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Chemisorption of oxygen onto activated carbon can enhance the stability of biological perchlorate reduction in fixed bed biofilm reactors

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ABSTRACT

Fixed bed biofilm reactors with granular activated carbon (GAC) or glass beads as support media were used to evaluate the influence of short-term (12 h) and long-term (23 days) increases of influent dissolved oxygen (DO) concentrations on biological perchlorate removal. The goal was to evaluate the extent by which chemisorption of oxygen to GAC can enhance the stability of biological perchlorate reduction. Baseline influent concentrations were 50 μg/L of perchlorate, 2 mg/L of acetate as C, and 1 mg/L of DO. Perchlorate removal in the glass bead reactor seized immediately after increasing influent DO concentrations from 1 to 4 mg/L since glass beads have no sorptive capacity. In the biologically active carbon (BAC) reactor, chemisorption of oxygen to GAC removed a substantial fraction of the influent DO, and perchlorate removal was maintained during short-term increases of influent DO levels up to 8 mg/L. During long-term exposure to influent DO concentrations of 8.5 mg/L, effluent perchlorate and DO concentrations increased slowly. Subsequent exposure of the BAC reactor bed to low DO concentrations partially regenerated the capacity for oxygen chemisorption. Microbial analyses indicated similar microbial communities in both reactors, which confirmed that the differences in reactor performance during dynamic loading conditions could be attributed to the sorptive properties of GAC. Using a sorptive biofilm support medium can enhance biological perchlorate removal under dynamic loading conditions.

1. Introduction

Perchlorate (ClO_4^-) is an oxidizing anion, which is commonly used in the form of ammonium perchlorate in rocket fuels, air bags, road flares, and other industrial applications (Urbansky, 1998). Since the introduction of an analytical method that can measure perchlorate accurately at μg/L levels (USEPA, 1997), perchlorate has been reported to be present in many drinking water sources (Gullick et al., 2001). Removal of perchlorate from drinking water sources can be achieved using abiotic processes, such as ion exchange (Roquebert et al., 2000; Urbansky, 1998), reverse osmosis (Urbansky, 1998),

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electrodialysis (Roquebert et al., 2000), and tailored activated carbon (Chen et al., 2005; Parette and Cannon, 2005), in addition to a range of biological processes. Biological reduction of perchlorate is carried out by perchlorate-reducing bacteria which can use perchlorate as an electron acceptor (Achenbach et al., 2001; Coates et al., 1999; Rikken et al., 1996). Compared to abiotic processes, biological processes can convert perchlorate to non-toxic chloride without generating waste streams that contain high concentrations of perchlorate or brines from regenerating ion exchange resins. Another advantage of biological treatment is that, in addition to perchlorate, other contaminants such as nitrate and bromate can be reduced in the same system (Nerenberg and Rittmann, 2004). While the reduction of these other contaminants is desirable, these oxidized compounds will compete with perchlorate for electron donors. In perchlorate-contaminated drinking water, the dominant competing electron acceptors are typically oxygen and nitrate. Microbial reduction of perchlorate is inhibited by high concentrations of oxygen and nitrate (Coates and Achenbach, 2004) and the application of biological processes for drinking water treatment may be problematic in case of variable influent oxygen or nitrate concentrations.

Biological removal of perchlorate has been evaluated in biofilm reactors using different carrier media including plastic (Min et al., 2004), sand (Min et al., 2004), Celite (Losi et al., 2002), and granular activated carbon (GAC) (Brown et al., 2002) for fixed bed reactors, and sand and GAC for fluidized bed reactors (McCarty and Meyer, 2005; Sutton, 2006). Other reactor configurations include membrane diffuser biofilm reactors (Nerenberg et al., 2002) and ion exchange membrane bioreactor (Matos et al., 2006). Advantages of using GAC as a carrier medium include the widespread application of GAC in drinking water treatment plants where existing GAC filters can easily be retrofitted to operate as biologically active carbon (BAC) reactors. In 2004, the California Department of Health Services issued a conditional approval of biological removal of perchlorate from drinking water sources using fixed bed BAC (CADHS, 2004).

Not only can GAC be used to support the growth of biofilms, but sorption by GAC has been shown to complement biological removal in BAC reactors under dynamic loading conditions (Hanaki et al., 1997; Herzberg et al., 2003; Jaar and Wilderer, 1992; Sutton, 2006). Based on mathematical modeling, Herzberg et al. (2003) showed that the sorptive capacity of GAC can be beneficial by serving as a temporary sink for contaminants and then allowing biological degradation of the sorbed contaminants. They demonstrated that sorption, intraparticle diffusion, and desorption resulted in increased biofilm activity on the GAC compared to non-absorbing carrier media. Kim and Logan (2000), however, pointed out a potential problem related to using GAC as a temporary sink. They observed increased effluent perchlorate concentrations after backwash and redistribution of the GAC within the reactor, and attributed increased effluent concentrations to the desorption of perchlorate from GAC. A better understanding of the interactions between sorption, desorption, biological processes, and reactor operation is needed to make use of the sorptive capacity to improve reactor performance (Sutton, 2006).

In addition to the direct benefits of acting as a temporary sink of target contaminants, the sorptive capacity of GAC should be able to enhance biological perchlorate removal indirectly by lowering the concentration of oxygen, the competing electron acceptor, through chemisorption. Molecular oxygen can be irreversibly removed by interacting with the GAC surface (Abuzaid and Nakhla, 1994; Prober et al., 1975): one oxygen molecule and two carbon atoms form two C—O bonds (Zhu et al., 2000). Also, oxygen can be removed by reacting with surface C=O groups to form carboxylic acid groups (Prober et al., 1975). Prober and coworkers showed that chemisorption of oxygen can sustain as much as 6000 bed volumes with 10–40 mg oxygen removed per g of carbon. However, it is not clear to what extent this capacity can be regenerated through physical, chemical, or biological processes. The purpose of the current study was to examine how chemisorption of oxygen on GAC affects biological perchlorate reduction in a BAC filter. To study the specific effects of chemisorption, two identical laboratory-scale biofilm reactors were operated using GAC or glass beads as sorptive or non-sorptive carrier media, respectively. The effects of the sorption capacity of the GAC were evaluated by comparing oxygen and perchlorate removal during short- and long-term exposure to increased influent dissolved oxygen (DO) concentrations and during electron donor failure conditions.

2. Materials and methods

2.1. *Reactor setup and influent composition*

The two laboratory-scale fixed bed biofilm reactors had an inner diameter of 2.4 cm and a length of 14 cm, which resulted in an empty bed volume of 63.4 mL. One reactor was filled with GAC (Norit model RO 0.8, Amersfoort, The Netherlands); the other reactor was filled with glass beads (1-mm glass beads, etched using 0.25% HF for 1 h to allow for a better adhesion of bacteria). Both reactors were operated in an upflow mode with completely mixed bulk-phase conditions by adding a recirculation loop with a flow rate ($Q_{recirculation}$) five times of the influent flow rate ($Q_{influent} = 2.7$ mL/min). This corresponds to an empty bed contact time of 23.5 min. The BAC reactor was seeded using biomass collected from two other BAC reactors: one had been fed Urbana (IL) tap water amended with acetate at a concentration of 2 mg/L as C and 50 μg/L perchlorate (Brown et al., 2002), the other had been fed Urbana groundwater amended with 50 μg/L perchlorate (Lin, 2004). Sorption capacities of the GAC for perchlorate and oxygen were exhausted before initial start-up by recirculating water containing 50 μg/L of perchlorate and saturated by oxygen through the reactor. The glass bead reactor was seeded using biomass from a previously operated 3-mm glass bead reactor, which had been seeded with biomass from the BAC reactor used in the current study.

The synthetic influent was prepared with deionized water and contained 50 μg/L perchlorate, 0.15 mg/L of NH_4Cl as N, and 0.5 mM phosphate buffer to maintain a pH of 7.5. The influent DO level was adjusted to values between 1 and 8.5 mg/L by purging the influent with N_2 gas. After purging, the influent was isolated from ambient air using a floating lid.