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Sonochemical degradation of malachite green in water

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ABSTRACT

In this study, removal of malachite green (MG), a cationic triphenylmethane dye, by 300 kHz ultrasound was investigated. The effects of operating parameters such as initial dye concentration, ultrasound power and initial pH on the sonochemical degradation were studied. The initial rate of MG degradation and hydrogen peroxide formation as a function of initial concentration were determined. The obtained results show that the degradation rate increases with increasing initial dye concentration up to a plateau. The rate of hydrogen peroxide formation decreases with increasing substrate concentration and reaches a minimum, followed by almost constant production rate for higher MG concentrations. The dominant degradation mechanism is the reaction of substrate with •OH radicals both at the gas bubble–liquid interface and in the bulk solution. Sonochemical degradation of MG occurs via two competitive processes: N-demethylation and destruction of the conjugated structure. The degradation rate increased proportionally with increasing ultrasonic power, but decreased with the increase of initial pH value from 2 to 7. In the presence of 10 mg/L Fe(II), the initial degradation rate of MG became 2 times larger for initial dye concentration of 5 mg/L and 1.5 times larger for initial substrate concentration of 10 mg/L, respectively.

1. Introduction

Advanced oxidation processes (AOPs) have been widely investigated to develop novel and green technologies for wastewater treatment, in particular to the degradation and mineralization of organic pollutants found in wastewater streams and in accumulated effluent [1]. The most widely investigated AOPs are H_2O_2/Fe^{2+} (Fenton), $H_2O_2/Fe^{2+}(Fe^{3+})/UV$ (photo-Fenton), H_2O_2/Fe^{3+}-oxalate, Mn^{2+}/oxalic acid/ozone, photocatalysis $TiO_2/h\nu/O_2$, ozone/H_2O_2, ozone/UV and H_2O_2/UV [2]. Although above techniques make use of different reaction systems, the principle underlying all techniques is production of •OH radicals, which are extraordinary oxidizing species with an oxidation potential of 2.5 eV.

A new AOP that has emerged in the recent past is ultrasound. When ultrasound is applied to a liquid medium, the molecules or particles oscillate at their mean positions. The molecules are pushed together in the compression period and drawn apart in the rarefaction period because the variation of the acoustic pressure follows a sinusoidal pattern. If the applied pressure is large enough to break the molecular interaction, a cavity is formed. This process is termed the acoustic cavitation. Even though the tensile strength of water is very large (that requires a negative pressure of approximately 1500 atm), cavitation events can occur under fairly low pressure conditions (<20 atm) due to the presence of the dissolved gas molecules acting as the nuclei for cavitation. Once a cavitation bubble is formed, it starts to increase its size due to rectified diffusion or bubbles coalescence unless it is dissolved. It is believed that extreme conditions, such as high temperatures of over several thousand Kelvin and high pressures of over several hundred atmospheres, form inside cavitation bubble when it undergoes the last compression period [3–7]. Under these extreme conditions, water molecules are thermally dissociated to hydrogen and hydroxyl radicals ($H^\bullet$ and $^\bullet OH$), and with other species present, various other radicals may form (reactions (1)–(5)) [3,4].

$$H_2O \rightarrow H^\bullet + {}^\bullet OH \qquad (1)$$

$$O_2 \rightarrow 2\,O \qquad (2)$$

$$H^\bullet + O_2 \rightarrow {}^\bullet OOH \qquad (3)$$

$$O + H_2O \rightarrow 2\,{}^\bullet OH \qquad (4)$$

$$H^\bullet + O_2 \rightarrow {}^\bullet OH + O \qquad (5)$$

In the absence of any solute, these primary radicals of sonolysis mostly recombine to form hydrogen peroxide that is released in the medium (reactions (6) and (7)).

$$2\,{}^\bullet OH \rightarrow H_2O_2 \qquad (6)$$

$$2\,{}^\bullet OOH \rightarrow H_2O_2 + O_2 \qquad (7)$$

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Sonolytic degradation in aqueous phase involves several reaction pathways and zones such as pyrolysis inside the bubble and/or at the bubble–liquid interface, and hydroxyl radical-mediated reactions at the bubble–liquid interface and/or in the liquid bulk [4,8–12].

With rapid industrialization, the civilian and commercial sectors are facing daunting environmental problems related to the remediation of hazardous waste and contaminated groundwater. A number of large and medium sized industries do not have adequate effluent treatment facilities, as they cannot afford enormous investments in pollution control equipment. Many of the toxic pollutants contained in wastewater discharge from these industries are recalcitrant and not amenable to conventional aerobic biological treatment. Examples of such pollutants are the dyes in the wastewater discharge from various industries. Synthetic dyes are widely used in various fields, such as leather, paper, and textile, and their discharge into natural waters causes environmental problems, related to their carcinogenicity, toxicity to aquatic life and undesirable esthetic aspect. Dyes are classified into various groups such as acidic, basic, azo, diazo, and anthroquinone, on the basis of their chemical structure. At present, approximately 10,000 different dyes and pigments are in industrial use, with total estimated annual global consumption of 1 million tonnes [13]. Most of these dyes are difficult to decolorize due to their complex chemical structure and synthetic origin. These dyes are biorefractory and do not undergo effective degradation using conventional biological techniques.

Malachite green (MG), a cationic triphenylmethane dye, was chosen as a typical representative pollutant. MG is traditionally used as a dye for materials such as silk, leather and paper in industry and has emerged as a controversial agent in aquaculture [14]. Eating fish contaminated with MG poses a significant health risk to human beings since it has many toxic effects, such as, carcinogenesis, mutagenesis [15], chromosomal fractures, teratogenicity and respiratory toxicity [16]. Therefore, treatment of wastewater containing MG becomes a hot spot of current research.

Many researchers have studied the effectiveness of low frequency ultrasound for the removal of MG from aqueous media [17–20]. However, it seems that the application of high frequency ultrasound to the treatment of water contaminated by MG still needs further research. Additionally, the effect of pH on ultrasonic degradation of MG was not established.

The purpose of the present work was to determine the efficiency of high frequency ultrasound (300 kHz) in the process of MG removal from aqueous solution. Experiments were conducted to investigate the effects of various operational parameters on the performance of treatment system.

2. Materials and methods

2.1. Materials

The cationic basic dye (C.I. 42000; Basic Green 4), malachite green oxalate salt, (molecular formula $C_{52}H_{56}N_4O_{12}$, FW 929), was obtained from Sigma–Aldrich and used without further purification. The structure of this dye is shown in Fig. 1. In this work, all chemicals were of analytical grade and were used without any further purification.

The dye solution was prepared by dissolving the MG dye in distilled water to produce a stock solution of 500 mg/L. This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations.

2.2. Reactor

Experiments were conducted in a cylindrical water-jacketed glass reactor in order to control the temperature. Ultrasonic waves (300 kHz) were emitted from the bottom of the reactor through a piezoelectric disc (diameter 4 cm) fixed on a Pyrex plate (diameter 5 cm). The temperature of the solution was monitored using a thermocouple immersed in the reacting medium. The temperature inside the reactor was maintained at 25 ± 1 °C by circulating cooling water through a jacket surrounding the cell. Acoustic power dissipated in the reactor was estimated using standard calorimetric method [21,22]. The reactor was periodically sampled for analysis.

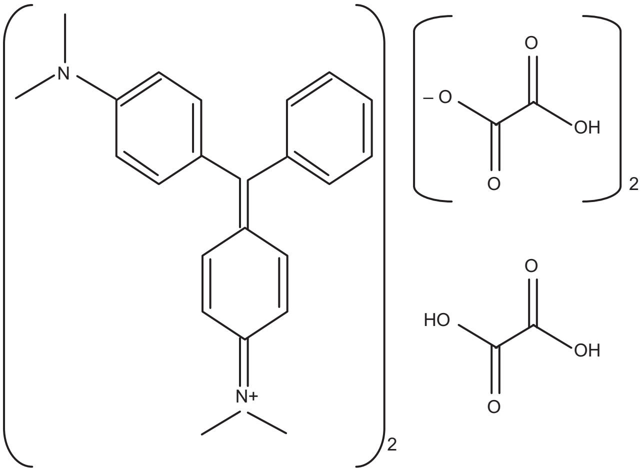

Fig. 1. Chemical structure of malachite green.

2.3. Analytical methods

The efficiency of the proposed process was evaluated by monitoring MG degradation by measuring absorbance at 618 nm using a UV–visible spectrophotometer (Jenway 6405). The wavelength resolution and the bandwidth were, respectively, 1 and 0.5 nm. The length of the optical path in glass cell was 1 cm. Therefore, the concentration of the MG in the reaction mixture at different reaction times was determined by measuring the absorption intensity at 618 nm and from a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard MG solution with known concentrations. In some cases, a proper dilution was necessary to obtain a well measurable absorption.

Hydrogen peroxide concentrations were determined using the iodometric method [23]. Sample aliquots taken from the reactor were added in the quartz cell of the spectrophotometer containing potassium iodide (0.1 M) and ammonium heptamolybdate (0.01 M). The mixed solutions were allowed to stand for 5 min before absorbance was measured. All experiments were carried out at least three times.

3. Results and discussion

3.1. Sonolytic degradation of MG

As shown in Fig. 2, the application of high frequency ultrasound (300 kHz and 60 W) to 300 mL of the aerated MG solution with initial dye concentration of 5 and 10 mg/L reduced the initial substrate concentration. The MG concentration decreased exponentially with sonication time following apparent first-order kinetics. Besides the degradation process, hydrogen peroxide productions were measured both in the absence and presence of MG (5 and 10 mg/L). The formation of hydrogen peroxide was found to increase linearly with time of ultrasonic irradiation. It is noteworthy that in the presence of dye, the hydrogen peroxide production was lower compared to that in the aerated substrate free water. The reaction of hydroxyl radicals with MG competes with $^\bullet$OH radical combination (reaction