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Comparative efficiencies of the degradation of Crystal Violet using UV/hydrogen peroxide and Fenton's reagent

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Abstract

The kinetics of the photo-decoloration of Crystal Violet (CV) imparted by UV/H_2O_2 process and also by Fenton's reagent were investigated. Negligible effects were observed in the presence of either UV light or H_2O_2 alone. As expected, the Fenton-mediated decoloration occurred much faster than the photolytic process. The effects of dye concentration, hydrogen peroxide concentration, pH and the presence of various ions on the decoloration rate were also studied. The extent of decoloration of the dye was found to be independent of pH. The rate of decoloration of the dye that occurred in both the photolytic as well as in the Fenton's methods was found to fit first-order kinetics. A mechanism is suggested for the degradation of the dye. The effect of anions that are normally present in dye effluent on the degradation of the dye was also investigated. Unexpectedly, hydrogen phosphate ions were found to dramatically inhibit the Fenton-mediated decoloration of the dye, whereas they had a minor effect on the photolytic degradation system. The other ions tested had equal minor inhibitory effects on dye degradation by both the methods.

Keywords: Crystal Violet; Decoloration; Photolytic oxidation; UV/H_2O_2; Fenton's reagent

1. Introduction

Many different types of synthetic dyes such as azo, vat, nitro, indigo, etc., are widely used for different purposes in paper and pulp manufacturing, plastics, printing and textile industry [1–3]. The effluent from these industries, when it contains substantial amounts of such dyes, causes not only coloration of water, but also poses a threat to aquatic life [4]; furthermore, their presence in drinking water constitutes a potential human health hazard [5,6]. It is therefore essential either to remove the dyes from water or to treat them in such a way so as to minimize their effects on the environment and also to decolorize the water.

Different approaches have been suggested to remove dyes from aqueous solution including adsorption, biological decoloration, coagulation, advanced oxidation processes (AOP), photo-Fenton reaction, ozone treatment and hypochlorite treatment [7–14]. A very simple approach which can be commonly utilized is the photolytic oxidation of such solutions. In many cases, this method is readily applicable due to the UV content of sunlight. On the other hand, the decoloration of dye using Fenton's reagent has been reported in the literature and has shown promising results [15–17]. In this paper, we wanted to examine the relative efficiencies of two different AOP methods, namely UV/H_2O_2 and Fenton's for the degradation of the triarylmethane dye, Crystal Violet (CV); many of the parameters that affect dye decoloration rate, such as dye concentration, H_2O_2 concentration, and pH were also evaluated. Since many electrolytes are present in dye effluent, the kinetics of dye decoloration in both the presence and absence of various ions were determined.

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2. Experimental

2.1. Reagents

Crystal Violet (Fig. 1) was procured from Fluka and was used as received. Deionized water was used for all dye solutions. Hydrogen peroxide (35% w/w) was obtained from Merck and used at a final concentration of 1.67 mM, unless otherwise stated.

2.2. Preparation of samples and decoloration studies with UV/H_2O_2

Crystal Violet used in all the experiments was at a concentration of 22 μM in water (unless otherwise indicated). UV/vis studies were carried out using a CARY 50 UV/vis spectrophotometer, using a 1-cm quartz cell. All experiments were carried out in a 4-ml quartz cuvette as follows: 3 ml of 22 μM Crystal Violet solution was mixed with 50 μl of 0.1 M H_2O_2, and the mixture was then subjected to UV light (254 nm) produced using an Upland UVGL-58 lamp.

For experiments examining the effects of different ions on the decoloration of Crystal Violet, a final concentration of 0.5 mg/ml of three salts (sodium chloride, sodium sulphate, and sodium hydrogenphosphate) was added to the cuvette before the addition of H_2O_2. None of the electrolytes used had an effect on the pH or on the UV/vis spectra of Crystal Violet in the absence of UV light.

2.3. Preparation of samples and decoloration studies by Fenton's process

All experiments reported were carried out in a 4-ml quartz cuvette as follows: 3 ml of 50 μM Crystal Violet solution was mixed with 30 μl of 0.1 M $FeSO_4$/1 mM H_2SO_4. The Fenton chemistry reaction was initiated by the addition of 15 μl of 1 M H_2O_2 after which, absorbance scans were collected every 6 s, for a total of 2 min. The effects of different ions on the degradation of Crystal Violet were studied via the addition of a final concentration of 0.5 mg/ml of various salts to the cuvette before the addition of H_2O_2; none of the electrolytes had an effect on the Crystal Violet spectra in the absence of H_2O_2.

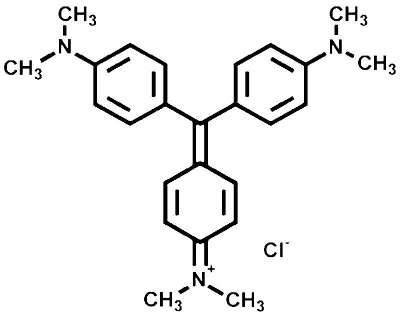

Fig. 1. Structure of Crystal Violet.

2.4. HPLC analysis of the discoloration/degradation samples

For HPLC analysis of the dye decoloration/degradation, 50 ml of dye solutions was taken either at time zero (right after the addition of H_2O_2 and no UV irradiation) or at 30 min of UV irradiation after the addition of H_2O_2, and the organic component of the mixture was extracted using chloroform. The organic layer was extracted again for a second time with chloroform, and then dried in a rotary evaporator. The dried substance (dye and/or degraded by-products) was then dissolved in 100% methanol and then used for HPLC analysis. The samples were run on C_8-Eclipse column (Agilent) using a 0–100% methanol (water as the base mobile phase) gradient over 30 min, at 1 ml/min, and analyzed by measuring the absorbance at 280 nm.

3. Results and discussion

Initially, experiments were carried out in the presence of either UV light or H_2O_2 alone; neither of these treatments had an effect on the absorption maxima of the dye solution and imparted no decoloration. However, decoloration of the dye occurred when it was subjected to UV light in the presence of H_2O_2, presumably due to the production of hydroxyl radicals, as shown below:

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \tag{1}$$

The hydroxyl radicals can in turn react with the dyes and lead to dye degradation:

$$^{\bullet}OH + Dye \rightarrow {}^{\bullet}Dye + H_2O \tag{2}$$

Further reactions in solution can then take place as a part of the overall scheme:

$$^{\bullet}Dye + O_2 \rightarrow Dye{-}O_2^{\bullet} \tag{3}$$

$$2Dye{-}O_2^{\bullet} \rightarrow 2Dye{-}O^{\bullet} + O_2 \tag{4}$$

$$Dye{-}O^{\bullet} + O_2 \rightarrow HO_2^{\bullet} + \text{products} \tag{5}$$

Additionally the peroxy radicals can also further react with the dye as follows:

$$HO_2^{\bullet} + Dye \rightarrow {}^{\bullet}Dye + H_2O_2 \tag{6}$$

For the decoloration studies, we monitored the decrease in the absorption peak at 582 nm; the time-dependent decrease in the dye concentration is shown in Fig. 2. The absorption data of the dye solution was fitted to the first-order rate equation.

$$\ln(A_t) - \ln(A_0) = -kt,$$

where k is the rate constant, t is the reaction time and A_0 and A_t are the initial and the final absorbance values of the dye solution, respectively. A plot of $\ln(A_t)$ versus time generated