Photodegradation of malachite green under simulated and natural irradiation: Kinetics, products, and pathways

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HIGHLIGHTS

- Photofate of malachite green was studied under simulated and natural irradiation.
- Favorable conditions for degradation were optimized by the orthogonal array design.
- Main ROS for the decomposition were determined by free radical quenchers.
- Fifty-three products were determined by LC–MS and GC–MS.
- Pathways were proposed with the aid of theoretical calculation.

ARTICLE INFO

ABSTRACT

In this work photodegradation rates and pathways of malachite green were studied under simulated and solar irradiation with the goal of assessing the potential of photolysis as a removal mechanism in real aquatic environment. Factors influencing the photodegradation process were investigated, including pH, humic acid, Fe^{2+}, Ca^{2+}, HCO_3^-, and NO_3^-, of which favorable conditions were optimized by the orthogonal array design under simulated sunlight irradiation in the presence of dissolved oxygen. The degradation processes of malachite green conformed to pseudo first-order kinetics and their degradation rate constants were between 0.0062 and 0.4012 h^{-1}. Under solar irradiation, the decolorization efficiency of most tests can reach almost 100%, and relatively thorough mineralization could be observed. Forty degradation products were detected by liquid chromatography–mass spectrometry, and thirteen small molecular products were identified by gas chromatography–mass spectrometry. Based on the analyses of the degradation products and calculation of the frontier electron density, the pathways were proposed: decomposition of conjugated structure, N-demethylation reactions, hydroxyl addition reactions, the removal of benzene ring, and the ring-opening reaction. This study has provided a reference, both for photodegradation of malachite green and future safety applications and predictions of decontamination of related triphenylmethane dyes under real conditions.

1. Introduction

Traditionally, malachite green (MG) is an organic dye for materials such as silk, leather, and paper. In recent decades, however, it has emerged as a controversial agent in aquaculture due to its role as an antibacterial and parasiticide agent, and its mutagenicity in *Salmonella typhimurium* TA98 reflected marked cytotoxicity and induced cell transformation and lipid peroxidation [1].

MG cannot undergo efficient biodegradation, because its BOD_5 is almost equal to zero. However, in aqueous solution, MG and MG leucocarbinol can convert into each other, the equilibrium being pH-dependent [2]. MG leucocarbinol not only spreads quickly across cell membranes, but also metabolizes into leucomalachite green (LMG) in fish muscles (Fig. 1). Being non-polar, LMG is found
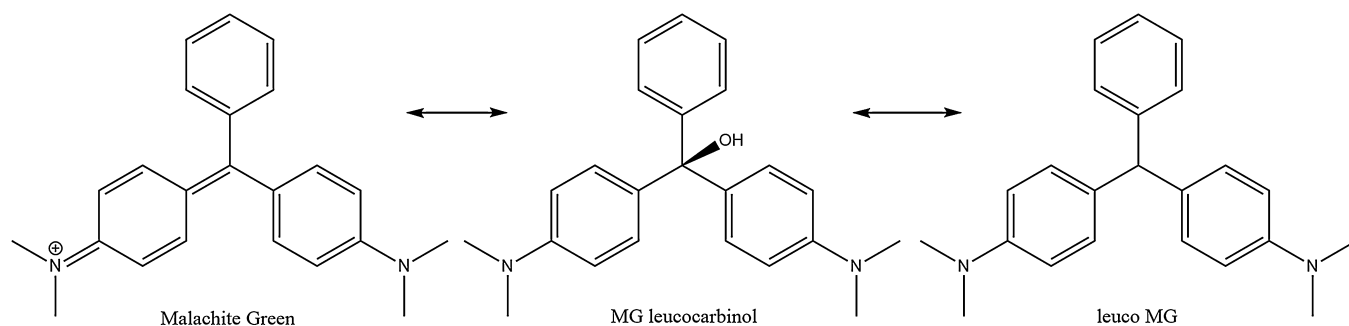
Fig. 1. Conversions between MG (left), MG leucocarbinol (middle), and LMG (right).

to be retained in catfish muscle longer ($t_{1/2} = 10$ days) [3] than MG ($t_{1/2} = 2.8$ days). In fishes' intestines, MG can be reduced to LMG metabolites, remaining in catfish muscle with a half-life of about 10 days and even longer in fat and organs [3]. The potential carcinogenic, genotoxic, mutagenic, and teratogenic properties of its metabolites were demonstrated in many animal species [4–7]. Consequently, it is not permitted in the USA and EU. Nevertheless, it is still widely used for fishery disinfection because of its low price and high efficiency, but few studies have been involved in its degradation in natural conditions. It is still indispensable to conduct thorough research on its transportation and transformation in natural and simulated waters.

Previous literature on degradation of MG indicated that pure oxidization, electrochemical treatment, and biodegradation had weaknesses, such as low degradation rate, high investment, etc. [8]. A number of studies focused on the photodegradation of MG by photocatalysis with TiO_2, $K_3PW_{12}O_{40}$, etc. [9–13]. Some researchers also studied the adsorption by different materials to remove MG from aqueous solutions [14,15]. However, the photodegradation of MG in the actual or simulated environment was rarely reported, except for one case that MG was photodegraded under merely natural sunlight [16].

Although MG possesses relatively low bioaccumulation and hydrolysis, it can be degraded by photolysis in water, which is the primary feature that draws our attention. Photolysis is an important removal pathway of organic compounds besides hydrolysis, adsorption, volatilization, and biodegradation owing to the ubiquitousness of light in natural processes. Direct photolysis occurs when the absorption spectrum of one compound overlaps with the solar emitting spectrum. Indirect photolysis takes place in the presence of reactive oxygen species generated from photosensitizers such as nitrate and dissolved organic matter. For those organic compounds unable to undergo direct photolysis, indirect photolysis plays a particularly important role. Several important reactive oxygen species are generated as a consequence of light absorption in the aquatic environment. $HO^\bullet$, $^1O_2$, $HO_2^\bullet/O_2^{\bullet-}$, $^3NOM^*$, and e_{aq}^- are prevalent and generally respond to oxidization of organic pollutants in the environment. It is expected that the photodegradation of MG could be accelerated, and it could be mineralized into CO_2 and H_2O under simulated and/or natural conditions.

Considering MG as a pollutant in dye wastewater and a bactericide for fish, it is crucial to investigate its transportation and transformation process under natural conditions. Never before has photodegradation of MG under simulated or natural conditions been reported. In this study, photodegradation of MG was explored under simulated and natural conditions. Experimental parameters such as pH, humic acid, cationic, and anionic ions were investigated by the orthogonal array design in an attempt to better understand the transformation process in water matrix. The photodegradation intermediates of MG have been identified by LC-ESI–MS and GC–MS. Possible mechanism of the solar photodegradation was proposed via kinetics, theoretical calculation, and identification of degradation products.

2. Experiment

2.1. Reagents

Malachite Green chloride, humic acid, isopropanol 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,4-benzoquinone (BQ), formic acid, ammonium acetate, and acetonitrile were used. For detailed information, please refer to the Supplementary material.

2.2. Orthogonal array design

In this work, the orthogonal array design was employed to investigate the extent of MG degradation under simulated natural environment. Moreover, the influencing factors and their importance for MG degradation under simulated natural conditions were also studied according to the orthogonal test results.

The ambient pH of natural waters varies from about 5 to 9 and pK_a of MG is 6.9 [2]. In the pH range of 5–9, the main species of ions in surface water are ferrous, bicarbonate, and nitrate [17]. The concentrations of the main ions were set based on literature and the data of main waters of China, i.e., the concentration of humic acid is between 0.3 and 30 mg/L [18]; Fe^{2+} is about 0.1 mM [19–21]; Ca^{2+} is 32.2 (the Yellow River) to 48.1 mg/L (the Yangtze River), HCO_3^- is 118 (the Yellow River) to 228 mg/L (the Yangtze River) [22], and NO_3^- is 0.1 to 1 mM [23,24]. Therefore, one L_{25} (5^6) orthogonal array design with six factors at five levels was performed to optimize the favorable conditions of photodegradation of MG under simulated and natural irradiation as in Table S1. The five levels for controlling factors are 5–8 for pH, 0–40 mg/L for humic acid, 0–0.12 mM for Fe^{2+}, 0–60 mg/L for Ca^{2+}, 0–200 mg/L for HCO_3^-, and 0–1.2 mM for NO_3^-. And the statistical software Minitab 16.0 was executed to process the data analysis.

Humic acid was considered because it is one of the most important light absorbers that may induce indirect photolytic transformations of organic pollutants in natural waters; iron in different speciations could be the source of $HO^\bullet$; Ca^{2+} represents the hardness of water and it is responsible for complexation and chelating; NO_3^- is an important ion affecting indirect photolysis and induces production of reactive radicals such as $HO^\bullet$, $NO^\bullet$, and $NO_2^\bullet$; HCO_3^- was considered one scavenger of $HO^\bullet$.

2.3. Degradation studies

Under the dark condition, the hydrolysis test was conducted as follows: a test tube with glass stopper containing 50 mL of 10 mg/L MG solution entirely enclosed by tinfoil was placed in a temperature-controlled reactor. The absorbance variation was measured by UV–vis spectrometer at regular time intervals, and