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Removal of multiple electron acceptors by pilot-scale, two-stage membrane biofilm reactors

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ABSTRACT

We studied the performance of a pilot-scale membrane biofilm reactor (MBfR) treating groundwater containing four electron acceptors: nitrate (NO_3^-), perchlorate (ClO_4^-), sulfate (SO_4^{2-}), and oxygen (O_2). The treatment goal was to remove ClO_4^- from ~200 μg/L to less than 6 μg/L. The pilot system was operated as two MBfRs in series, and the positions of the lead and lag MBfRs were switched regularly. The lead MBfR removed at least 99% of the O_2 and 63–88% of NO_3^-, depending on loading conditions. The lag MBfR was where most of the ClO_4^- reduction occurred, and the effluent ClO_4^- concentration was driven to as low as 4 μg/L, with most concentrations ≤10 μg/L. However, SO_4^{2-} reduction occurred in the lag MBfR when its $NO_3^- + O_2$ flux was smaller than ~0.18 g H_2/m^2-d, and this was accompanied by a lower ClO_4^- flux. We were able to suppress SO_4^{2-} reduction by lowering the H_2 pressure and increasing the $NO_3^- + O_2$ flux. We also monitored the microbial community using the quantitative polymerase chain reaction targeting characteristic reductase genes. Due to regular position switching, the lead and lag MBfRs had similar microbial communities. Denitrifying bacteria dominated the biofilm when the $NO_3^- + O_2$ fluxes were highest, but sulfate-reducing bacteria became more important when SO_4^{2-} reduction was enhanced in the lag MBfR due to low $NO_3^- + O_2$ flux. The practical two-stage strategy to achieve complete ClO_4^- and NO_3^- reduction while suppressing SO_4^{2-} reduction involved controlling the $NO_3^- + O_2$ surface loading between 0.18 and 0.34 g H_2/m^2-d and using a low H_2 pressure in the lag MBfR.

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1. Introduction

Perchlorate (ClO_4^-) causes serious health problems by inhibiting the transfer of iodide from the blood to the thyroid gland, which is required for the gland to produce hormones essential for growth and metabolism (Logan, 2001; Wolff, 1998). Although the US EPA has not yet established a maximum contaminant level (MCL) for ClO_4^-, it plans to regulate ClO_4^- under the Safe Drinking Water Act (USEPA, 2011), and some states have established cleanup levels ranging from 2 to 18 μg/L for ClO_4^- in drinking water (Gu and Coates, 2006).

While physical/chemical techniques – activated carbon, ion exchange, and chemical reduction (Coates and Achenbach, 2004; Matos et al., 2008) – can remove ClO_4^- from water, biological reduction reduces ClO_4^- to harmless chloride (Cl^-) and water (H_2O) (Van Ginkel et al., 1996). Perchlorate reductase (*pcr*ABCD) reduces ClO_4^- to chlorite (ClO_2^-) (Kengen et al., 1999), and chlorite dismutase (*cld*) further catalyzes the disproportionation of chlorite (ClO_2^-) to chloride (Cl^-) and oxygen (O_2) (Van Ginkel et al., 1996), which is subsequently reduced to H_2O. The *pcrA* gene encodes for the α subunit of perchlorate reductase, an enzyme that catalyzes the first step of perchlorate reduction to chlorite; it is specific to perchlorate reducers and is usually used to detect and quantify perchlorate-reducing bacteria (PRB) (Nozawa-Inoue et al., 2008).

The hydrogen-based membrane biofilm reactor (MBfR) has been applied successfully for microbial reduction of ClO_4^- (e.g., Nerenberg et al., 2002; Rittmann, 2007; Ziv-El and Rittmann, 2009; Zhao et al., 2011, 2013a; Ontiveros-Valencia et al., 2013). In the MBfR, hydrogen gas (H_2) diffuses through the walls of hollow-fiber membranes and serves as the electron donor, while ClO_4^- is an electron acceptor. The non-porous polypropylene walls allow H_2 to diffuse through them, which delivers the electron donor directly to the H_2-oxidizing bacteria. The non-porous walls also prevent H_2 bubbling, which might lead to biofilm detachment (Nerenberg et al., 2003). Besides ClO_4^-, many other oxidized contaminants can be simultaneously reduced in the MBfR: e.g., NO_3^- (Ziv-El and Rittmann, 2009; Zhang et al., 2009), SO_4^{2-} (Ontiveros-Valencia et al., 2012; Zhao et al., 2013a), selenate (SeO_4^{2-}) (Chung et al., 2006a), chromate (Chung et al., 2006b), and chlorinated solvents (Xia et al., 2011; Ziv-El et al., 2012). In addition to the MBfR, Ricardo et al. (2012) used an up-scaled ion exchange membrane bioreactor (IEMB) to achieve simultaneous removal of nitrate and perchlorate.

NO_3^- is an oxyanion commonly co-occurring with ClO_4^-, for example, in groundwater close to a military base that houses rockets (USEPA, 2001). The drinking water MCL for NO_3^- is 10 mg N/L (USEPA, 2009), because NO_3^- causes methemoglobinemia in infants. NO_3^- also spurs eutrophication of surface waters (Herman and Frankenberger, 1999). Respiratory NO_3^- reduction, or denitrification, is a very common and well-studied process (Hiscock et al., 1991) that can have different effects on ClO_4^- reduction (Coppola and McDonald, 2000; Giblin et al., 2000; Nerenberg et al., 2002; Choi and Silverstein, 2008; Zhao et al., 2011). Some previous studies have shown that nitrate inhibits ClO_4^- reduction, particularly when the electron donor was limiting (Herman and Frankenberger, 1999; Choi and Silverstein, 2008), although Nerenberg et al. (2002) showed that inhibition between nitrate and perchlorate reductions was trivial in a H_2-based MBfR as long as sufficient H_2 was available. Modeling by Tang et al. (2012a,b,c) predicted that a high-enough nitrate loading (>0.6 g N/m^2-d) strongly inhibits perchlorate reduction even if H_2 is not limiting, but a medium nitrate loading (0.1–0.6 g N/m^2-d) has no adverse effect on perchlorate removal in an MBfR biofilm.

SO_4^{2-} is another oxyanion that often occurs with NO_3^- and ClO_4^-. Although SO_4^{2-} is a natural constituent of water and is not normally considered as a contaminant (US EPA, 2012), SO_4^{2-} reduction usually is an unwanted process because its final product – hydrogen sulfide (H_2S) – is corrosive, odorous, and toxic (Odom, 1990). H_2S strongly inhibits denitrification (Dalsgaard and Bak, 1994), and SO_4^{2-} reduction inhibited ClO_4^- reduction in a previous MBfR study (Ontiveros-Valencia et al., 2013). Thus, SO_4^{2-} reduction normally should be suppressed when denitrification and ClO_4^- reduction are required.

Many waters also contain dissolved O_2. ClO_4^-, NO_3^-, and SO_4^{2-} reductions can be affected by O_2, since O_2 is the most favorable electron acceptor (Ziv-El and Rittmann, 2009). O_2 can inhibit SO_4^{2-} reduction, because most sulfate-reducing bacteria (SRB) are strictly anaerobic (Dolla et al., 2006), although a few SRB can tolerate low concentrations of O_2 (below 15 μM) (Marschall et al., 1993). O_2 at high concentration can inhibit denitrification, because denitrifying bacteria (DB) prefer to use O_2 as an electron acceptor over NO_3^- (Alefounder et al., 1981). O_2 seems to have different effects on PRB. Chaudhuri et al. (2002) reported that dissolved O_2 concentrations as low as 2 mg/L inhibited perchlorate reduction by *Dechlorosoma suillum*, but Song and Logan (2004) reported that *Dechlorosoma*. sp. KJ. recovered its ability to reduce ClO_4^- after dissolved O_2 exposure at ~8 mg/L for less than 12 h.

The interactions among the four electron acceptors have been studied to a degree with the MBfR. Ziv-El and Rittmann (2009) reported that the four electron acceptors had a clear H_2-utilization priority when H_2 supply was limiting in a H_2-based MBfR: $O_2 > NO_3^- > ClO_4^- > SO_4^{2-}$. Ontiveros-Valencia et al. (2012) reported that, without restriction on H_2 availability, SO_4^{2-} was reduced only when the NO_3^- surface loading was ≤0.13 g N/m^2-day, since DB can outcompete SRB in the biofilm (Tang et al., 2013). In a previous study, we compared ClO_4^- reduction with or without NO_3^- in an MBfR having a range of H_2 delivery capacities (Zhao et al., 2011). We found that, with sufficient H_2, a small NO_3^- loading (0.1 g N/m^2-d) had no effect on ClO_4^- reduction. Considering the fact that most PRB can use NO_3^- and ClO_4^- simultaneously as respiratory electron acceptors (Kengen et al., 1999; Xu et al., 2004) and that some PRB prefer NO_3^- as the electron acceptor (Giblin and Frankenberger, 2001), Tang et al. (2012a,b,c) generalized the interactions between NO_3^- and ClO_4^- reductions using a multispecies biofilm model. They predicted that low NO_3^- loading slightly promotes ClO_4^- reduction by providing more electron acceptor reduction for the PRB, but a high NO_3^- loading inhibits ClO_4^- removal. The dividing line between the cases depends on the permeability of the membrane and the H_2 pressure.

In this study, we evaluated a pilot-scale MBfR used to treat a groundwater contaminated with ClO_4^- (160–200 μg/L) and NO_3^- (8–9 mg/L NO_3^-–N), but also containing SO_4^{2-} at