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13. ABSTRACT ***(Maximum 200 Words)***

An electrochemical advanced oxidation process has been developed, utilizing electrodes which generate hydroxyl free radical (HO) by oxidizing water. All substrates tested are oxidized, mostly with reaction rates proportional to the corresponding rate constants for reaction with hydroxyl. All substrates tested in the process have been destroyed. Complete oxidation of substrate molecules is the rule, and products of partial oxidation are rarely detected. Because relatively large current efficiencies can be achieved, this process is attractive in regard to energy cost. No hydrogen peroxide or ozone is required.

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Electrochemical Advanced Oxidation Process Utilizing Nb-doped TiO_2 Electrodes

Abstract

An electrochemical advanced oxidation process has been developed, utilizing electrodes which generate hydroxyl free radical (HO•) by oxidizing water. All substrates tested are oxidized, mostly with reaction rates proportional to the corresponding rate constants for reaction with hydroxyl. All substrates tested in the process have been destroyed. Complete oxidation of substrate molecules is the rule, and products of partial oxidation are rarely detected. Because relatively large current efficiencies can be achieved, this process is attractive in regard to energy cost. No hydrogen peroxide or ozone is required.

Introduction

An electrochemical advanced oxidation process has been invented [1], wherein water is oxidized to produce hydroxyl free radical:

$$H_2O \rightarrow OH\bullet + H^+ + e^- \qquad \varepsilon_0 = +2.74V \qquad (1)$$

The anodes consist of a Ti-metal substrate with an oxide coating comprising TiO_2 doped with 4 mole % Nb or Ta in the +4 valence state [2]. The oxide coating is a heavily n-doped semiconductor, and the resulting electrodes have excellent corrosion resistance at the high potential needed to generate hydroxyl.

The electron transfer process at the surface of the anode are illustrated in Figure 1. It is fundamentally similar to electron transfer in photooxidation at a TiO_2 surface. When a large positive electrode potential is applied to the anode, a positive space charge forms just inside the metal oxide layer at its interface with the electrolyte, resulting in pronounced bending of the electron bands. When the doped conduction band inside the metal oxide lines up with the potential of the H_2O/ OH• couple, electrons tunnel into the conduction band, converting water molecules at the surface of the metal oxide to hydroxyl free radicals which remain bound at the oxide/electrolyte interface. The surface bound hydroxyls react with substrate molecules at the surface of the anode. Because electrons are removed from the interface, recombination is not an issue, and quite large current efficiencies are observed: up to 90% in laboratory test cells, and 25-35% in large prototypes that will soon be tested in industrial settings.

Structure of the Anodes

The electrodes are produced by baking a coat of TiO_2 doped with Nb on to a Ti-metal substrate under conditions that favor the +4 oxidation state of Nb. Methods to produce rod electrodes and disk electrodes for laboratory use are described in [2]. Subsequent improvements have allowed production of plate electrodes of Ti-sheet and porous electrodes of Ti-fiber. Exact coating compositions and coating procedures used to produce full-sized porous electrodes and details of electrode structure will be described in a patent application to be filed shortly.

Porous anodes are produced by coating bundles of 50μm diameter Ti fibers with the same doped oxide composition. The time needed for water to flow past a fiber is only 0.5ms, and the thickness of the diffusive boundary layer formed is on the order of 1 μm, allowing excellent mass transfer.

Process Kinetics

Kinetic data suggest that most of the hydroxyl produced by oxidation of water remains loosely bound to the surface of the anode until a substrate molecule comes by and reacts with it. Two kinetic regimes may be distinguished in the case that substrate is present:

(1) Reaction Limited Regime. Most commonly, the small steady state concentration of hydroxyl bound to the surface of the anode (N_{OH}) limits the rate of reaction. In this case,

$$V\, dC_s/dt = -\, k_s\, N_{OH}\, A_{an}\, C_s \qquad (2)$$

First order kinetics are observed, and the rate of reaction is proportional to N_{OH} which is a characteristic of the anode. In this case, more hydroxyl is produced at the anode than is required to fully oxidize the substrate molecules that reach the reaction zone; the excess is converted by further electrode reactions to O_2

(2) Current Limited Regime. In this case, enough substrate molecules reach the surface of the anode to consume all of the hydroxyl generated there. The rate of reaction is independent of substrate concentration (zero order kinetics), and is directly proportional to current through the cell multiplied by f_{OH}, which is the intrinsic current efficiency of the anode:

$$V\, dC_s/dt = -\, f_{OH}\, i\, A_{an} / (n\, F_0) \qquad (3)$$

The Current Limited Regime is encountered when

$$C_s > C_t = f_{OH}\, i / (n\, F_0\, k_s\, N_{OH}) \qquad (4)$$

The parameters N_{OH} and f_{OH} are easily determined in tests where C_s is much smaller or much larger than C_t, respectively. In principle, a Mass Transfer Limited Regime might also be encountered, but, in practice, mass transfer is never rate limiting in a properly designed cell.

Experimental results in the Rate Limited Regime

Experimental data for six substrates generated using flat plate electrodes at $i = 20$ mA cm^{-2} are presented in Figure 2. The electrolyte was 0.1M $NaHCO_3$ bubbled with CO_2 to maintain pH near 7. Figure 3 shows data for p-cresol and t-butylmethylether in 25 mM $NaHCO_3$ collected in batch mode in a test unit with fiber anodes.

Semilogarithmic plots for four of the substrates in Figure 2 and both substrates in Figure 3 are linear, indicating first order kinetics. The slopes vary in proportion to the rate constant for reaction with hydroxyl (k_s), diagnostic of the Reaction Limited Regime. The plots for azide and formate are curved, probably because they are both small anions present in relatively large concentration. Under these conditions, a large concentration of the substrate anion may be present in the electrical double layer at the surface of the anode. In calculating the "measured" rate constants for formate and azide presented in Figure 4, the initial values of the slopes of the corresponding plots in Figure 2 were used.

If one rate constant is taken as known, the other rate constants can be determined by comparing the slopes in a semilogarithmic plot. The rate constant of p-cresol was set equal to the literature value $k_s = 1.2 \times 10^{10}$ M^{-1} s^{-1} [4], and the other rate constants were determined in proportion to the slopes. Rate constants determined in this way are compared to literature values in Figure 4. The value determined for formate is too high by a factor of two, but the other values are in good agreement with literature values. Literature values for three substrates were not available, and the measured values are compared with known values of closely related compounds (open circles). The measured value for 2,2'-thiodiethanol is practically equal to the literature value for diethylsulfide, and the measured value for diisopropylmethylphosphonate is just smaller than twice the value for isopropanol. The measured value for 2,4-D is practically equal to the literature value for 4-chlorophenol.

The good correspondence between the rate constants determined from our data and values in the literature indicates that the substrates are, in fact, being destroyed by reaction with hydroxyl, rather than direct injection of electrons into the conduction band. Kinetic experiments of this kind compare favorably with other methods that have been used to determine k_s .

Application to Actual Waste Waters

Figure 5 depicts treatment of a waste water from a plating shop that contains cyanide and unknown organic compounds that contribute Chemical Oxygen Demand (COD). The favorable rate constant ($k_s = 7.6 \times 10^9$ M^{-1} s^{-1}) causes cyanide to be rapidly destroyed, while COD decreases more slowly. The slope of *log COD* vs. time decreases gradually, as the more reactive compounds are preferentially removed from the mix.

Figure 6 illustrates treatment of a sample of waste water from a machine shop using a small test cell with a rod electrode. This water is contaminated mostly with residues of water soluble cutting fluids washed from work pieces. This sample is representative of a very common industrial waste stream. A complex and poorly characterized assortment of organic and inorganic compounds are present in the water, and the major parameter of concern is COD. This test began in the current limited regime with $f_{OH} = 0.96$ and went over to the Rate Limited Regime as COD decreased.

Figure 7 illustrates removal of COD from a sample of shipboard wastewater that has been purified by mechanical separation of solids followed by membrane filtration (sample provided by the US Naval Surface Warfare Center, Carderock). The porous anode test unit was used. First order kinetics are clearly evident, as expected at small substrate concentration.

Prospects for practical application

Two different prototype water treatment units of 1 L/min and 4 L/min capacity have been built. They will soon be delivered to industrial sites for operational testing. These prototype units operate at about 30% current efficiency and 6V cell voltage, corresponding to 67 kw-hr/kgCOD destroyed. Work is continuing to improve electrode life, current efficiency, and reaction kinetics at small concentrations of substrate. At least a two-fold improvement in energy cost is expected as the electrodes and process conditions are optimized.

This process is expected to find application destroying contaminants at levels greater than other AOPs can handle at reasonable cost, starting with those discussed in the preceding section.

Definition of Symbols

A_{an} = active surface area of the anode
C_s = concentration of substrate (S) in solution
C_t = concentration of S at the transition between kinetic regimes
F_O = 96,485 Coulombs mole^{-1} = Faraday's constant
f_{OH} = moles HO• produced/ Faraday through the cell
i = current density at the surface of the anode (A cm^{-2})
k_s = rate constant for reaction of HO• with S
n = moles of HO• required to completely mineralize one mole of S
N_{OH} = concentration of HO• at the surface of the anode (moles cm^{-2})
t = time
V = volume of electrolyte

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Fig. 1. Electron transfer at the surface of the electrode.

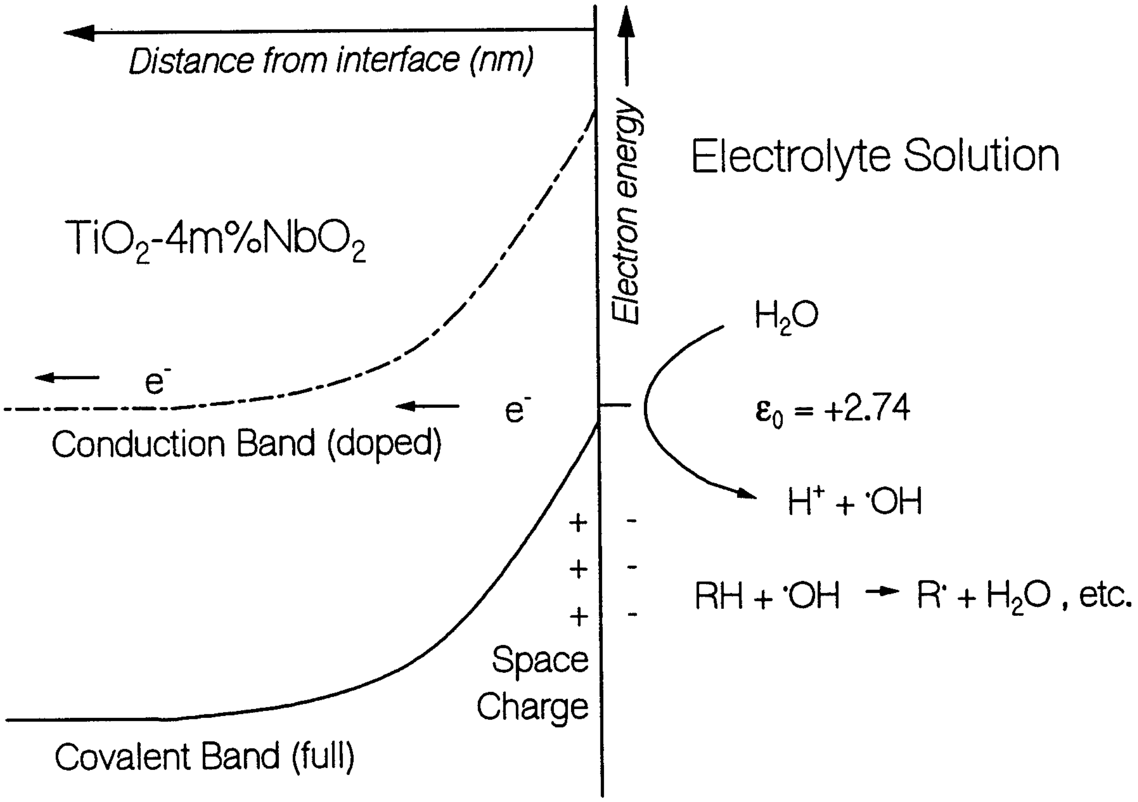

Fig. 2. Kinetic Data for Several Substrates

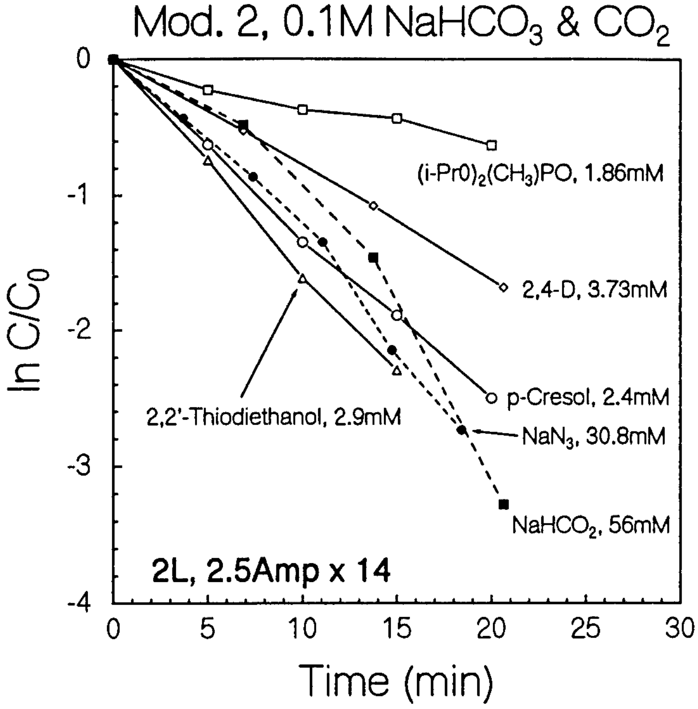

Fig. 3. Oxidation of p-Cresol and MTBE in Porous Anode Cell

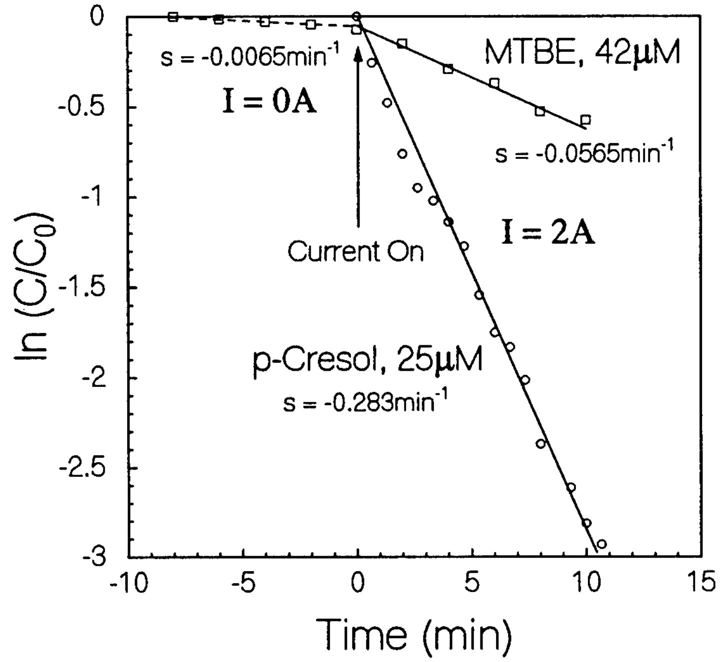

Fig. 4. Comparison of Rate Constants

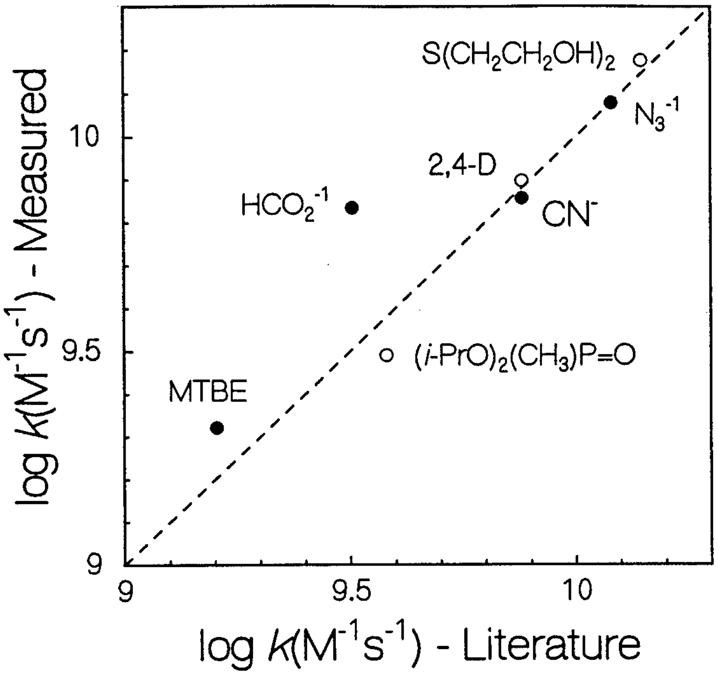

Fig. 5. Plating waste water

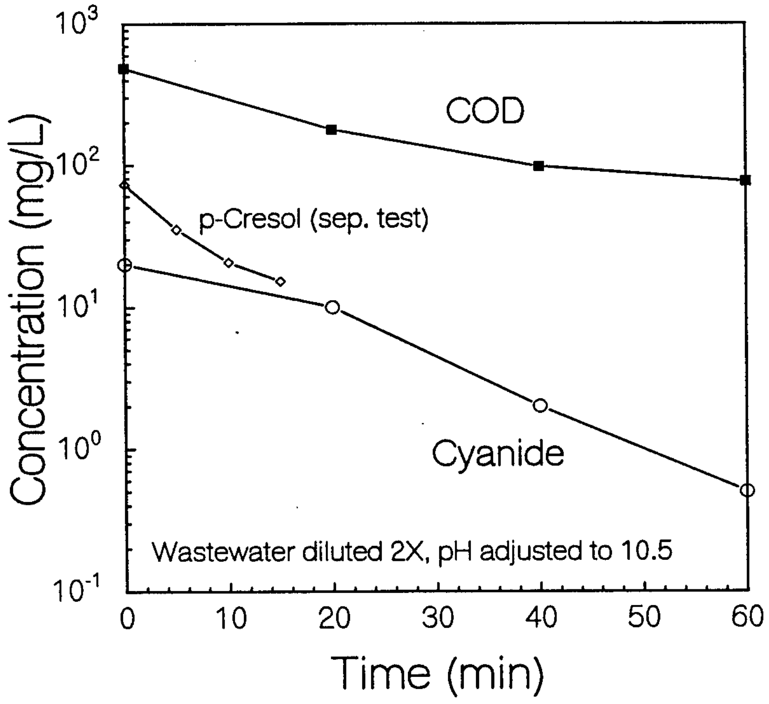

Fig. 6. Machine shop wastewater

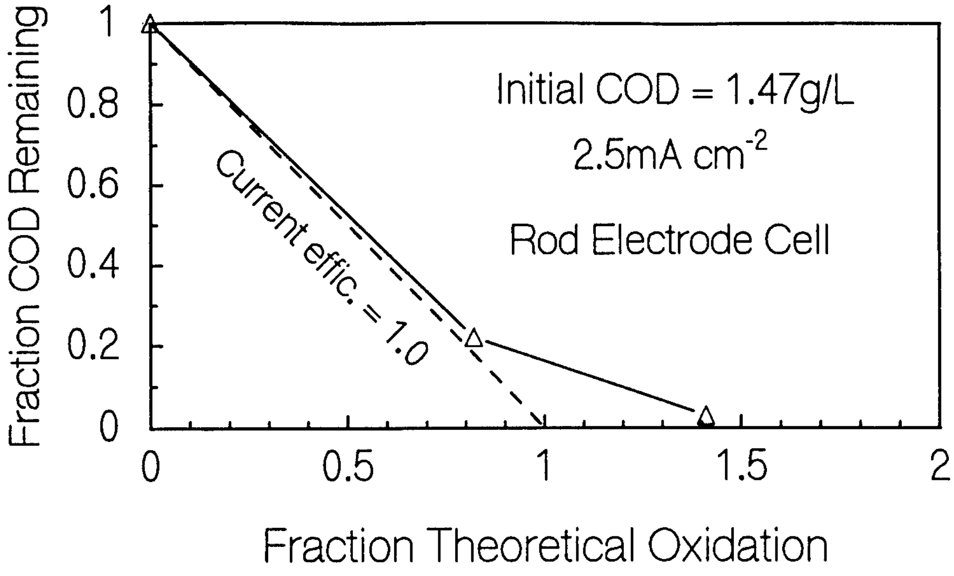

Fig. 7. Ultrafiltered black water.