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A biofilm model for assessing perchlorate reduction in a methane-based membrane biofilm reactor

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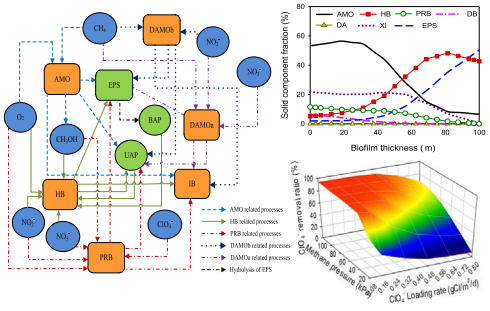
HIGHLIGHTS

- A model describing perchlorate reduction in a methane-based MBfR was developed.
- The model was verified by experimental data under different operational conditions.
- The stratified microbial distribution in the biofilm was reveal by model analysis.
- Over 80% perchlorate removal efficiency can be achieved with proper P_{CH4} and L_{ClO4}.
- The perchlorate reduction could be affect by nitrate and nitrite concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Perchlorate (ClO_4^-) is recognized as an important contaminant in surface water and groundwater, which would pose health risks at very low concentrations. A methane-based membrane biofilm reactor (MBfR) has been successfully demonstrated for perchlorate reduction, which provided an alternative solution for perchlorate remediation with low cost. In this work, a multispecies biofilm model was developed to evaluate perchlorate reduction in the methane-based MBfR under different operational conditions. The model was calibrated and validated using the experimental data from the long-term operation of the MBfR at seven distinct stages. The results suggested that the developed model could satisfactorily describe perchlorate reduction and denitrification performances in the MBfR ($R^2 > 0.9$). The modeling results provided insight into the microbial community distribution in the biofilm, with aerobic methanotrophs and perchlorate reduction bacteria being mainly located at the membrane side (~60%) and heterotrophic bacteria being situated near the liquid side (~50%). The model simulations indicated that over 80% of perchlorate removal efficiency could be achieved through controlling the optimal combinations of methane pressure (P_{CH4}) and perchlorate loading (L_{ClO4}) (e.g., applying a P_{CH4} of 30 kPa at a L_{ClO4} of 0.08 g Cl/m^2/d). In addition, the perchlorate reduction would be inhibited by the presence of nitrate and nitrite in the MBfR, which should be appropriately controlled during the future practical application of the promising process.

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1. Introduction

Perchlorate salts, including ammonium, potassium and sodium perchlorate have been widely used in rocket fuels, pyrotechnics, matches, munitions and many other industries [1,2]. These perchlorate salts usually have high solubilities and would be readily dissociated in water producing perchlorate anion, which is relatively nonreactive and stable, but extremely mobile in aqueous systems [3]. Perchlorate (ClO_4^-) is recognized as an important contaminant in surface water and groundwater, as it would pose health risks at very low concentrations and is difficult to remediate from the water. It can interfere with the body's iodine intake, consequently inhibiting thyroid hormone production, which is thought essential for growth and development [4]. Therefore, the U.S. Environmental Protection Agency is in the process of evaluating a maximum contaminant level (MCL) for perchlorate in the range of 1–18 μg/L [5].

Many previous studies have been carried out to investigate the remediation of perchlorate in water through microbiological reduction [6–8]. A recent study, for instance, reported a successful example of microbial perchlorate removal in a methane-based membrane biofilm reactor (MBfR) [9]. In this study, methane was supplied into lumens of hollow-fiber membranes and further permeated through the non-porous walls into biofilms attached on outer surfaces of membranes. Meanwhile, perchlorate in wastewater was diffused into biofilms, where perchlorate reduction bacteria (PRB) developed and the microbial perchlorate reduction took place. The result showed that the biofilms could reduce up to 5 mg/L ClO_4^- to a non-detectable level when methane delivery was not limiting. While, under the methane limiting condition, the removal of perchlorate could be interfered by the presence of nitrate and nitrite in water.

As methane is an inexpensive and widely available carbon source, its utilization for perchlorate remediation could largely reduce the cost, compared with other methods such as chemical reduction and iron exchange [2,10]. Also, it proposed a promising solution for energy recovery from the wastewater system, because methane is a key product of the anaerobic digestion of biosolids [11,12]. Although, the utilization of methane has potential risks due to its relatively low explosion limit [13], the application of the "bubble-less" membranes could enhance the operational safety by preventing methane losses to the atmosphere. In addition, as methane is a potent greenhouse gas, using methane for perchlorate reduction could potentially alleviate the greenhouse gas emission from the wastewater treatment system [14,15]. Therefore, the application of methane-based MBfR for perchlorate remediation has a good prospect of practical application. In this regard, a mathematical model for describing perchlorate reduction in the methane-based MBfR is highly desirable to facilitate its full-scale application. The comprehensive investigation into this promising system, especially into the effect of different operational parameters on perchlorate removal, is also required to potentially improve the system performance.

The experimental investigation implied that the microbial perchlorate removal in the methane-based MBfR system could be affected by three key operational parameters, i.e., the methane pressures, perchlorate loadings and nitrate or nitrite loadings [9]. These parameters governed the perchlorate removal not only by directly affecting the perchlorate reduction rate, but also by influencing the development of PRB in the biofilm. In the biofilm, the possible competition and promotion mechanisms mainly include: i) The competition between PRB and heterotrophic bacteria (HB) for the same electron donor [16,17]; ii) The competition between different microorganisms and associated products for space in the biofilm [18]; iii) The competition within PRB between nitrate/nitrite and perchlorate for the same resources such as electrons and possibly reductase enzymes [19]; and iv) the promotion of the growth of PRB through their utilization of nitrate or nitrite [20]. Because of multiple mechanisms, microbial species, and substrates in the methane-based MBfR system, the links between these operating parameters and perchlorate removal are not straightforward. In this case, multispecies biofilm modeling is advantageous for quantitatively integrating the microbiological and physical phenomena that control the perchlorate removal in the methane-based MBfR.

This study aimed to develop a multispecies biofilm model to predict the perchlorate removal in the methane-based MBfR system under different operational conditions. The developed model comprehensively considered the interaction between different microbial processes in the biofilm as well as the gas delivery characteristics through the membrane substratum in the reactor. The model was calibrated and validated using the experimental data from a long-term operated methane-based MBfR at different operational stages. The effect of key operation parameters on the perchlorate removal was then investigated using the validated model. It is expected that the established model could provide supports for the further development of the methane-based MBfR for efficient perchlorate remediation.

2. Material and methods

2.1. Development of the biological processes model

The key biological processes occurred in the biofilm of the MBfR was considered based on the experimental observations [21], which were summarized in Fig. 1. In the biofilm, the methane could be aerobically oxidized by methanotrophs (AMO) with oxygen in the influent. The oxidation product, methanol, was then severed as the electron donor for perchlorate reduction and heterotrophic denitrification with the respiration of PRB and HB. On the other hand, methane could also be anaerobically oxidized by denitrifying anaerobic methane oxidation (DAMO) bacteria or archaea using nitrate and nitrite as electron acceptor in the biofilm where oxygen could not be penetrated to. The anaerobic methane oxidation coupled to perchlorate reduction was not included in this work, as so far there still no direct evidence to prove the occurrence of such process in the system. Through aforementioned oxidation or reduction processes, the microorganisms gained energy to synthesis new biomass, and meanwhile to produce extracellular polymeric substances (EPS) and substrate-utilization-associated products (UAP) [22]. The formed EPS could be hydrolyzed into biomass-associated products (BAP). The BAP and UAP could be both used by HB as organic electron donors with nitrate or nitrite as their electron acceptors. All microorganisms involved in the system are subject to endogenous respiration, with the production of inert biomass (IB) and the reduction of the electron acceptors to gain energy for cell maintenance.

According to the biological processes described above, the developed biological model includes seven particulate species, i.e., AMO (X_{AMO}), HB (X_{HB}), PRB (X_{PRB}), DAMO bacteria (X_{DB}), DAMO archaea (X_{DA}), EPS (X_{EPS}) and inert biomass (X_I), and eight soluble species, i.e., methane (S_{CH4}), oxygen (S_{O2}), perchlorate (S_{ClO4}), nitrate (S_{NO3}), nitrite (S_{NO2}), methanol (S_{CH3OH}), UAP (S_{UAP}), and BAP (S_{BAP}), as listed in Table S1. The unit was g N/m^3 for all nitrogen species, g Cl/m^3 for perchlorate and g O/m^3 for oxygen, while concentrations of other compounds were quantified based their chemical oxygen demand (COD) equivalent, i.e., g COD/m^3. The stoichiometric matrix of the model was summarized in Table S2 (SI). The rates of the growth and endogenous respiration of microorganisms were modelled using Monod-type kinetics while hydrolysis of the EPS was simulated through first-order kinetics [22,23].