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Removal of dissolved methane and nitrogen from anaerobically treated effluents at low temperature by MBR post-treatment

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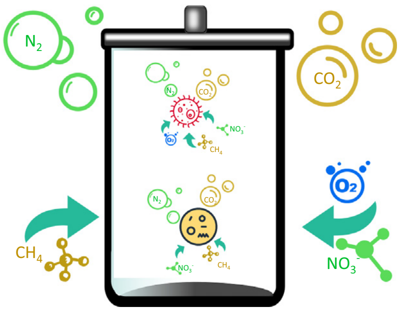
HIGHLIGHTS

- The effluent of a UASB, with dissolved methane and nitrogen, was treated in an MBR.
- Dissolved oxygen and recycle ratio influenced nitrogen and methane removal rates.
- A fraction of nitrogen and up to 80% dissolved methane were removed in the MBR.
- FISH/batch assays revealed anaerobic/aerobic methane oxidation organisms presence.

GRAPHICAL ABSTRACT



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ABSTRACT

Sewage treated anaerobically at low temperature contains dissolved methane, which should be removed in order to reduce greenhouse gas emissions (GHG). In this research, a membrane bioreactor (MBR) post-treatment was proposed that is able to simultaneously remove methane and nitrogen by implementing newly discovered biological processes involving methane oxidation coupled to denitrification. Up to 95% of methane was removed at 17–23 °C. Moreover, biological treatment partially removed nitrogen, up to 15–20 mg TN L^{-1}, by coupling methane oxidation and denitrification. This study opens the door to reducing the GHG impacts associated to the anaerobic treatment of sewage in temperate and warm climates countries. The elimination of the majority of the dissolved methane, suspended solids and the remaining biodegradable COD of the anaerobically treated effluents, converted this treatment as friendly from the ecological point of view, reducing part of the nitrogen contained in sewage.

1. Introduction

Anaerobic wastewater treatment has been considered a suitable option for treating municipal wastewater in areas with warm climates. COD removal rates ranging from 60% to 80% can be achieved when applying anaerobic wastewater treatment at 20–25 °C and with organic loading rates (OLR) of approximately 2–3 kg COD·m^{-3}·d^{-1} [1,2]. In the last few years, research on anaerobic treatment of wastewater has been considered a promising research area as a consequence of its attractive benefits. The absence of aeration, lower sludge production and its applicability over a wider range of OLR values compared to traditional technologies such as conventional activated sludge (CAS) make this treatment worthy of further investigation. Moreover, methane-rich biogas is obtained that can be profitably used to produce energy.

In anaerobic conditions, a considerable fraction of the total methane produced, more than 60% at low temperatures, is dissolved in the effluent [3]. In the case of sewage treatment, a

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Nomenclature

AMO-D	aerobic methane oxidation coupled to denitrification
CAS	conventional activated sludge
COD	chemical oxygen demand
CSRT	continuous stirred reactor tank
DAMO	denitrification coupled to anaerobic methane oxidation
DHS	down-flow hanging sponge reactor
DO	dissolved oxygen concentration, mg $O_2 \cdot L^{-1}$
FISH	fluorescence in situ hybridization
GHG	greenhouse gas
HRT	hydraulic retention time
MBR	membrane bioreactor
MBfR	membrane biofilm reactor
MRR	methane removal rate, $mgCH_4 \cdot L^{-1} \cdot d^{-1}$
NIST	The US National Institute of Standards and Technology
NRR	nitrogen removal rate, $mgN \cdot L^{-1} \cdot d^{-1}$
OLR	organic loading rate, kg $COD \cdot m^{-3} \cdot d^{-1}$
ORP	oxidation reduction potential, mV
ORR	oxygen removal rate, $mgO_2 \cdot L^{-1} \cdot d^{-1}$
PLC	programmable logic controller
UASB	upflow anaerobic sludge blanket
R	recycle stream
SAD_m	membrane specific air demand, $m^3 \cdot m^{-2} \cdot h^{-1}$
SRT	solids retention time
TSS	total suspended solids
TMP	transmembrane pressure, mbar
TN	total nitrogen
VFA	volatile fatty acids
VS	volatile solids
VSS	volatile suspended solids
WWTP	wastewater treatment plant
Y_{obs}	observed biomass yield, kg $VSS \cdot kg\ COD^{-1}$

range between 20 and 60% has been reported [4]. Methane can be easily stripped off in the typical aerobic post-treatment, as observed in a study of GHG emissions after anaerobic treatment in a full-scale WWTP in Japan [5]. Methane has been classified as a harmful GHG, with a warming potential 34 times that of CO_2 in a 100-year scenario. Methane related to anaerobic waste and wastewater treatment is responsible for 2.8% of the world' overall GHG emissions [6]. This fact reflects a considerable environmental issue, one that argues against the use of anaerobic technologies compared with CAS treatments [7]. To diminish these GHG emissions, the dissolved methane present in anaerobically treated effluents should be eliminated, thereby addressing the targets set forth during the 2015 Climate Change Conference in Paris [8].

To reduce the impacts of anaerobic treatments, alternative post-treatments should be installed. There are expensive alternatives already available. One option is the combustion of stripped-off methane; another is catalytic methane oxidation, well known for its remarkable efficiency [3]. Recently, biological solutions are being developed to reduce methane content that act directly in the effluent [9,10].

At the end of the last century, it was demonstrated the use of methane as a carbon source for biological denitrification [11]. The overall process can be accomplished by using aerobic or anaerobic methane-oxidizing microorganisms [12]. Aerobic methanotrophs are able to convert methane into oxidized species such as methanol, formaldehyde or acetate, compounds that are fully soluble in water. These methane oxidation products can be employed as a carbon source by heterotrophic denitrifying microorganisms in a subsequent reaction. This process is known as aerobic methane oxidation coupled to denitrification (AMO-D) and has been described by the summarized reaction below [13].

$$CH_4 + 1.1\ O_2 + 0.72\ NO_3^- + 0.72\ H^+ \rightarrow 0.36\ N_2 + CO_2 + 2.36\ H_2O \tag{1}$$

Modin et al. [14] developed a lab scale membrane biofilm reactor (MBfR) with a liquid volume of 0.8 L, achieving elimination rates of 21 and 8 $mg \cdot L^{-1} \cdot d^{-1}$ of methane and nitrogen, respectively, exclusively through this via.

In the absence of oxygen, specific, recently discovered microorganisms are able to couple denitrification to anaerobic methane oxidation (DAMO) [12]. This process can be carried out either using nitrite and DAMO bacteria (*Candidatus Methylomirabilis oxyfera*) or nitrate and DAMO archaea (*C. Methanoperedens nitroreducens*) [15].

$$\text{DAMO archaea}: \ CH_4 + 4\ NO_3^- \rightarrow 4\ NO_2^- + CO_2 + 2\ H_2O \tag{2}$$

$$\text{DAMO bacteria}: \ CH_4 + 8/3\ NO_2^- + 8/3H^+ \rightarrow 4/3\ N_2 + CO_2 + 10/3\ H_2O \tag{3}$$

A consortium of anammox, DAMO archaea and DAMO bacteria was discovered [15]. DAMO archaea were responsible for reducing nitrate into nitrite, and then anammox and DAMO bacteria competed for nitrite. In the long term, it seems that the anammox bacteria outcompete the DAMO bacteria and the latter tend to disappear [16]. The simplified stoichiometry of the anammox process is summarized below [18].

$$\text{Anammox}: \ NH_4^+ + NO_2^- \rightarrow N_2 + 2\ H_2O \tag{4}$$

Unfortunately, these newly discovered DAMO microorganisms are characterized by extremely slow growth rates of approximately 1–2 weeks [19]. Moreover, it seems that the capacity of DAMO enrichment reactors, which relies on sedimentation of the biomass from the treated water, could be limited by the tendency of these microorganisms to be washed out with the effluent. Kampman et al. [20] conducted an enrichment experiment in a sequencing batch reactor and stated that DAMO microorganisms were washed-out with the effluent, limiting the nitrogen removal rate below 35 $mgN \cdot L^{-1} \cdot d^{-1}$ enrichment Due to this fact, bioreactor configurations for preventing biomass washout, such as membrane filtration or biofilms, have to be considered. This problem has been overcome by installing a membrane, resulting in a maximum nitrogen removal rate (NRR) of 36 $mgN \cdot L^{-1} \cdot d^{-1}$ [21]. Very recently, it was observed at lab scale a DAMO activity of 40 $mgN \cdot L^{-1} \cdot d^{-1}$ [22]. Moreover, it was developed a lab-scale hollow fiber membrane biofilm reactor with a surprisingly high NRR of 684 $mgN \cdot L^{-1} \cdot d^{-1}$ [17]. This value has not been replicated in further studies at similar or larger scales. In a previous study, it was studied the same system than in the current work, using dissolved methane as an electron donor for denitrification in a 180 L pilot-scale UASB with a pre-anoxic MBR system [23]. Methane removal rates (MRR) were approximately 150 $mgCH_4 \cdot L^{-1} \cdot d^{-1}$. NRR of 79 $mgN \cdot L^{-1} \cdot d^{-1}$ were observed, although different nitrogen removal processes were observed.

With this outline, the aim of this study was to demonstrate the feasibility of an innovative bench-scale MBR post-treatment for the "eco-friendly" treatment of low-strength UASB effluents at approximately 20 °C. This work focused intensively on minimizing the GHG emissions associated with dissolved methane which appears in the effluent of UASB reactors at these relatively low tempera-