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Electrochemical degradation of malachite green with BDD electrodes: Effect of electrochemical parameters

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ABSTRACT

The dye malachite green (MG) has found extensive use all over the world in the fish farming industry as a fungicide. It has been suspected to be genotoxic and carcinogenic and it has now become a highly controversial compound due to the risks it poses to the consumers of treated fish. In this context, electrochemical oxidation of malachite green (MG) has been studied on a one-compartment batch reactor employing a boron-doped diamond (BDD) as anode and a stainless steel as cathode. The effects of several experimental parameters, such as current density, pH initial and supporting electrolyte were investigated. The optimal conditions were determined such as a current intensity of 32 mA cm^{-2}, strongly acidic pH (pH = 3), and Na_2SO_4 as a good supporting electrolyte. Under these conditions, a degradation efficiency of 98% was obtained after 60 min of electrolysis and 91% of chemical oxygen demand (COD) removal after 180 min of electrolysis.

1. Introduction

Day by day growing dye consumption and usage of new kind of dyes by the textile industry are producing increasing amounts of waste. The industry faces a big environmental problem with approximately 10 000 registered different types of dyes and 7×10^5 ton consumption per year [1]. When 10–15% of these dyes are given to aqueous environments, it is obvious how great the rate of pollution is [2–5]. Malachite green (MG) is a cationic triphenylmethane dye also called basic green 4, and it contains three groups of aryls. It is extensively used as biocide in the aquaculture industry because of its effectiveness and relatively low cost against important protozoal and fungal organisms [6,7]. This chemical can be used also for coloring silk, wool, cotton, jute, leather, paper, and plastics and in acrylic industries such as in dyes [8]. Furthermore, it is employed as a food additive and a medical disinfectant. Malachite green is classified as Class II Health Hazard because it was found to be toxic to human cells and might cause liver tumor formation and also pose a serious risk to aquatic life [9,10]. It is very unlikely that adverse effects will result by eating fish with very low levels of malachite green and leucomalachite green detected. However, due to its availability and low cost, it is still used in certain countries with less restrictive laws for non-aquaculture purposes [8]. More intense physical/chemical conditions are needed in order to remove dyes from wastewater [11,12]. In recent years, advanced oxidation processes (AOPs) have emerged as potentially powerful methods which are able to transform the recalcitrant pollutants into harmless substances [13] and which almost rely on the generation of very reactive free radicals and very powerful oxidant, such as the hydroxyl radical, $HO^{\cdot}$ (redox potential = 2.8 V vs. SHE) [14]. When generated, these radicals react rapidly and usually indiscriminately with most organic compounds, either by addition to a double bond or by abstraction of a hydrogen atom from organic molecules [15]. The resulting organic radicals then, react with oxygen to initiate a series of degradative oxidation reactions that ultimately lead to mineralization products, such as CO_2 and H_2O [16].

The results of electrochemical degradation of some organic and inorganic compounds in effluent streams started a new field in electrochemistry, known as electrooxidation [17]. The main advantage of this technology is its efficiency to remove pollutants from wastewater without adding any chemical and at a lower cost than any technology used, which is an important issue in water treatment. Electrochemical oxidation or anodic oxidation (AO) is the most popular electrochemical AOP for water remediation [18]. This technique is done by means of indirect and/or direct anodic reactions in which oxygen is transferred from the solvent (water) to the product to be oxidized. The main characteristic of this treatment is that it uses electrical energy as a vector for environmental decontamination.

Recently, the electrolysis of organic pollutants by use of boron-doped diamond (BDD) electrodes has received growing attention and a considerable number of laboratories investigating this material for wastewater treatment and the number of related publications have rapidly increased during the last two decades [19–22]. It is a new

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electrode material that possesses overpotential to oxygen emission which is more important than the oxides of the other metals that were used at this period. This type of electrode offers most of the desirable properties required for AOPs such as, a great chemical and electrochemical stability which enhances the average lifetime of this material and makes it a useful treatment for almost any kind of wastewater, high resistance to corrosion, high thermal stability, chemical inertness, low background current, good electrical conductivity and large potential window between oxygen and hydrogen evolution [23–26]. During electrochemical degradation by BDD electrodes, the organic chemicals are destroyed or converted by either direct or indirect oxidation process. The schematic of this process is illustrated in Fig. 1.

During direct anodic oxidation or direct electron transfer to the anode (Fig. 1.a), the chemicals are initially adsorbed on the surface of the anode where they are degraded by the anodic electron transfer reaction [18]. In the indirect anodic oxidation or mediated electrochemical oxidation (Fig. 1.b), strong oxidants such as hypochlorite chlorine, ozone, or hydrogen peroxide are electrochemically generated. The pollutants are then degraded by the oxidation reaction with these strong oxidants [28,29].

Ngamukot et al. [30] are the first to report concerning the electroanalysis of malachite green and leucomaalchite green by using BDD thin film electrode for the oxidative detection.

The aim of this work was to test the feasibility of electrochemical method for the degradation of malachite green (MG) using BDD anodes. The influence of different electrochemical parameters such as current density, initial pH and supporting electrolyte composition on the efficiency of the electrochemical process. In terms of color and COD removal. Energy consumption and average current efficiency 'ACE' are also calculated in order to optimize operative conditions.

2. Materials and methods

2.1. Reagents

The dye, malachite green oxalate (MG), chemical formula $C_{46}H_{50}N_4.3C_2H_2O_4$, $M_W = 929.02$ g mol^{-1}, $\lambda_{max} = 617$ nm (extinction coefficient = 1.5×10^5 M^{-1} cm^{-1}), was supplied by Riedel-de Haën. Stock solutions were prepared by dissolving accurately weighed samples of the dye in ultrapure water to give a concentration of 1000 mg L^{-1} and diluting when necessary. It was protected from light and stored at 20 °C. The chemical structure of malachite green oxalate is shown in Fig. 2.

Electrolytes of 0.1 mol L^{-1} of the following salts: $NaNO_3$, NaCl and Na_2SO_4 were studied as support electrolytes and were purchased from Merck. The electrolytic medium was made basic or acidic as required by the addition of aqueous NaOH (0.1 M) or H_2SO_4 (0.1 M); respectively, and was supplied by Sigma-Aldrich. Ultrapure water was used throughout this study. It is purified with a Milli-Q water ion-exchange system (Millipore C0) to give a resistivity of 1.8×10^7 Ω cm.

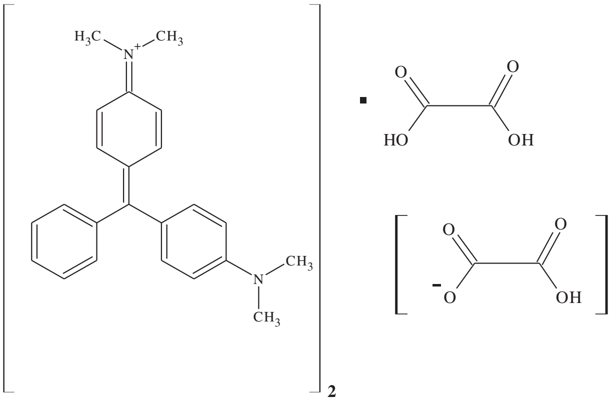

Fig. 2. Chemical structure of malachite green.

2.2. Electrolytic system

The experiment was conducted in a DiaCell (type 500); a single compartment electrolytic cell with parallel plate electrodes manufactured by Adamant Technologies. The anode is monopolar Si/BDD and the cathode is stainless steel. The active surface is a 12.5 cm^2 rectangular surface (50 × 25 mm) and the interelectrode gap was about 3 mm. The current intensity was provided by power supply (Fig. 3.). The anodic oxidation was performed in galvanostatic mode. The BDD electrodes were subjected to auto cleaning procedure during 30 min in H_2SO_4 (1 M) after each experiment to remove adsorbed molecules at the electrode surface and then rinsed with distilled water until the pH of water became neutral.

The dye solution was placed in a glass reactor of 1 L and the closed circulation of the solution was provided to a plain of a peristatic pump and the flow rate was set according to the intensity of the impressed current as indicated in Table 1. The degradation of malachite green dye was carried out in a volume of 1 L aqueous solution of MG 20 mg L^{-1} during 180 min.

2.3. Analytic methods

The samples were withdrawn from the reactor at different desired electrolysis times and the color removal of the MG was evaluated by measuring the decrease absorbance at 617 nm using a single beam UV–Visible spectrophotometer (Spectronic UV–Vis) following the equation:

$$A = \log I_0 = \log \frac{100}{T} = \varepsilon\, c\, l$$

where A is absorbance (no unit of measurement), ε is molar absorptivity (dm^3 mol^{-1} cm^{-1}), c is molar concentration (mol dm^{-3}), and l is path length (cm).

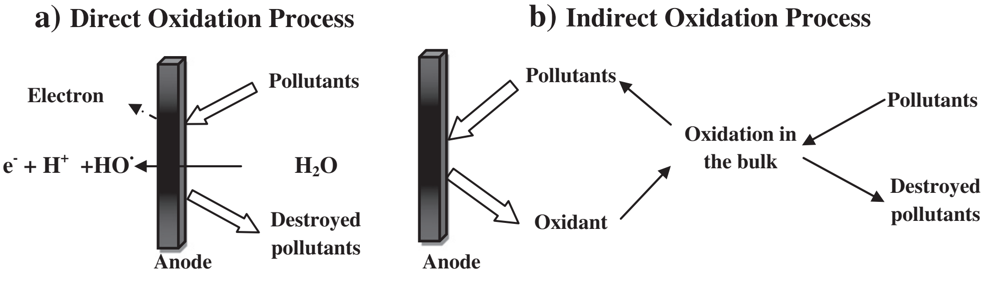

Fig. 1. Schematic of pollutant removal pathways during electrochemical oxidation [27].