Chapter 6
In-Situ Oxidative Degradation of Emerging Contaminants in Soil and Groundwater Using a New Class of Stabilized MnO_2 Nanoparticles

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ABSTRACT

Emerging Organic Contaminants (EOCs) such as steroidal estrogen hormones are of growing concern in recent years, as trace concentrations of these hormones can cause adverse effects on the environmental and human health. While these hormones have been widely detected in soil and groundwater, effective technology has been lacking for in-situ degradation of these contaminants. This chapter illustrates a new class of stabilized MnO_2 nanoparticles and a new in-situ technology for oxidative degradation of EOCs in soil and groundwater. The stabilized nanoparticles were prepared using a low-cost, food-grade Carboxymethyl Cellulose (CMC) as a stabilizer. The nanoparticles were then characterized and tested for their effectiveness for degradation of both aqueous and soil-sorbed E2 (17β-estradiol). Column tests confirmed the effectiveness of the nanoparticles for in-situ remediation of soil sorbed E2. The nanoparticle treatment decreased both water leachable and soil-sorbed E2, offering a useful alternative for in-situ remediation of EOCs in the subsurface.

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1. INTRODUCTION AND BACKGROUND

EOCs in Environment

With the development of more powerful analytical tools, our ability to detect contaminants in water at the trace levels (ng/L-μg/L) has been greatly improved. As a result, a host of emerging organic contaminants (EOCs) have been revealed in water bodies (Pal, Gin, Lin, & Reinhard, 2010). Over the last decade or so, increasing attention has been placed on various endocrine disrupting chemicals (EDCs) including pharmaceuticals and personal care products. Typically, these EOCs are physiological toxic but remain unregulated or are undergoing the regulatory process (Rivera-Utrilla, Sanchez-Polo, Ferro-Garcia, Prados-Joya, & Ocampo-Perez, 2013). EDCs can interfere with hormonal and homeostatic system functions. Steroidal estrogens are one class of EDCs, of particular environmental concern are endogenous estrone (E1), 17β-estradiol (E2), and estriol (E3) released by human and wildlife, as well as synthetic 17α-ethinylestradiol (EE2), which has been used in almost all oral contraceptive pills. When released into the environment, these hormones may cause a wide range of adverse effects including abnormal development, reproductive disorders, sexual disorders as well as cancers in wildlife and humans (Colborn, Saal, & Soto, 1993; Diamanti-Kandarakis et al., 2009). Of the estrogen hormones, E2 has been a major concern for its physiological effects at lower concentrations than other steroid hormones (Shore & Shemesh, 2003). For instance, the male Japanese medaka was found to produce female specific proteins when exposed to E2 at 5 ng/L (Tabata et al., 2001). E2 has been detected in aqueous environment at concentrations above 10 ng/L, which is above the lowest observable effect level (LOEL) for some fish and plants (Shore & Shemesh, 2003). A resent U.S. Geological Survey detected various reproductive hormones in 139 streams sampled across 30 states, of which E2 was found in 10% of the 139 streams at a maximum concentration of 0.1 μg/L (Kolpin et al., 2002). The analysis of 112 samples in 59 groundwater sites in Austria detected E2 in more than 50% of the samples with a maximum concentration of 0.79 ng/L (Hohenblum et al., 2004).

Estrogens in the environment originate from humans, livestock, wildlife, and pharmaceuticals. Municipal wastewater discharge is considered one of the major sources of hormones in the aquatic system as current wastewater treatment processes could not completely remove these hormones (Baronti et al., 2000; Rosenfeldt & Linden, 2004; Ternes et al., 1999). Animal manure represents another major source of estrogens. Large amounts of estrogen and testosterone can leach from manure piles, and besides, land application of animal wastes contributes significant amounts of hormones to soil (Finlay-Moore, Hartel, & Cabrera, 2000; Shore & Shemesh, 2003).

The mobility of estrogens is generally low and they are easily bound to soil. However, low concentrations of estrogens were reported to breakthrough in porous media and release into groundwater, which are high enough to cause harmful effects (Hohenblum, Gans, Moche, Scharf, & Lorbeer, 2004; Kolodziej, Harter, & Sedlak, 2004; Vulliet, Wiest, Baudot, & Grenier-Loustalot, 2008).

Conventional EOCs Treatment Methods

Oxidation-reduction or "redox" reactions play an important role in transformation and/or speciation of organic chemical and redox-active inorganic contaminants, such as EOCs, nitrate, perchlorate, chromate and uranium in both natural and engineered systems. Researchers have explored various treatment processes, primarily oxidation-based processes, to reduce environmental estrogenicity of estrogens in waters.