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Inhibition factors in biofilm N removal systems treating wastes generated by amine based CO_2 capture

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ABSTRACT

We have previously shown that biological nitrogen removal by pre-denitrification as illustrated may be a feasible approach for treating wastes generated by amine based CO_2 capture. In order to identify limiting factors for successful up-scaling, we first compared the nitrifying activity of moving bed biofilm reactors (MBBR) with or without chronic exposure to organic loading in the form of acetate while monitoring population dynamics in the biofilms by pyro-sequencing. Our results show that the long-term abundance of heterotrophic bacteria is an essential factor in inhibition of nitrification efficiency. Secondly, the inhibition potential of the commonly applied amines monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA), methyldiethanolamine (MDEA), piperazine (Pip), as well as MEA based reclaimer waste (RW) were tested on separate nitrifying and denitrifying MBBRs. Results show that nitrification was inhibited by 50% at EC_{50} concentrations from 9 to 120 mM, whereas denitrification was stimulated by all compounds at concentrations up to 100 mM. Nitrifying biofilms long-term adapted to organic loadings were 5–20 times more sensitive towards inhibition than those maintained without organic feeding, by both MEA and by organic loading. The crucial factor for the total process is therefore maintaining nitrification by avoiding overloading of amines or other organics in the second reactor.

1. Introduction

Carbon capture and storage (CCS) is increasingly receiving attention as a measure to mitigate greenhouse gas emissions. In post combustion CO_2 capture, the most commonly applied scrubbing solvent is still monoethanolamine (MEA), but recently a full scale plant was set in operation at Boundary Dam, Canada, based on a mixed diamine system (Stéphenne, 2014). Many different blended systems have also been suggested, among them phase change systems (Pinto et al., 2014). For medium to high pressure applications promoted methyldiethanolamine (MDEA) and sterically hindered and cyclic amines such as 2-amino-2-methyl-1-propanol (AMP), often mixed with piperazine (Pip) are applied for CO_2 capture.

In such amine based CO_2 capture plants, the aqueous amine solution is subject to oxidative and thermal degradation, carbamate polymerization, as well as side reactions with flue gas impurities (Gouedard et al., 2012; Bello and Idem, 2005; Goff and Rochelle, 2004; Lepaumier et al., 2011a,b; Supap et al., 2011; Davis and Rochelle, 2009; Vevelstad et al., 2011, 2013, 2014; Fredriksen and Jens, 2013). In order to keep the capture capacity up, high molecular weight degradation products and heat stable salts are separated from the intact solvent in a reclaimer unit and removed as so called 'reclaimer waste' (Goff and Rochelle, 2004; Wang et al., 2015). The resulting degradation products vary among the amines in quality, quantity and toxicity (Fredriksen and Jens, 2013; Eide-Haugmo et al., 2009; Rohr et al., 2013; McDonald et al., 2014). MEA-based waste composition and treatment options were recently reviewed by Nurrokhmah et al. (2013a) and Nurrokhmah et al. (2013b), concluding secondary biological treatment to be the most economical option (Nurrokhmah et al., 2013a). Despite the fact that various amines applied in CCS have their distinct properties, they all end up as waste containing ammonia as well as more or less toxic nitrogenous organic degradation products.

Biological nitrogen removal is based on the sequential aerobic microbial oxidation of ammonia to nitrate, followed by anoxic reduction of nitrate to inert molecular nitrogen, denoted nitrification and denitrification, respectively (Zhu et al., 2008). Both microbial consortia have widely different substrate requirements as well as growth kinetics. Nitrification is facilitated by two groups

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of chemolithoautotrophic bacteria – the ammonia oxidizing bacteria (AOB) and the nitrite oxidizing bacteria (NOB). Contrary to these bacteria, the denitrifying bacteria are heterotrophic and may grow much faster. The nitrification step may thus be less robust, both because the nitrifiers are more sensitive towards environmental changes and require longer periods to recover from operational disturbances due to their slow growth rates (Wagner and Loy, 2002).

Our recent studies on MEA (Hauser et al., 2013a) and MEA based reclaimer waste (Hauser et al., 2013b) have proven the feasibility of applying biological nitrogen removal (BNR) on such waste streams at a lab-scale (Hauser et al., 2014). In our applied pre-denitrification set-up, the waste is first treated in the anoxic denitrification reaction and then enters the aerobic nitrification reactor (see TOC graphic). All organic matter which is biodegradable under denitrification conditions may be oxidized in the first step, and most of MEA is hydrolyzed to ammonia with acetaldehyde as the first organic intermediate (Ndegwa et al., 2004). This effluent is then led to the aerobic nitrification reactor, where the influent ammonia is oxidized via nitrite to nitrate. MEA and other organics still present may be oxidized by oxygen and further degraded, stimulating heterotrophs also in this reactor step. The average MEA and chemical oxygen demand (COD) removal achieved were 98 ± 1 and $71 \pm 1\%$, respectively (Hauser et al., 2013b).

In moving bed biofilm reactors (MBBR), the bacteria grow as a biofilm on polyethylene carriers (Rusten et al., 2006). It has been shown that the nitrifying biofilm is stratified, whereas the NOB are located in the inner part of the biofilm and the AOB are closely associated with heterotrophic bacteria throughout the biofilm (Okabe et al., 1999). This is advantageous for the nitrifying bacteria in terms of shear stress protection, but on the other hand this stratification can lead to suffocation of the inner located bacteria due to oxygen limitation. This competition for space between heterotrophic and nitrifying autotrophic bacteria in the diffusive gradient of biofilms has been well documented (Nogueira et al., 2002; Vogelsang et al., 2002). Especially, in presence of an external carbon source, the fast growing heterotrophic bacteria on the surface may outcompete the slow growing autotrophic for oxygen and space. This factor must be considered when evaluating the treatment of amines and amine based reclaimer waste by biofilm reactors. As the amine represents an available carbon source for heterotrophs, it might significantly change the composition of the biofilm, depending on availability and toxicity of the amine.

Although several studies on amines used in CCS address the biodegradability (Eide-Haugmo et al., 2009) and potential toxic effect on humans (McDonald et al., 2014; Rohr et al., 2013), none of them assess the inhibiting effect of amines on bacteria, as involved in nitrification or denitrification. This information is essential to model process parameters in detail and consequently develop cost efficient waste treatment systems with high operational stability.

The main scope of this study is to identify the most essential inhibitory factors relevant for an up-scaled process. Therefore, three moving bed biofilm reactors (MBBR) were operated for 48 days in continuous mode. Reactor 1 was run as a control to confirm process stability, while chronic exposure to organic loading was tested in duplicate in order to verify reproducibility. To study inhibition and the effect on the relative abundance of nitrifying bacteria within the nitrifying biofilm over time, the bacterial communities were characterized by pyrosequencing of 16S rDNA amplicons. The sequence data were used for determining the relative abundance of ammonia and nitrite oxidizing bacteria.

Furthermore, inhibition tests of selected amines and organic loading (sodium acetate) were performed in batch tests to determine the EC_{50} (effect concentration where the activity reaches 50%) on the rate-limiting nitrifying step, as well as on the denitrifying biofilm. Our choice of amines represents a primary (MEA), secondary (DEA), tertiary (MDEA), sterically hindered (AMP) and heterocyclic amine (piperazine). Additionally, the effect of increased heterotrophic bacteria within the nitrifying biofilm was verified by re-testing MEA toxicity after long-term exposure to sodium acetate.

2. Material and methods

2.1. Experimental set-up

3 1 L (ht: 15 cm, diameter: 9 cm) moving bed reactors made of glass, with water-jackets (connected to a Cole-Parmer Polystat water bath set to 25 °C) were set-up in continuous flow. All reactors were mechanically mixed at a speed of 250 rpm. The influent was fed with a peristaltic pump at a hydraulic retention time (HRT) of 6 h. Air was supplied through a sparger and an O_2 electrode (Oxi 3315, WTW) was used to measure the dissolved O_2 level at every sampling. The pH was controlled by a Consort Controller R301 (reactors 1 and 2) or (Ingold pH amplifier) (reactor 3) and adjusted by automatic addition of 0.5 M and 0.3 M HCl or NaOH, respectively. To avoid high salinity, pH ranges were set to 7.3–7.8 for the nitrification and 6.8–7.3 for the denitrifying reactor.

2.2. Inocula and media

The biofilm was grown on polyethylene carriers (Standard AnoxKaldnes K1; Rusten et al., 2006). Inoculum for the nitrifying biofilm originated from a municipal wastewater treatment plant in Trondheim and enriched under nitrifying conditions until steady state. The denitrifying biofilm was inoculated with sludge from the same facility without a previous enrichment process. Both biofilms had previously been exposed to MEA (Hauser et al., 2013a) and MEA based reclaimer waste (Hauser et al., 2013b). For the chronic exposure to organic loading, reactors 1 and 2 were inoculated with biofilm used to treat MEA based reclaimer waste (Hauser et al., 2013b) and reactor 3 to biofilm which had been short-term exposed to MEA. The basal medium composition for nitrification was as follows (g/L): $(NH_4)_2SO_4$, 0.236; K_2HPO_4, 0.4; $NaHCO_3$, 1.0; 10 mL/L trace metal solution containing (g/L): $MgSO_4{\cdot}7H_2O$, 2.5; $CaCl_2{\cdot}2H_2O$, 1.5; $FeCl_2{\cdot}4H_2O$, 0.2; $MnCl_2{\cdot}2H_2O$, 0.55; $ZnCl_2$, 0.068; $CoCl_2{\cdot}6H_2O$, 0.12; $NiCl_2{\cdot}6H_2O$, 0.12; and EDTA, 2.8; 0.384 g/L sodium acetate anhydrous, equivalent to 300 mg/L COD was added to reactors 2 and 3 from day 11 onwards. Reactor 1 was used as a control receiving no organic loading. For the inhibition tests under denitrifying conditions, the basal medium was prepared in deaerated water, containing (g/L): K_2HPO_4, 0.533; NH_4Cl, 0.253; KNO_3, 4.0; yeast extract, 0.05; ethanol, 1.0; 10 mL/L trace metal solution as described above.

2.3. Chemical analyses

Samples were taken every 2–3 days with syringes (BD Plastipak) and filtered with 0.45 μm filters (Sarstedt) to remove suspended biomass. All concentrations of NH_4^+—N, NO_3^-—N, NO_2^-—N and chemical O_2 demand (COD) were determined with assays from Hach-Lange for water quality (Hach Lange, Germany), procedures were carried out according to manufacturers' instructions.

2.4. Analyses of microbial community

Standardized biofilm samples were collected by picking one MBBR carrier with forceps from each of the 3 reactors every 3–5 days, and the samples immediately frozen at −20 °C without any buffer or pretreatment. DNA was extracted by using a Power Soil DNA Isolation Kit (MO BIO Laboratories, California), and the 16S v4 region was amplified by a semi-nested PCR protocol for pyrosequencing (Vik et al., 2013).