Chemical Engineering Journal 343 (2018) 484–491

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Application of the oxidation reduction potential (ORP) for process control and monitoring nitrite in a Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO)

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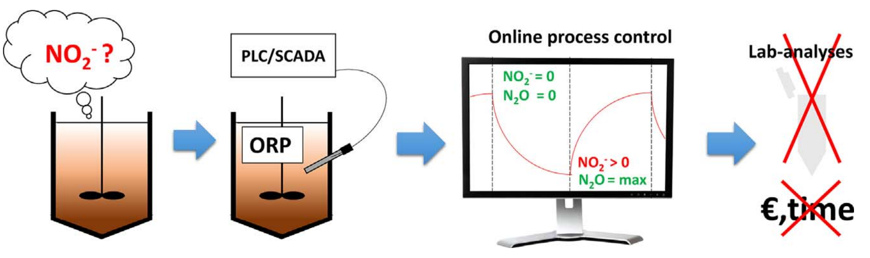
HIGHLIGHTS

- Long-term investigation about the ORP in a nitrous denitritation process.
- Demonstration of the potential of the ORP as nitrite surrogate parameter.
- Determination of ORP ranges for nitrite elimination and high nitrous oxide yields.
- Development and validation of an ORP gradient based process automation strategy.
- Determination of optimal COD/N ratios under real feed-stream conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Process control
Nitrite
Nitrous oxide
Energy recovery
Oxidation-reduction-potential
Coupled Aerobic-anoxic Nitrous Decomposition Operation

ABSTRACT

Energy recovery from nitrogen via nitrous oxide by applying e.g., the Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO), is a potential key to more sustainable and energy-efficient wastewater treatment facilities. In this study, laboratory-scale investigations were conducted for the second stage of a continuously operated CANDO process over 84 cycles to test and validate the oxidation reduction potential (ORP) as operational control variable. The ORP was investigated to optimize effluent nitrite (NO_2^-) concentrations, nitrous oxide (N_2O) yields and overall process conditions under real feed-stream conditions. Characteristic deviations for stable operational conditions, underload and overload could be derived based on representative cycles. The results revealed that continuously increasing ORP deviations are correlated to the abundance of nitrite in anoxic reaction periods and that the depletion of nitrite and nitrous oxide correlates with switching from a positive to negative ORP gradient. These observations were supported by investigating the dynamics of relevant process parameters of a single cycle. Ultimately, the reactor was successfully operated under dynamic conditions i.e., different chemical oxygen demand to nitrite ratios (COD/N) ratios, and automatically controlled by applying an ORP gradient of −1 mV/min over 20 min as termination criterion for anoxic reaction periods. This operation resulted in stable and reliable NO_2^- elimination. Additionally, previous observations concerning the necessity of a COD/N ratio of 4 could be confirmed concerning optimal N_2O yields. A COD/N ratio of 5 compromised the N_2O yield to a higher nitrogen removal rate.

1. Introduction

In conventional biological wastewater treatment, heterotrophic denitrification is a key element of the nitrification/denitrification process for nitrogen removal. Throughout this operation, a considerable portion of the carbonaceous oxygen demand is utilized as reducing

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https://doi.org/10.1016/j.cej.2018.03.038
Received 17 December 2017; Received in revised form 12 February 2018; Accepted 7 March 2018
Available online 08 March 2018

equivalents for nitrate reduction (7.6 kg_{COD}/kg_N) [1]. As a result, in conventional biological nutrient removal treatment configurations the energy recovery potential contained in organic constituents (on average 1.93 kWh/m^3) [2] is limited to the required denitrification capacity. To decouple denitrification from chemical oxidation demand (COD) consumption and hence, to increase energy recovery potentials, the application of alternative microbial pathways or short-cuts in the microbial metabolism are promising and are being pursued [3]. Based on these pathways, processes like for instance, partial nitritation/deammonification (PN/D) [4–6], nitritation/denitritation [7,8], or the Coupled Aerobic-anoxic Nitrous Decomposition Operation (CANDO) [9] have been developed. Beside the advantage of a lower organic carbon demand, also the oxygen demand can be reduced by up to 60% compared to conventional nitrification [10] by constraining the aerobic processes to the oxidation of ammonium to nitrite (NO_2^-) instead of nitrate (NO_3^-). However, to trigger these alternative pathways, tight process control is essential. Operation of a PN/D system, for instance, was achieved by online-control and three feed-back control loops regarding mixed ammonium concentration, dissolved oxygen and pH [11]. An additional example are full-scale granular reactors [12] for PN/D, which are operated with continuous aeration and online monitoring of effluent ammonium and nitrite concentrations. Similar to this study, an oxidation–reduction potential (ORP) based control strategy called ‘Swinging ORP’ has been developed for the operation of a single-stage PN/D system [13].

As in most of these alternative nitrogen removal technologies, the first stage of the CANDO process, is a nitritation ($NH_4^+ \rightarrow NO_2^-$) stage. In the second stage, nitrite is biologically reduced to nitrous oxide ($NO_2^- \rightarrow N_2O$) [9,14] for subsequent harvesting and energetic utilization. Considering the carbon savings, 4.6 kg_{COD}/kg_N can be saved for anaerobic treatment compared to conventional denitrification [15]. The opportunity of intended nitrous oxide co-combustion with biogas further increases the on-site energy recovery potential. Considering the chemical reaction enthalpy of the decay of N_2O, theoretically 37% more energy can be generated by substituting O_2 by N_2O during biogas combustion [9]. Additionally, the combustion of N_2O to CO_2-neutral nitrogen gas potentially reduces the carbon footprint of nitrogen removal processes. Presently, N_2O emissions, which exhibit a CO_2-equivalent of approximately 300 [16], are of concern, especially in N/DN systems [17,18], but also in conventional nitrification/denitrification systems, N_2O emissions contribute a considerable share of up to 80% to the carbon footprint [19].

Considering process control of the CANDO process, in a previous study [15] dissolved oxygen and effluent ammonium concentrations were successfully applied in a closed control loop for automated operation and control of the nitritation stage. For the nitrous denitritation stage, however, reactor control strategies so far have only been time control based [14,15,20].

Because the SBR cycle of the nitrous denitritation stage is characterized by alternating anaerobic/anoxic conditions, the application of the ORP is promising for operational control. Previous studies investigating the ‘Swinging ORP’ concept already correlated low nitrite and nitrate concentrations with low ORP values in anoxic or anaerobic reaction periods [13]. In the CANDO process, a complete elimination of nitrite in anoxic phases of the nitrous denitritation process is essential for maintaining high N_2O yields and effluent quality [15]. In this respect, it is also worth mentioning that residual NO_2^- concentrations are reduced to nitrogen gas in subsequent cycles, which increases the demand of organic reducing equivalents in the nitrous denitritation stage [3]. Hence, tight monitoring of NO_2^- concentrations would facilitate efficient energy recovery, effluent quality control and maintaining stable operation also under varying process conditions.

The currently available measurement technologies for online NO_2^- measurement are based on ion-selective electro-chemical [21] or spectral absorption principles [22]. However, the typically applied concentration range of 0–300 $mg_{NO2\text{-}N}/L$ is not provided by commercially available systems [14,15,20]. Additionally, regarding maintenance requirements ORP probes are cheaper and do not rely on compensating probes for e.g., chloride or potassium. They are robust, have proven suitability for operational control [23–26], and provide the possibility to judge about an anaerobic system states as well [27]. However, operational absolute values are typically process specific and not readily transferable to other systems, because they are very much depending on the feed matrix and operating conditions [13]. However, characteristic deviations of the ORP were investigated in relation to NO_2^- and N_2O under continuous real-feed stream conditions in an operating nitrous denitritation stage of a CANDO system. Additionally, deviations for stable operation, overload and underload were derived in time-controlled operation. Ultimately, the application of the ORP as a control variable was successfully validated and process automation of a nitrous denitritation stage could be demonstrated successfully for the first time. The application of the ORP for process control will potentially enable more efficient and economically viable process control in lab- and full-scale applications, especially considering the currently required effort of lab analyses for nitrite concentration measurements. Additional assessments concerning the performance and a nitrogen mass-balance were part of a previous long-term investigation regarding the operation of the CANDO process under real feed-stream conditions [15].

2. Materials and methods

2.1. Reactor setup

An automated bioreactor system has been designed and operated for the nitritation and subsequent nitrous denitritation processes [15]. The reactors were equally designed with a reaction volume of 12 L. The configuration for both systems comprised stirrer (IKA-Werke GmbH, Staufen, Germany) and peristaltic feed and dosing pumps (Watson-Marlow, Falmouth, Great Britain). Additionally, a heat exchanger (Huber Kältemaschinenbau AG, Offenburg, Germany) was installed to temper the nitritation stage (31 °C). The second stage comprised three additional peristaltic pumps (Heidolph Instruments, Schwabach, Germany) to add carbon feed and coagulant (5% iron-III-chloride), and to withdraw effluent volumes. For aeration of the first stage and N_2O removal, fine bubble aeration stones were installed at the reactor bottom. Gas stripping was conducted with technical grade nitrogen gas (purity 99.5%, Linde, Munich, Germany).

2.2. Substrates and inocula

Feed samples were collected at the municipal wastewater treatment plant Garching, Germany, with a treatment capacity of 31,000 population equivalents. The wastewater is screened on-site behind the inlet of the plant by a 4-mm drum screen. Primary effluent samples were collected weekly behind the screen and stored at 4 °C. The samples exhibited COD and NH_4-N concentrations of 468 ± 55 mg_{COD}/L and 54.7 ± 5.3 mg_N/L (Table 1), respectively, throughout the period investigated.

Digester reject water served as nitritation feed and was collected from storage tanks at WWTP Garching. The centrate contained ammonium concentration of 1074 ± 173 $mg_{NH4\text{-}N}/L$ and 359 ± 51.7 mg_{COD}/L (COD/N ratio = 0.33). The nitritation stage of the laboratory system was operated mainly to produce the nitrogen feed for the second stage. Detailed information about the operation are documented elsewhere [15].

Throughout the investigations, the nitrous denitritation feed (nitritation effluent) contained 965 ± 65.1 $mg_{NO2\text{-}N}/L$ on average after the first stage (Table 1) and hence, exhibited a suitable quality. Both stages were inoculated prior to this study as described previously [15].