234f Quantification of Reductive Species Produced by High Voltage Electrical Discharges in Water

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Advanced oxidation processes (AOP) are rapidly gaining importance for the degradation of minute concentrations (ppb to ppm range) of chemical and biological pollutants [1-5]. These technologies as the name suggests are primarily involved in the oxidation of pollutants utilizing a highly non-selective and reactive oxidant hydroxyl radical. However hydroxyl radical isn't the only reactive species produced in advanced oxidation processes. The generation of molecular species such as hydrogen peroxide, hydrogen, oxygen, other oxidative species such as hydroperoxyl radical and reductive species such as hydrogen radical, superoxide radical anion and aqueous electrons (in some processes) have also been documented [6-9]. The presence of reductive species in a highly oxidizing environment offers the possibility that in mixture of aqueous contaminants some pollutants or a component of certain pollutants degrade by reductive mechanisms. Some of the earlier work has demonstrates the role of reductive species in the degradation of compounds with high electron affinity, primarily chlorinated compounds and compounds containing nitro groups [10-12]. The reactive species associated with reductive degradation are different in different AOP's. Modified Fenton's process produces superoxide radical anion that causes degradation of carbon tetrachloride while the species responsible for a component of DNT degradation in photolytic ozonation (O3/UV) system is ethanol radical, a reductive species formed on reaction of ethanol with hydroxyl radical [10,12]. Radiation and photo-catalytic studies have quantified reductive species such as superoxide radical anion by the use of selective probes such as tetranitromethane (TNM), nitroblue tetrazolium chloride (NBT) and ferricytochrome c [13-16]. Sonochemical studies have shown an increase in phenol degradation when carbon tetrachloride was used as a scavenger of the hydrogen atom [11]. Pulsed electrical discharge is a form of AOP in which high voltage electrical discharge is used to degrade pollutants by production of various reactive species in the liquid and gaseous phase [17-19]. The efficacy of this technology in degrading a wide spectrum of chemical and biological contaminants has been demonstrated 20-23]. The production of the following reactive species due to aqueous phase discharges has been demonstrated: hydroxyl radicals, hydrogen radical, oxygen radical (using emission spectroscopy), hydrogen peroxide (chemical methods), hydrogen and oxygen (GC-TCD)[24-26]. This work focuses on quantification of reductive species formed due to generation of pulsed electrical discharge in water. The motivation behind this work are previous studies that show hydroxyl radical attack alone can't account for TCE degradation observed due to pulsed electrical discharges (i.e. non-hydroxyl radical particularly reductive mechanisms might be responsible) and the quantification of hydrogen and oxygen gas which can account for the considerable production rate of hydrogen radical and superoxide radical anion respectively[26,27]. The likely reductive species produced by pulsed electrical discharge are hydrogen radical and superoxide radical anion since the generation of aqueous electrons hasn't been demonstrated. Two probes tetranitromethane (TNM) and nitroblue tetrazolium chloride (NBT) are to qualitatively and quantitatively demonstrate the production of reductive species. Competition experiments between the probe compounds are conducted to demonstrate qualitatively the production of reductive species. Experiments are conducted to understand the role of various parameters such as: concentration of probes, applied voltage, initial solution conductivity, and the initial solution pH on the production of reductive species.

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