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Coupled photocatalytic-biodegradation of 2,4,5-trichlorophenol: Effects of photolytic and photocatalytic effluent composition on bioreactor process performance, community diversity, and resistance and resilience to perturbation

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ABSTRACT

Sequentially coupled advanced oxidation-biodegradation systems have proven effective for treating a variety of wastewaters, but in several cases the pretreatment did not improve, or even hindered, subsequent biodegradation. Therefore, investigating the relationship between advanced oxidation pretreated effluent and subsequent bioreactor performance can help to optimize these systems. Here, a photocatalytic reactor was used to produce four unique effluents from 2,4,5-trichlorophenol (TCP) by varying light wavelength, catalyst presence, and reaction time, demonstrating that the conditions of photocatalytic pretreatment can be tuned to achieve a variety of treatment objectives. The photocatalytic effluents were characterized for chemical oxygen demand (COD), chloride release, aromaticity, and residual TCP concentration. The four effluents were normalized to 40 mg COD/L, combined with biological medium components, and fed to continuous bioreactors. Bioreactors were assayed for COD removal, TCP removal, optical density (OD), and microbial diversity via denaturing gradient gel electrophoresis. In general COD removal in the bioreactors increased as aromatic character of the photo-effluent decreased, but the least aromatic effluent performed poorly indicating the nuanced relationship between photoreactor effluent composition and bioreactor performance. While neither indicator of community diversity, richness nor evenness, correlated with COD removal or biomass accumulation, each effluent produced a unique community as indicated through similarity indices. All conditions demonstrated strong overall TCP removal. After two weeks at steady state, the reactors were perturbed with a 120-μM spike of TCP. Overall the most aromatic photoeffluent produced the most resistant community to the perturbation, while the optimum effluents at steady state

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produced communities with poor resistance in terms of biomass accumulation and COD removal. These results highlight the tradeoffs between steady state performance and resistance to perturbation that are necessary to optimize a combined advanced oxidation-biodegradation treatment strategy.

1. Introduction

Biorecalcitrant organic compounds can pass unchanged through conventional wastewater treatment, while inhibitory organic compounds can impair process performance. Physical treatments that remove or concentrate these contaminants still require degradation of the sequestered compounds. Chemical treatments, such as advanced oxidation processes (AOPs), are effective for transforming many of these contaminants, but chemical treatment alone is often not a viable alternative (Scott and Ollis, 1995). Therefore, robust treatment processes that degrade biorecalcitrant and inhibitory organic compounds while adequately reducing the chemical oxygen demand (COD) are of practical interest. Coupled photocatalytic-biological treatment, here termed photobiocatalysis, is a novel technology that can meet these goals (Mantzavinos and Psillakis, 2004; Oller et al., 2011). A general photobiocatalytic treatment scheme for the ideal case of complete removal of an inhibitory substrate is shown in Fig. 1.

Past work has illuminated the potential and pitfalls for sequentially coupled chemical-biological treatment systems. Fenton's reagent and combined Fenton's/UV oxidation systems were extensively studied for use in treating wastewaters (Tony et al., 2009; Yoon et al., 2001) and as pretreatments for coupled systems (Chamarro et al., 2001; Rodriguez et al., 2002). Photo-Fenton systems improved the biodegradability of *p*-nitrotoluene-*o*-sulfonic acid (p-NTS) (Bandara et al., 1997; Pulgarin et al., 1999) and 5-amino-6-methyl-2-benzimidazolone (AMBI) (Sarria et al., 2001), both present in dye-manufacturing wastewaters, as well as di-(2-ethylhexyl)-phthalate (Chung and Chen, 2009) and pesticides (López et al., 2010). On the other hand, photo-Fenton systems also produced effluents that were not susceptible to biological degradation (Alaton et al., 2004; Parra et al., 2000) or resulted in incomplete mineralization (Bandara et al., 1997). Similarly, ozone, ozone/H_2O_2, UV, and UV/H_2O_2 showed promise as chemical pretreatments in some cases (Alaton et al., 2004; Amador et al., 1989; Dantas et al., 2008; El-Mamouni et al., 2002; Rubalcaba et al., 2007; Stern et al., 1997; Stowell et al., 1992; Zeng et al., 2000; Zhang et al., 2010a), but did not increase biodegradability in others (Adams and Kuzhikannil, 2000; Cokgor et al., 2004; Kitis et al., 2000). Thus, combined treatment systems have potential but require a greater understanding of the characteristics that render a pretreated effluent readily biodegradable.

Titanium dioxide (TiO_2) photocatalysis has been used to transform several toxic organic compounds, including phenols (Lin et al., 2011), methyl vinyl ketone (Manilal et al., 1992), chlorinated hydrocarbons (Choi and Hoffmann, 1996; Wiltowski et al., 2001; Zuo et al., 2006), and an insecticide (Tomašević et al., 2010). It has been used as a pretreatment in coupled treatment systems for degrading surfactants (Tanaka and Ichikawa, 1994), surfactant washwaters (Maillacheruvu et al., 2001), dyes (Aye et al., 2004; Jonstrup et al., 2010), phenols (Li et al., 2011; Marsolek et al., 2008; Zhang et al., 2010b) and herbicides (Parra et al., 2002). TiO_2 photocatalysis has proven successful for degradation of chlorinated phenols, a priority class of compounds that are targeted in the current work (Gray and Stafford, 1994; Lapertot et al., 2006; Li et al., 2011; Skurlatov et al., 1997; Stafford et al., 1997a,b; 1993,).

In this work, we use 2,4,5-trichlorophenol (TCP) as the model contaminant. The history and public-health impact of TCP are typical of chemicals on the USEPA's Persistent Bioaccumulative Toxics list. While TCP is not a proven carcinogen (de Mesquita et al., 1993), there have been increased mortality and cancer rates in people exposed to elevated TCP levels (Thörn et al., 2000), and, the metabolites of TCP are possible initiators of DNA strand breaks (Juhl et al., 1991).

Research on the fate of chlorophenols in wastewater treatment plants suggests that, as long as the concentrations are very low (e.g., μg/L), the chlorophenols can be mineralized (Céspedes et al., 1996; Dahlen and Rittmann, 2002a, b; Makinen et al., 1993; Parker et al., 1994). However, this ability may be compromised following step or spike increases in the concentration of highly chlorinated phenols. This concept is in line with our previous work on TCP biodegradation (Marsolek et al., 2007), which suggests that concentrations greater than 40 μM are largely biorecalcitrant and that TCP inhibits respiration by non-adapted communities in direct proportion to its concentration.

As shown above, while a large body of research details the potential of coupled photocatalytic-biological treatment, there has not yet been a systematic investigation tying individual photocatalytic effluents to subsequent biological process performance, particularly in regards to impacts on the microbial community. Some studies have investigated the impact of pretreated wastewater on microbial community composition (Ballesteros Martín et al., 2011), but an information gap exists regarding the impact of different substrate compositions from the pretreatment on the performance and microbial ecology of the biological reactor, and how to optimize pretreatment effluent composition for subsequent biological performance.

In this work we produced and characterized four unique photoreactor effluents from degradation of TCP and subsequently fed them to continuous aerobic bioreactors. The bioreactors were monitored at steady state for performance (chemical oxygen demand (COD) removal, biomass accumulation) and changes in the microbial communities (richness, or number of operational taxonomic units, and evenness, or the relative equality of the community distribution). The