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Comparative degradation studies of Malachite Green and Thiazole Yellow G and their binary mixture using UV/H_2O_2

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ABSTRACT

Wastewater effluents of many industries are usually composed of dye mixtures and their removal poses a significant challenge. The present study reports on the use of an advanced oxidation process namely UV/H_2O_2 to degrade Malachite Green (MG) (k = 0.0518 min^{-1}) and Thiazole Yellow G (TYG) ($k = 0.0367$ min^{-1}), and their binary mixture in aqueous solutions. Interestingly, it was seen that the photolytic degradation of dyes in binary solution was slower (by 10% for MG and by 46% for TYG) than that in neat solutions under comparable conditions. The total organic carbon analysis (TOC) was also carried out in both the neat dyes (38.5% decrease for MG and 13% decrease for TYG), and in mixture the TOC change was 40%. HPLC analyses confirmed the formation of intermediates in both individual dye solutions, which were however not seen in binary mixtures. The present work shows that dye mixtures behave very differently than neat dyes, and highlights the importance of studying complex dye mixtures and the possible deleterious interactions between dye intermediates during the remediation process.

Keywords: Dyes; Degradation; Advanced oxidation process; TOC; Wastewater

1. Introduction

Organic synthetic dyes are one of the many chemicals which are being used in various industrial processes. Their use in various types of industrial and other applications results in the discharge of these chemicals in the environment which poses a threat to aquatic life as well as contaminates the water bodies. Thus, it is essential to remove such dyes from solution at the point of discharge. In this regard, various physical processes are used which include filtration, sedimentation, adsorption, coagulation, etc. [1–4]. Advanced oxidation processes (AOPs) are commonly used for degrading various pollutants as the techniques show promising results. These processes can be easily carried under mild operational conditions of temperature and pressure; in many cases, it results in total mineralization of the pollutants without any waste disposal problem.

There are various types of AOPs which are widely used; these include the UV photolytic technique [5], Fenton process [6], photo-Fenton process [7],

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ozonation process [8], sonolysis [9], photocatalytic approach [10], and radiation-induced technique [11]. Many researchers have also successfully used the enzyme-based approaches for dye degradation [12]. All these techniques are versatile in nature and can facilitate the conversion of contaminants to less harmful compounds such as oxygenated organic products and low-molecular weight acids. A common denominator in all these techniques is that all of them when employed to solutions produce highly reactive hydroxyl radicals ($^{\bullet}OH$) at a certain stage which are strong oxidizing agents and are actively responsible for the destruction of pollutants. Due to their high standard reduction potential ($E^{\circ} = 2.31$ V), these radicals are able to eventually oxidize almost all organic compounds to carbon dioxide and water.

Amongst the many techniques employed in the AOP approaches, UV/H_2O_2 is simpler to use and is more environmental friendly. The hydrogen peroxide molecules upon irradiation by UV light generate hydroxyl radicals [5].

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad (1)$$

Hydroxyl radicals are very strong oxidizing agents and thus can react with the organic dye molecules to produce intermediate species which can lead to the decolorization of the dye solution.

$$^{\bullet}OH + \text{dye} \rightarrow {}^{\bullet}\text{Product} \quad (2)$$

Since many industrial applications use mixtures of dyes, it is therefore important to understand the degradation of dye mixtures which may result in the formation of new products. Moreover, the intermediates produced during the degradation of one component may affect the degradation of the other component.

Irrespective of the techniques used, dye removal and degradation will result in intermediates and smaller compounds which under ideal conditions should mineralize. Degrading a mixture of dye from solution can become a complicated process as it can lead to wide variety of new compounds which are not present in the degradation of a single dye. The significance and complexity of the problem have drawn the attention of various researchers [13–16]. In this study, (UV/H_2O_2) processes was applied to study the degradation of a mixture of a binary dye solution consisting of Thiazole Yellow G (TYG) and Malachite Green (MG) which belongs to the azo and triaryl methane family, respectively. These two dyes were chosen because they have a significant difference in their λ_{max} values and it makes it easier to monitor their absorbance values over time. Degradation studies were carried under optimized conditions followed by HPLC and total organic carbon (TOC) analyses to differentiate the behavior of individual dye and dye mixture during the UV/H_2O_2 process.

2. Experimental

2.1. Preparation of samples

MG and TYG were procured from Sigma-Aldrich and were of high purity. Their structures are shown in Fig. 1. Stock solution of 2,000 ppm for both the dyes was prepared in a 250 mL flask by dissolving an appropriate amount of the dye in deionized water. Necessary dilutions of this stock were further done as per the requirement of the experiment. Hydrogen peroxide (35% w/w) was obtained from Merck and was diluted in water as necessary right before use.

2.2. Decoloration studies with UV/H_2O_2

Dye degradation reactions were carried out by applying UV/H_2O_2 to a buffered dye solution. The mixture was subjected to UV light (254 nm) for various time intervals using an Upland UVGL-58 lamp. The instrument operates at 0.12 A with a UV power output of 6 W at 365 and 254 nm; however, the lamp was selectively used in the 254 nm output mode (by using appropriate cut-off filters) for these studies. The light intensity was calculated to be 300 W/m^2. The decoloration studies were carried out by exposing 50 mL of dye solution in a beaker held at a distance of 4 cm from a stand-mounted UV lamp. At appropriate time intervals, an aliquot of the solution was removed from the beaker and scanned for changes in absorbance

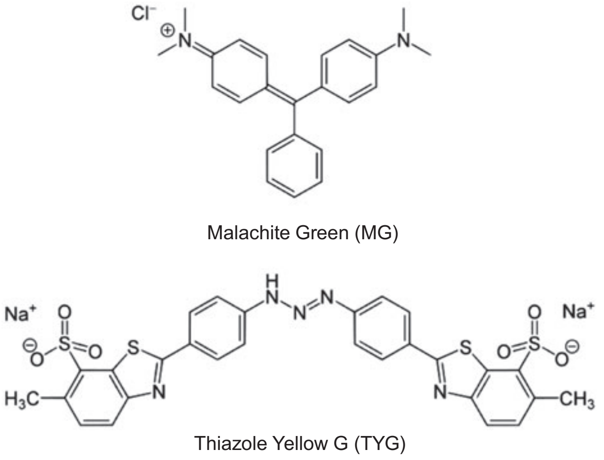

Fig. 1. Chemical structures of MG and TYG dyes.

values. Spectrophotometric measurements were made using a CARY 60 UV/vis spectrophotometer using a 1-cm quartz cell. Since it is well established that AOPs generally work well at dilute dye concentrations [6], it was found that 15 ppm was the optimum value for MG, whereas for TYG, the optimum value was found to be 45 ppm. The % degradation for the dye was calculated by observing the changes in λ_{max} (618 nm for MG and 402 nm for TYG) of the solution. For dye mixture, 15 ppm of MG and 45 ppm of TYG were mixed together and subjected to UV/H_2O_2. For pH studies, the dye solution was prepared in 33.33 mM universal citrate–phosphate buffer adjusted to specific pH. These buffers did not cause any change in the λ_{max} of the dye. Photolytic oxidation studies were done in duplicate at 25 ± 2°C and the average values were used.

2.3. HPLC analysis of the discoloration–degradation samples

For HPLC analysis of the dye decoloration–degradation, samples of dye solutions were taken at time zero (right after the addition of H_2O_2 and no UV irradiation) and at the end of the experiment [17]. Briefly, an Agilent HP 1100 liquid chromatography system, (Agilent, USA) with an Agilent Zorbax SB-C18 column 150 × 4.6 mm packed with 5 μm particle size, coupled to a diode array detector (Agilent, USA) was used to monitor dye degradation intermediates. The mobile phase consisted of solution A (0.1 M ammonium formate (pH 6.7) and solution B (1:1 acetonitrile/methanol), and a gradient from 0 to 80% B in 40 min at the flow rate was 1 mL/min was used to obtain the chromatographs.

2.4. TOC analysis

TOC analyses were carried out using GE Sievers Inno-Vox TOC analyzer properly calibrated with fresh standards. The dye samples tested were 0% degradation sample which consisted of 100 ppm dye in water (adjusted to pH 4 by using HCl), and 100% degradation sample which was exactly the same as the 0% sample but contained 1 mM H_2O_2. Analyses were carried out in triplicates and the values were calculated as TOC values normalized to 0% dye degradation sample. Similarly, the mixture consisting of two dyes namely MG and TYG was analyzed in the same way.

3. Results and discussion

In the present work, the degradation and kinetics of H_2O_2-assisted photochemical oxidation of neat MG and TYG, and their mixtures were investigated. The degradation of the dyes and their mixtures in solution was monitored by measuring the change in absorbance of dye sample solutions over a time period. Initial experiments were carried out to optimize the degradation parameters such as dye concentration, amount of H_2O_2 and pH. The optimized conditions were then applied to the binary dye mixture. Additionally, TOC analyses were carried out to compare the values in neat dye solutions and their mixtures. Both neat dyes and their mixtures after degradation were also subjected to HPLC analysis to compare the difference in the formation of various intermediates.

3.1. Effect of pH on dye degradation

Dye degradation is well known to be pH-dependent [6,7,12]. In order to optimize this parameter, UV/H_2O_2-mediated dye degradation was studied at different pH values (from 3 to 9), while keeping the other conditions same (MG = 15 ppm, TYG = 45 ppm, buffer = 33.33 mM, H_2O_2 = 0.175 mM, temperature = 25°C). The results are shown in Fig. 2. These experiments showed that the dye degradation is highly dependent on the pH of the solution; the % degradation changes by changing the pH from 3 to 9. At pH 9, the dyes showed significantly poor degradation. The optimum pH for dye degradation appeared to be pH 4, for both the dyes, where 40% of MG dye could be degraded in 10 min as compared to 30% of TYG in the same time period. Since both the dyes showed more degradation at pH 4, thus the same pH value was used in the mixture of dye for degradation purposes. This finding underscores the usefulness of the optimization of this parameter to degrade industrial effluents which may have varying pH.

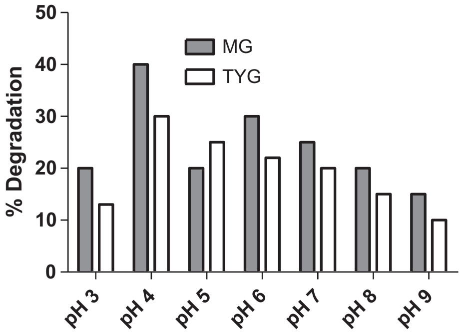

Fig. 2. Percent degradation of dye with changing pH under optimized conditions (MG = 15 ppm, TYG = 45 ppm, H_2O_2 = 0.175 mM, temperature = 25°C, and time = 10 min).

3.2. Effect of hydrogen peroxide concentration on dye degradation

Since the reaction uses H_2O_2 as a source of furnishing $^{\cdot}OH$ radicals which are responsible for carrying out the degradation, it is important to optimize its concentration in the reaction as well. A simplified reaction scheme for the photochemical oxidation of the dye is given below:

$$H_2O_2 + h\nu \rightarrow 2\ ^{\cdot}OH \tag{3}$$

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecule to produce intermediates which can cause the decoloration and degradation of the original solution [18]:

$$^{\cdot}OH + \text{dye} \rightarrow\ ^{\cdot}P \tag{4}$$

where $^{\cdot}P$ is the radical product.

In homogeneous media, the lifetime of the hydroxyl radicals is approximately 70 ns, with a diffusion coefficient of $2.5 \times 10^{-5}\ \text{cm}^2/\text{s}$ and can only diffuse a distance of almost 180 Å [19]. It is, therefore, most probable that the reaction of hydroxyl radicals occurs in its vicinity only. The concentration of H_2O_2 was kept at an optimum level due to the fact that at high concentrations, the solution undergoes self-quenching of $^{\cdot}OH$ radicals by added amounts of H_2O_2 to produce $HO_2^{\cdot}$ radicals.

$$H_2O_2 + {}^{\cdot}OH \rightarrow H_2O + HO_2^{\cdot} \tag{5}$$

The peroxy radicals ($HO_2^{\cdot}$) produced as a result of the above reaction can also enter in other reaction pathways [20].

$$2HO_2^{\cdot} \leftrightarrow H_2O_2 + O_2 \tag{6}$$

$$^{\cdot}P + O_2 \rightarrow {}^{\cdot}PO_2 \tag{7}$$

$$^{\cdot}PO_2 + {}^{\cdot}P \rightarrow 2PO^{\cdot} \tag{8}$$

$$PO^{\cdot} + PH \rightarrow POH + {}^{\cdot}P \tag{9}$$

Thus one can assume that H_2O_2 acts as a pseudo-catalyst in this case. If the concentration of hydrogen peroxide used is too low, the degradation will becomes less; however, a very high peroxide concentration can irreversibly cause the $^{\cdot}OH$ radicals to combine together and this will again lead to lesser degradation. In this regard, experiments were carried out to optimize the H_2O_2 concentration while keeping the other parameters constant. The results showed the optimum H_2O_2 concentration to be 0.175 mM.

3.3. Kinetics of photolytic decoloration

The decoloration of dye solutions was also subjected to kinetic analysis. The absorbance value obtained in each case was subjected to first-order kinetics, which in its usual form is given by

$$\ln\ (A_t/A_0) = -k \times t \tag{10}$$

where A_0 is the initial absorbance value of the dye solution, A_t is the concentration at time t, and k is the apparent rate constant. A plot of Abs versus time (t) was plotted as shown in Fig. 3. The apparent rate constant (k) obtained from the slope of the

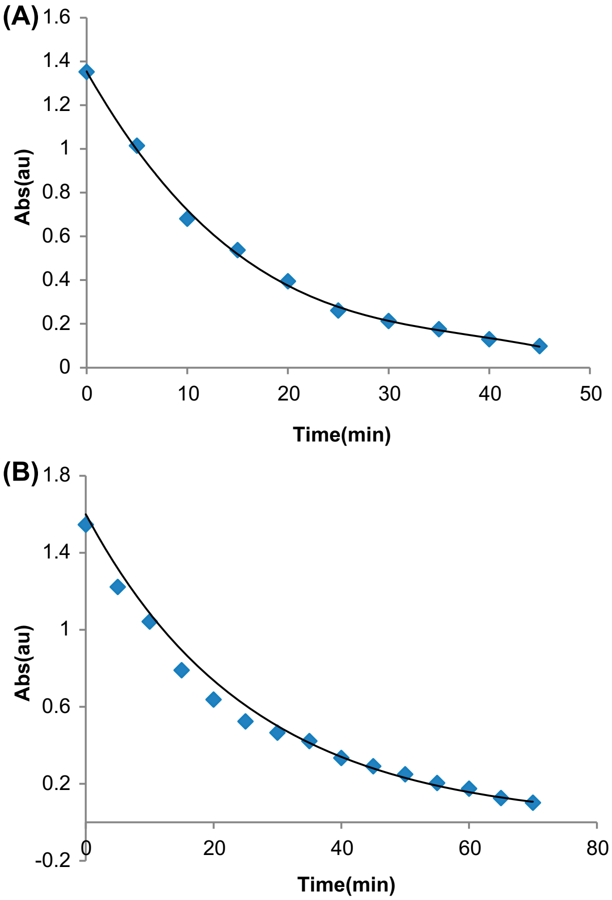

Fig. 3. Change in absorbance value with time of the neat dyes: (A is MG, B is TYG. MG conc. = 15 ppm, TYG conc = 45 ppm, H_2O_2 = 0.175 mM, temperature = 25°C, and pH = 4).

plot was 0.0518 and 0.0367 min^{-1} for MG and TYG, respectively.

The photolytic decoloration of same concentration of binary dye solutions under UV/H_2O_2 is shown in Fig. 4. The decoloration rates of the dyes in mixture were also found to be different as compared to that in neat dye solution. The k_{app} values for both dyes in binary solutions were also calculated according to Eq. (8) and were to be 0.0469 and 0.0198 min^{-1} for MG and TYG, respectively. It can be seen that photolytic decoloration of individual dye in binary solution is slower than that in single solution under comparable conditions. This may be due to the reason that in mixtures the rate of decoloration is influenced by the presence of a second dye which acts as an additive. Also, the difference between the photolytic decoloration rates of MG and TYG in binary solutions becomes smaller compared to the cases of single solutions, although MG still has a faster photolytic decoloration rate in mixed solution than TYG. This is termed as the retarded effect. A similar observation has been reported for the photodegradation rates of Reactive Red 2 (RR2) and Acid Orange7 (AO7) in binary solutions. The rate in mixture becomes smaller as compared to the cases of single solutions, although RR2 still has a faster photodegradation rate than AO7 [21].

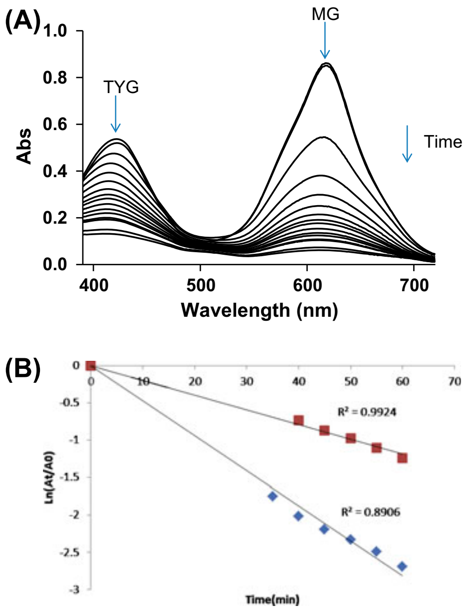

Fig. 4. (A) Change in absorbance value of MG + TYG mixture. (B) Degradation of MG (shown as ♦) and TYG (shown as ■) in a mixture of two dyes [MG conc in mixture = 15 ppm, TYG conc in mixture = 45 ppm H_2O_2 = 0.175 mM, temperature = 25℃, and pH = 4].

3.4. Measurement of TOC

The mineralization of organic carbon of both dyes individually and in same concentration mixture was investigated by the TOC measurement during the degradation of the solution at pH 4. The TOC amount changed significantly (38.5% decrease in the case of MG and 13.0% in the case of TYG) as shown in Fig. 5. When the two dyes were mixed and analyzed for TOC values, it was found that the TOC amount decreased by 40% as shown in the above figure. These results displayed that there is a little increase in mineralization of dyes in binary system than the single solution for the two dyes. Similar changes in TOC values have been reported in the literature where mixtures of dyes were investigated [22].

3.5. HPLC studies

To confirm that the decoloration observed was in fact due to dye degradation, samples were taken from the UV/H_2O_2 treatment of TYG and MG dyes, and monitored by HPLC. Fig. 6 shows the chromatograms of both the dyes, neat dye solutions (time 0), and degraded dye solutions (45 min for MG & 70 min for TYG). As can be seen from the HPLC profiles, new peaks were observed in both the cases when the dyes were degraded. In the case of MG, the new peaks can be attributed to the series of *N*-de-methylated intermediates of MG dye as methyl groups are removed one by one as a result of ·OH attack on the dye molecule [23]. In the case of TYG, the new products observed in the HPLC profile could not be identified in the present study.

When the two dyes were mixed and subjected to UV/H_2O_2 treatment, the HPLC chromatogram showed an entirely different picture as shown in Fig. 6. All the metabolites seen in the case of individual dye degradation disappeared in the mixture chromatogram. This is

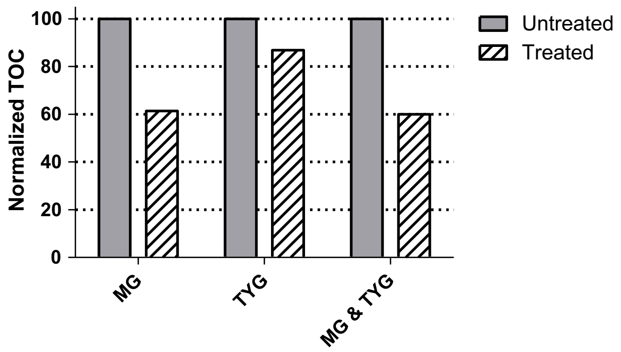

Fig. 5. Normalized TOC in 0 and 100% degraded neat dye samples and in dye mixture of MG + TYG.

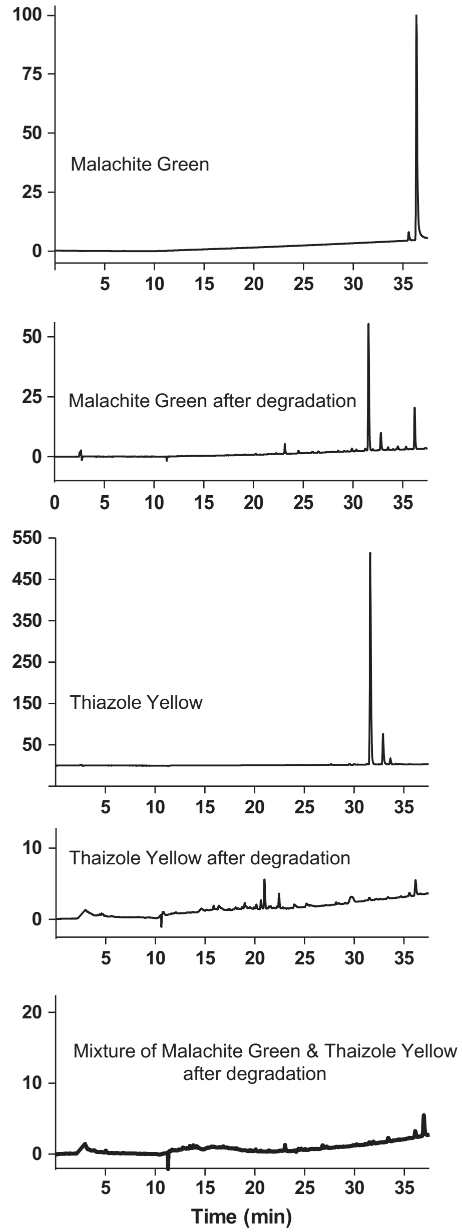

Fig. 6. HPLC profiles for individual dye (MG and TYG) degradation and their mixture.

an interesting observation and suggests that dyes in a mixture behave very differently than individual neat solutions. This is also consistent with our kinetics data showing very different behavior of dyes when mixed together.

4. Conclusion

MG and TYG were degraded as neat dyes and also in mixture using UV/H_2O_2 advanced oxidation process. The degradation behavior was monitored using UV–Vis spectrophotometer and HPLC. The degradation and mineralization efficiency of the process were influenced by the initial concentration of dyes as well as hydrogen peroxide used in the process. TYG degraded much slower as compared to MG, both in neat solution and in dye mixtures. TOC results showed a little increase in mineralization of dyes in binary system as compared to neat dyes. HPLC results of the dye mixture were different from the individual HPLC profiles of the two dyes. This might be due to the interaction of the intermediate products which may influence the course of the degradation pathway.

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