of nitrogen present in tannery wastewater resulted as compatible with the application of biogas biological treatment through autotrophic denitrification.

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