

Electrochemical Oxidation of the Xanthene Dye Rhodamine 6G by Electrochemical Advanced Oxidation Using Pt and BDD Anodes

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Abstract: Aqueous solutions of Rhodamine 6G (R6G), one of the more used xanthene dye, were treated by hydroxyl radicals (OH) electrocatalytically generated through the electro-Fenton process, a powerful and environmentally friendly electrochemical method. Platinum (Pt) or boron-doped diamond (BDD) anodes were used with a carbon-felt cathode. The effect of anode nature and applied current on the degradation and mineralization kinetics was investigated. The applied current value of 500 mA was found as optimum operating parameter for both anodes under our operating conditions. Kinetic data of R6G disappearance follow the pseudo-first order reaction decay process. The rate constant of the oxidation reaction between R6G and hydroxyl radicals was determined by competition kinetics method and found as $3.41 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The mineralization efficiency was found very high with both anodes reaching 99% and 98% for BDD and Pt respectively at 500 mA. Oxalic acid was identified as ultimate end-product before complete mineralization. The two secondary amine groups of R6G were converted mainly into NH_4^+ ions whereas NO_3^- ions are released to the solution at relatively low proportion.

Keywords: Rhodamine 6G, Advanced oxidation process, Hydroxyl radical, Boron-doped diamond, Electro-Fenton process, Mineralization.

INTRODUCTION

The major current environmental concern with dyes revolves around the potential carcinogenic health risk that they or their degradation intermediates present to humans. Thus, the appropriate treatment of dyes wastewaters for removing both colour and dye compounds is important for the protection of natural waters. Several physicochemical and biological methods have been proposed to eliminate synthetic dyes. Several physicochemical processes such as chemical oxidation [1-3], coagulation/flocculation [4-6] and electrocoagulation [7-9] are used to remove dyes from water. Chemical oxidation using conventional oxidizing agents are generally inadequate because of their low oxidation power against persistent organic pollutants, and the potential formation of oxidation reaction intermediates that can be more toxic than the initial pollutants. Physical processes are separatives, not degradatives. Biological treatments based on anaerobic/aerobic degradation [10-13] are often not effective because of the recalcitrant nature of dyes, or because of their toxicity to micro-organisms, making biological treatment inefficient.

The synthetic organic dyes, of which the major parts are recalcitrant in nature, are used universally in many different manufacturing processes. The dyes are released into the environment in industrial effluents and are highly visible even at low concentration. The color is one of the most obvious indicators of water pollution by dyes.

Hazardous xanthene dye, Rhodamine 6G (R6G), is widely used as a dye for silk, cotton, wool, bast fibers, paper, leather, and plastics [14], as tracing agent in water pollution studies [15], and as an adsorption indicator, especially in very acid solutions. Xanthene dyes, based on fluorescein- and rhodamine-like structures, are known to have intensive fluorescence and therefore have a great

relevance as molecular probes for bio-analytical application and for cellular imaging. As a dye and a fluorescent probe, R6G is also used in research on mitochondrial [16] and synaptosomal functions, in laser surgery [17], as an insecticide [18], in microbiology [19], and in drug screening [20]. Essentially, this compound is used only as a functional dye.

Hazardous xanthene dye, R6G, induces sister chromatid exchanges (SCEs) and chromosomal aberrations in cultured CHO (Chinese hamster ovary) cells and has incidence of keratoacanthomas of the skin [21]. The carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity to humans and animals have been experimentally proven [22-23].

In recent years, there has been growing interest in finding better way to degrade recalcitrant organic pollutants by developing advanced oxidation processes (AOPs). These processes are based on *in situ* generation of hydroxyl radicals (OH) that are powerful oxidizing agent and able to mineralize any organic pollutants [24, 25]. Several studies have shown that the oxidation of organic compounds can be achieved by using the Fenton's reagent (H_2O_2 , Fe^{2+}) or electrochemical/photochemically assisted Fenton's reaction. The Fenton's reagent is known as precursor of the hydroxyl radical (reaction 1) which is the second most strong oxidant known after fluorine (which can not be used in aqueous media), having a very high oxidation potential ($E^\circ(\text{OH}/\text{H}_2\text{O}) = 2.80 \text{ V/SHE}$) that make it able to non-selectively react with organics to give hydroxylated or dehydrogenated derivatives until their complete mineralization, i.e., their transformation into CO_2 , H_2O and inorganic ions [26-29]. Among these processes, the heterogeneous photocatalysis [30, 31] and heterogeneous Fenton-like degradation [32, 33] were already applied to removal of R6G from wastewater.

Among the electrochemical advanced oxidation processes, the electro-Fenton process is the most popular one. This indirect electrochemical method consist of the continuous production of hydrogen peroxide in the bulk of treated solution by two electron reduction of dissolved O_2 and simultaneous re-generation of Fe^{2+} by one electron reduction of Fe^{3+} (initially introduced at a catalytic

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