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Anodic oxidation of isothiazolin-3-ones in aqueous medium by using boron-doped diamond electrode

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ABSTRACT

Electrochemical degradation of biocide compound, isothiazolin-3-ones, was studied in aqueous medium, with Na_2SO_4 supporting electrolyte using boron-doped diamond (BDD) anode. The redox response of isothiazolin-3-ones at BDD was examined by cyclic voltammetric study. The degradation of isothiazolin-3-ones and its mineralization trend were monitored by UV–vis spectrophotometric method and total organic carbon (TOC) analyzer, respectively. The effect of operating parameters such as applied current density, biocide concentration, electrolyte pH and nature of supporting electrolytes (Na_2SO_4, $NaNO_3$ and NaCl) on degradation rate was studied in detail. It was established that the hydroxyl radicals (•OH) generated at BDD surface were responsible for the degradation and the mineralization of the biocide contaminant. The rate of degradation was almost independent of electrolyte pH but became faster as the applied current density increased and the biocide concentration decreased. The kinetic studies revealed that the biocide decay follows a pseudo-first-order rate. The apparent rate constant for the oxidation of isothiazolin-3-ones was determined to be $2.65 \times 10^{-4}\ s^{-1}$ at an applied current density of 25 mA cm^{-2} in the presence of 0.1 mol dm^{-3} Na_2SO_4 at pH 6.0. A poor mineralization efficiency was observed in the case of NaCl as supporting electrolyte which cause in-situ generation of chlorine based mediated oxidants such as Cl_2 and OCl^- which have negligible influence in mineralizing the isothiazolin-3-ones compared to peroxodisulfate ($S_2O_8^{2-}$) oxidants that formed in the case of Na_2SO_4. The oxidizing ability of the BDD anode was compared with those of Pt and glassy carbon anodes under similar experimental conditions.

1. Introduction

In recent years, research on negative consequences of chemicals used as pesticides, biocides, fertilizers etc., which caused increased health problems to humankind and the decline in the population of aquatic species, has become more significant among environmental scientists. Isothiazolin-3-ones, known biocides, have been found to exhibit biological activity towards several kinds of microorganisms. The isothiazolin-3-one compounds such as 5-chloro-2-methyl-4-isothiazolin-3-one (CMI) and 2-methyl-4-isothiazolin-3-one (MI) are highly bioactive especially their chloro derivative CMI. These are used as preservatives for increasing the shelf life of latex paints [1] in pharmaceutical/self hygiene products (sunscreens, shampoos, baby wipes and creams/lotions/gels), cosmetics (moisturizers, eye shadows, and make-up removers), toiletries and, household and industrial products (detergents, printing inks, fabric softeners, and adhesives). Additionally, they are being used in metal working fluids, slimicides of cooling towers, paper mills, recirculating chillers, cutting oils and jet heating fuels [2]. Despite their versatile applications, epidemiological studies proved that these isothiazolin-3-ones, even at a very low concentration (0.2%), can create allergic contact dermatitis to humankind [3–5]. The source of contamination of these compounds in the natural water body system is due not only to its application, but also to the contaminated wastes that are released from the manufacturing industries. Mitigating the problem of isothiazolin-3-ones is really a tough task and a nightmare to environmental scientists as its natural decay in the biotic system is a very slow process and the average time taken is predicted to be several days to weeks [6,7]. The continued increase in the production of these compounds for mandate applications increases their load in the water environment [1]. A couple of attempts have been tried for the natural degradation of isothiazolin-3-ones, in aqueous media, as a function of temperature and pH [8–9]. At pH > 8.5, the half-life period was found to be 4.6 days at 40 °C and it increased to 46 days when the temperature falls down to 24 °C. In a pH controlled (neutral pH) photolytic degradation under natural sunlight, the half-life was determined as 158 h and 266 h for MI and CMI, respectively. Hence, the problem caused by the contamination of isothiozoline-3-ones cannot be mitigated by natural degradation and the biological approach. Thus, an

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effective and viable treatment technique is needed to mineralize the biocide material in to completely harmless products. In an attempt of a biodegradation of CMI with two different initial concentrations viz. 0.3 and 0.03 mg l^{-1}, the respective CO_2 evolution was measured as 38 and 62% after 28 days [10]. The successful removal of isothiazolin-3-ones from aqueous solution was achieved [11] by heterogeneous photocatalysis technique. However, the main drawback for using photocatalysts is the difficulty in separating the semiconducting fine particles from the treated solution.

Emerging technologies such as advanced oxidation processes (AOPs) using novel electrodes are proved to be a promising one owing to the in-situ production of •OH that results in total mineralization of persistent organic contaminants in aqueous system. The •OH species is a powerful oxidizing agent and its fast non-selective reaction with organic pollutants gives dehydrogenated or hydroxylated intermediates that can undergo complete mineralization into CO_2, H_2O and fragmented inorganic ions [12–14]. Among the AOPs, electrochemical oxidation has been proved to be an effective technique which offers many advantages such as low operational cost and high mineralization efficiency compared to other known chemical and photochemical processes [12,15–17]. Electrochemical oxidation allows the destruction of organic pollutants of an aqueous system by •OH formed at the surface of a high oxygen overvoltage anode (M) from water decomposition.

$$M(H_2O)M(^{\cdot}OH) + H^+ + e^- \tag{1}$$

The application of electrochemical AOPs using a state-of- the art electrode material viz. boron doped diamond (BDD) has received great attention [18] as it exhibits the following important features; (i) an inert surface with a less adsorptive nature towards •OH; (ii) remarkable dimensional stability; (iii) corrosion resistive properties with greater durability; (iv) low and stable background current [19] and (v) an extremely wide potential window in aqueous and non-aqueous media [20]. The much higher oxygen overpotential of BDD compared to conventional electrodes (Pt, graphitic carbon electrodes and metal oxide coated electrodes such as SnO_2, PbO_2, RuO_2, etc.) favors the large production of •OH on its surface thus making the BDD anode more effective in mineralizing the organic pollutants [21–23]. This fact has been proved by many recent studies on the degradation of several organic dyes and pollutants in aqueous media using a BDD anode that showed a complete mineralization into CO_2 and H_2O [23–28]. Thus, the anodic oxidation technique using BDD could be an appropriate choice for the treatment of water containing isothiazolin-3-one compounds. To the best of our knowledge, there has not been any work addressing the degradation of isothiazolin-3-ones by an electrochemical approach.

Hence, in the present study, the degradation of iosthiazolin-3-ones from aqueous media was tried using BDD electrode. The influence of experimental parameters such as the initial concentration of the biocide, applied current density, electrolyte pH and different supporting electrolytes on the rate of degradation of isothiazolin-3-ones was systematically examined. Also, a comparative study with Pt and glassy carbon (GC) anodes was made to confirm the superior oxidation power of the BDD electrode. A reaction sequence for the mineralization of iosthiazolin-3-ones at BDD was proposed.

2. Experimental

2.1. Materials

ZONEN-C, biocide solutions, containing CMI (10.65%) and MI (3.31%) with magnesium nitrate as stabilizer, were obtained from Chemicrea (Japan) as gift samples. Magnesium stabilizes isothiazolin-3-ones by forming adducts through oxygen of carbonyl group. The electrolyte salts, organic solvents and other chemicals used in this study purchased from Kanto chemicals were of high purity and used as such. The boron source, B_2O_3 (99.9%) was from KOJUNDO Chemical Laboratory. The high purity water, obtained from Millipore Milli-Q system, was used for the preparation of all the solutions. Diluted H_2SO_4 or NaOH solutions were used for adjusting the pH of the electrolyte solution.

BDD anode was prepared by a microwave assisted plasma chemical vapour deposition (MPCVD) technique (Model AX2115, Astex Corp.) on p-Si(111) substrates. The fabrication process detail is described elsewhere [29]. The conditions for the fabrication of BDD thin film on a Si substrate are; temperature — 540 °C; pressure — 70 Torr; carrier gas — ultra pure H_2; carbon and boron source — mixture of acetone and methanol (9:1 *v*/*v*) having B_2O_3 with a B/C ratio of 10^4 ppm; and deposition time — 24 h. The thickness of the film fabricated was 20 μm. The electrode surface was cleaned by sonication in ethanol followed by deionized water. The other working electrodes viz., Pt and GC were procured from Nilaco Corporation, Japan.

2.2. Electrolytic studies

The molecular weight of CMI and MI is 149.59 and 115.1 g/mole, respectively. The gift sample obtained for this study (referred as isothiazolin-3-ones) was an aqueous mixture of CMI and MI with a ratio of 3:1. The sample was pale yellow in color with a density of 1.02 g/cm^3. The working concentration used in this study was a mixture of 5.5×10^{-4} mol dm^{-3} of CMI and 1.7×10^{-4} mol dm^{-3} of MI. Since both the compounds have an almost identical structure (as seen in Fig. 2) and showed similar trends of photocatalytic degradation [11], the total concentration of isothiazolin-3-ones in the mixture was conveniently taken as 7.2×10^{-4} mol dm^{-3}, for easy interpretations, predictions and calculations of reaction kinetic studies. The working volume of isothiazolin-3-one (7.2×10^{-4} mol dm^{-3}) solution was 220 mL with a supporting electrolyte concentration of 0.1 mol dm^{-3}.

A computer controlled electrochemical work station (potentiostat/galvanostat — Model HZ-5000, Hokuto Denko Ltd., Japan) with an undivided three electrode reaction cell was used for all the electrochemical studies. The working, counter and reference electrodes were BDD, Pt and $Hg/Hg_2Cl_2 \cdot KCl$ (sat.) (SCE), respectively. Deposition of BDD thin film was made over a square shape Si wafer (2 cm × 2 cm). The ohmic contact was made on the pristine side of the Si wafer using gold and silver paste. Upon making ohmic contact, the pristine side was completely masked using adhesive tape. The surface area of the BDD thin film, i.e., the area exposed to the electrolyte was then measured to be exactly 4 cm^2. The Pt strip used as a counter electrode was a rectangle type (1 cm × 2 cm) with an effective surface area of 4 cm^2. The inter electrode gap between the working and counter electrode was maintained as 1 cm. The degradation experiments were conducted at galvanostatic mode under uniform stirring. For anodic oxidation experiments using Pt and GC electrodes, the respective cathode material was BDD and Pt with a constant surface area. The temperature of the electrolyte solution was maintained at 25 °C by a thermo-regulated water bath.

Prior to every experimental run, an anodic polarization was carried out for the BDD electrode in 0.1 mol dm^{-3} H_2SO_4 solution at 100 mA for a period of 10 min while Pt was soaked in HNO_3 for 10 min to remove any kind of deposition and/or impurities from the surface. The constant cell potential during the galvanostatic electrolysis indicated that the activity of the electrode was unaltered and retained throughout the experiment.

2.3. Analyses

The degradation trend of the isothiazolin-3-ones with respect to electrolysis period was monitored in terms of the intensity of the absorbance peak (λ_{max} observed at 273 nm) using a UV–vis spectrophotometer (Hitachi U-2000). The reproducibility of the obtained results was confirmed by a duplicate run with an error % of ± 2. The electrolyte pH was measured with a TOA HM-30S pH meter. The mineralization of the isothiazolin-3-ones solution was followed from the decay of