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Degradation of Calmagite by H_2O_2/UV/US, H_2O_2/US, H_2O_2, and US process

Necati Menek [a,*], Ceren Uğurlar [a], Okan Uçarlı [b], Yeliz Karaman [c], Sasha Omanovic [d], Saloumeh Ghasemian [d]

[a] Ondokuz Mayıs University, Sciences and Arts Faculty, Department of Chemistry, 55139 Kurupelit-Samsun, Turkey
[b] Giresun University Espiye Vocational School, Medical Imagining Techniques, Giresun, Turkey
[c] Sinop University, Sciences and Arts Faculty, Department of Chemistry, 57000 Sinop, Turkey
[d] Mc Gill University, Engineering Faculty, Department of Chemical Engineering, Montreal-Quebec H3A 0C5, Canada

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KEYWORD

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Rate constants and kinetics;
Reaction Mechanism

Abstract 1-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid is known as Calmagite. In this study, the degradation of Calmagite in H_2O_2/UV/US, H_2O_2/US, H_2O_2, and US processes were investigated separately and each was compared among themselves. The concentration of H_2O_2, initial dye concentration, pH, UV light, and also ultrasonic sound significantly influenced the degradation of Calmagite and these parameters were optimized. For the azo dye tested, more than 98% of degradation in H_2O_2/UV/US, H_2O_2/US, and H_2O_2 processes was reached in 20, 40, and 60 min, respectively in Britton Robinson buffer media at pH = 11.0. The proposed degradation pathways of Calmagite were established from the ·OH mediated degradation of this azo dye. The first-order rate kinetics best fit the degradation of Calmagite.

1. Introduction

Azo compounds are widely used., especially textile dyes in industry, coloring agents in pharmaceuticals and food industry, etc. [1–3]. Azo compounds are dyestuffs that contain azo or more than one azo bond as the chromophore group attached to aromatic structures. They acquire different characteristic features by bonding different substituent groups such as hydroxyl, amino, and sulfonato [4–6]. As a result of the dyeing process of the textile industries, waste dyestuffs contaminate all water and water resources. Azo dyes substances are very stable in the aquatic environment and generally do not degrade under ambient conditions. Because of their high stability under sunlight and high resistance to biodegradation in aerobic conditions, they are hardly extracted by conventional wastewater treatment methods [4–6].

It is very difficult to clean the wastewater from the dyeing processes of cotton textiles with the help of activated sludge. The color of the dyes remains due to their non-biodegradable nature. There are many physical and chemical methods to remove the color of the dye, such as coagulation/flocculation, activated carbon adsorption and reverse osmosis, and similar methods. [7–10]. However, the latest methods,

* Corresponding author.
E-mail address: nmenek@omu.edu.tr (N. Menek).
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removal of paint impurities can cause new problems. Therefore, techniques that cause complete destruction of dyestuffs must be used. It has been successfully applied to purify different pollutants in water using UV radiation and hydrogen peroxide. The elimination mechanism in the degradation of the dye in the UV / H_2O_2 process is based on the formation of a highly reactive hydroxyl radical (•OH) [10–16]. •OH has a strong oxidizing property due to its high oxidation potential therefore, it is preferred to be used for water purification [17].

In our present work, it has been reported that the effect of optimum experimental parameters on the degradation of Calmagite (1-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid), in H_2O_2/UV/US, H_2O_2/US, H_2O_2, and US processes. The aim of this work is to study the degradation of Calmagite by •OH and propose its reaction mechanism. Calmagite concentration, UV light, pH, ultrasonic sound, and the effect of hydrogen peroxide on dye degradation were investigated for optimum experimental conditions.

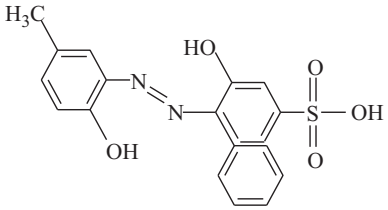
2. Experimental

2.1. Materials

1-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid known as Calmagite (M.W = 358.37 g/mol) textile dye was obtained from Sigma Aldrich. The chemical structure of the dye is shown in Scheme 1. The commercially available H_2O_2 (33%) was also obtained from Sigma Aldrich. Acetic acid (Merck, 100%), phosphoric acid (Merck, 85%), boric acid (Gehalt/Assay, 99.8%) and sodium hydroxide were used in order to prepare Britton-Robinson (BR) buffer solution [3,18].

2.2. Devices

A Jenway 3040 ion analyzer was used to monitor the pH of buffer solutions. Degradation experiments were carried out in Britton-Robinson buffer solution (pH: 2.0–12.0) at room temperature. For UV light experiments, the irradiation was provided using a long wave UV lamp (366 nm, 8 W mercury lamp) and a short wave UV lamp (254 nm, 8 W mercury lamp) in a Camag UV Cabinet-4 placed on a magnetic stirrer. Photocatalytic degradation was monitored by measuring the absorbance of the samples using a UV–Vis Spectrophotometer. Spectra were recorded using a Jenway 6105 UV–Vis Spectrometer from 190 to 800 nm using a 1 cm quartz cuvette. Ultrasonic effect experiments were carried out in Branson-2210 brand (40 Hz) ultrasonic bath.



Scheme 1 Chemical structure of commercial azo dye of Calmagite.

2.3. Procedures

All experimental studies have been examined out in 200 mL stock dye solutions prepared at appropriate concentrations using deionized water. Different amounts of chemicals were used in different solution media for the degradation of Calmagite and also each parameter was optimized. Experimental parameters and related changes are given in detail in the result and discussion section.

3. Results and discussion

3.1. UV–Vis spectrum of Calmagite

Solutions of Calmagite prepared in water media in the 1.40×10^{-4} M – 1.40×10^{-5} M concentration range, have been measured by the UV spectrophotometer device, and the UV–Vis absorption spectra and absorbance values are taken against the concentrations are given in Fig. 1. Two characteristic absorption bands are observed in the UV–visible region with maxima at 530–540 nm (about 535 nm) and 280 nm. Absorption bands at 280 nm and 535 nm belong to the benzene and azo groups, respectively [8,9]. According to Fig. 1, as the dye concentration increases, the absorbance values increase.

3.2. Effect of pH

The pH of solution media plays an important role in the degradation of various azo dyes pollutions and reaction of degradation because oxidation potential of •OH radical is affected by the change in pH [19]. Two absorption bands were observed in the visible region at different pH values. UV–Vis spectra of $2.1x10^{-5}$ M Calmagite in Britton-Robinson buffer media at pH = 3.0, 5.0, 7.0, 9.0, and 11.0 are given in Fig. 2. The bands at 535 nm and 605 nm correspond to the H_2In and HIn^- formation, respectively [9] (Fig. 2):

$$H_2In + H_2O \rightleftharpoons HIn^- + H_3O^+ pK_{a2} = 2.34 \quad (1)$$

$$HIn^- + H_2O \rightleftharpoons In^{2-} + H_3O^+ pK_{a1} = 7.91 \quad (2)$$

The effect of pH on the degradation of Calmagite by H_2O_2 was studied in the pH range 3.0–11.0 (Fig. 3) 100 mM H_2O_2 was added to the Calmagite solution with an initial concentration

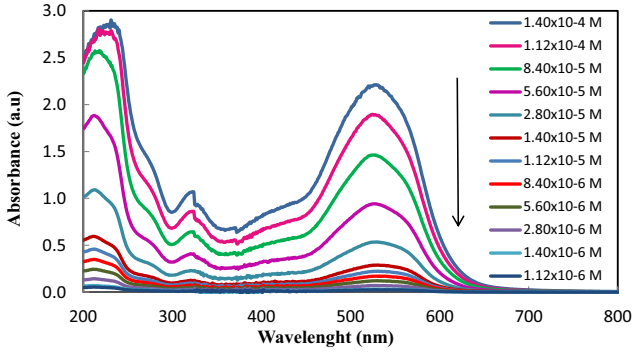


Fig. 1 UV–Vis spectra of Calmagite in water at different concentrations.

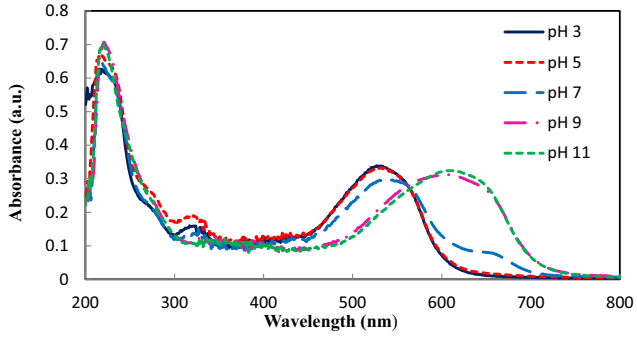


Fig. 2 UV–Vis spectra of Calmagite at different pH values.

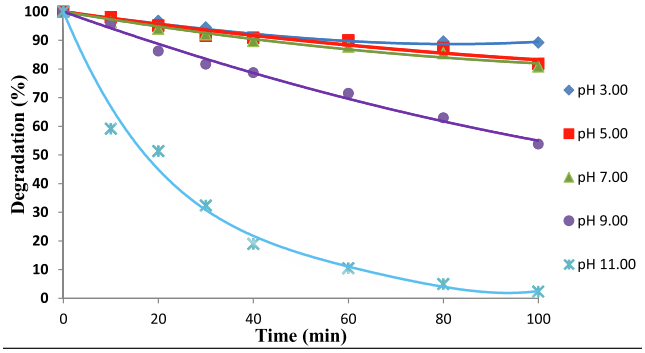


Fig. 3 The degradation percentage of $2.1x10^{-5}$ M Calmagite by 100 mM H_2O_2 solution in Britton-Robinson buffer at different pH values.

of $2.1x10^{-5}$ M and the solution was mixed homogeneously with a magnetic stirrer. The percentage of degradation of Calmagite depending on time is given in Fig. 3.

As given in Fig. 3, the degradation rate of Calmagite at pH = 11.0 is higher than other pH values. It is observed that the intensity of the chromophore band because of the visible light decreases exponentially with time and almost disappears after about 100 min at pH = 11.0, resulting in complete decolorization of the solution. This exponential decrease of the absorbance of Calmagite is given by Eq. (3):

$$ln\left(\frac{C}{C_0}\right) = -kt \tag{3}$$

where C_0 and C, are initial, the concentration at t (time), and k is the degradation rate constant. The logarithmic plot of normalized dye concentration as a function of time gives straight lines as Fig. 4.

The degradation rate constants have been determined by using Eq. (3). At pH = 3.0, 5.0, 7.0, 9.0 and 11.0 degradation rate constants at room temperature are calculated as 0.0014, 0.0020, 0.0022, 0.0060 and 0.0380 min^{-1}, respectively. As given in Fig. 5, the degradation rate is approximately constant at pH < 9.0 but increases exponentially at pH ≥ 9.0. pH = 11.0 is found that the optimum media for efficient removal of Calmagite by H_2O_2.

Chemical oxidation of organic species such as azo dyes in the presence of H_2O_2 occurs as a result of the reactions of ·OH and $HO_2^{\cdot}$ radicals. Literature studies have found that

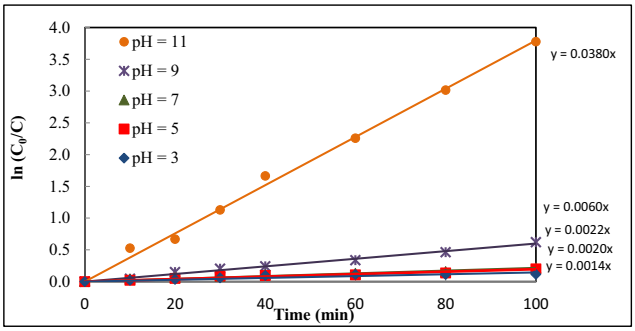


Fig. 4 The first order representation of Calmagite concentration change with time at various pH in the presence of H_2O_2. The initial dye concentration was $2.1x10^{-5}$ M.

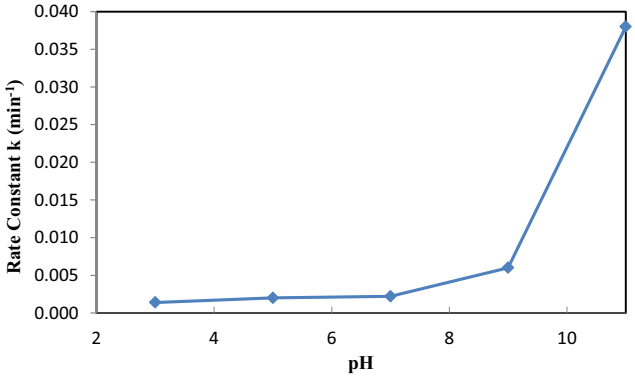


Fig. 5 Degradation rate constant of Calmagite versus pH values by H_2O_2 process. Initial dye concentration was $2.1x10^{-5}$ M Calmagite.

pH has an effect on the degradation of dyes. However, in the process of degradation, the ·OH radicals and dyes change depending on their acid-base forms. In the strong basic solution, the ·OH radicals dissociate to the less reactive $O^{\cdot -}$ radicals [13] (Eq. (4)):

$$HO^{\cdot} \leftrightarrow H^+ + O^{\cdot -} pH = 11.9 \tag{4}$$

In the study mentioned above, azo dyes were generally investigated in the range of pH: 3.0–11.0. However, their degradation reactions depend on the relative reactivity of the different species and the pH of the solution.

At high pH values, the concentration of hydrogen peroxide conjugated anions increases (Eq. (5)):

$$H_2O_2 \leftrightarrow HO_2^- + H^+ pKa = 11.6 \tag{5}$$

The oxidizing species of hydroperoxy anion (HO_2^-) is also formed in the alkaline medium. This HO_2^- anion reacts with ·OH radical and residual H_2O_2, consequently lowering the removal rate (Eqs. (6) and (7)) [20]:

$$2H_2O_2 + HO^- 2H_2O + O_2 + HO^{\cdot} \tag{6}$$

$$2HO^{\cdot} + 2HO^- \rightleftharpoons 2H_2O + O_2^- \tag{7}$$

Generally, perhydroxile ion is occurred and then perhydroxile radical has entered to reaction with H_2O_2, in alkaline media. Superoxide radical ions have been occurred at end of the reaction. These ions have played role in the degradation of the dye

and very reactive species in reaction media [21] (Eqs. (8) and (9)):

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad (8)$$

$$HO_2^- + H_2O_2 \rightarrow OH^- + O_2^{\cdot-} + H_2O \quad (9)$$

3.3. Effect of the Calmagite concentration

Degradation of Calmagite was investigated for different concentrations of dyes at pH = 11.0 which is the optimum value. The decolorization experiments were carried out with initial dye concentrations of 0.7×10^{-5}, 2.1×10^{-5}, and 3.5×10^{-5} M at pH = 11.0 in BR buffer media. These initial concentrations were mixed with 100 mM H_2O_2 by a magnetic stirrer for different times in the range of 0–180 min. Variations of the degradation percentage for different dye concentrations are shown in Fig. 6.

Degradation rate constants of Calmagite have been calculated by using Eq. (1) for different dye concentrations. As given in Fig. 7, the slopes of the graph of ln C/C_0 versus time represent the rate constants.

Degradation of Calmagite by H_2O_2 has been investigated in BR-Buffer media at pH = 11.0 as given in Fig. 8. As shown in Fig. 8, the apparent rate constant values for degradation decreased, by increasing the initial dye concentration. 2.1×10^{-5} M dye concentration has been chosen optimum for the degradation reaction, based on the literature studies. Depending on the literature, the decrease in Calmagite removal and rate with the increase in concentration can be explained as follows: I) As the number of Calmagite increases, the amount of ·OH radical per Calmagite decreases II) Due to the nature of the degradation, the degradation products increase as the initial concentration of Calmagite increases, resulting in a competition of Calmagite and its degradation products for ·OH radical [22,23]. This explains the decreased ·OH radical activity in working media with increasing dye concentration [24] 2.1×10^{-5} M dye concentration has been chosen optimum for the degradation reaction which is based on the literature studies.

The pseudo-first-order plot for different concentrations (0.7×10^{-5}, 2.1×10^{-5}, and 3.5×10^{-5} M) of Calmagite, as given in Fig. 7. The results from the data show that at a low concentration of dye, the rate of degradation is high with the apparent rate constant k, while there is a decrease in the degradation rate constant at high dye concentration. The optimum value in the degree of degradation was obtained with a Calmagite concentration of 2.1×10^{-5} M (Figs. 6 and 7). The change of rate constants was determined for every one of the dye concentrations. Because the molecule form of Calamgite has been changed aggregation or misceleus effect [8].

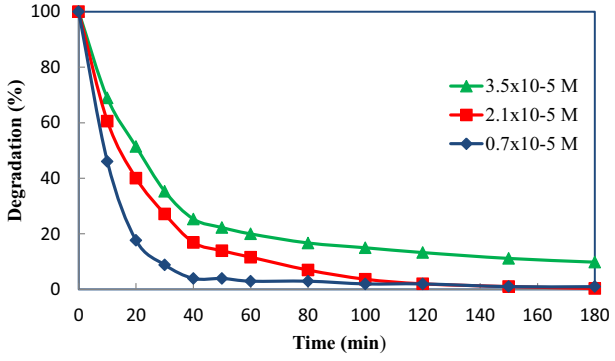


Fig. 6 Changes in the degradation percentage of various Calmagite concentrations in Britton Robinson buffer pH = 11.0 media by 100 mM H_2O_2.

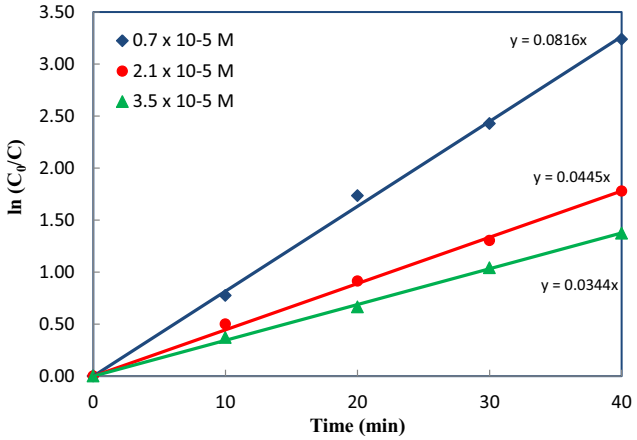


Fig. 7 The first-order representation of Calmagite degradation for different dye concentrations BR buffer at pH = 11.0 by 100 mM H_2O_2.

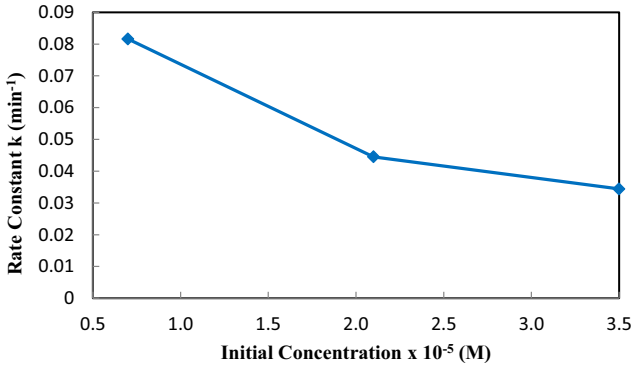


Fig. 8 Changes in degradation rate constant with the initial concentration of Calmagite (2.1×10^{-5} M) in BR buffer at pH = 11 in 100 mM H_2O_2 media.

3.4. Effect of H_2O_2 concentration

The effect of H_2O_2 on the degradation of Calmagite has been also investigated. For this purpose, 2.1×10^{-5} M Calmagite where is in BR buffer at pH = 11.0 that is the optimum condition for dye degradation is treated with 5, 10, 50, 100, and 200 mM H_2O_2 for different reaction times. Figs. 9 and 10 give the changes in Calmagite's percent of time degradation and first-order degradation rate constant as a function of the initial H_2O_2 concentration. A linear correlation was observed for degradation of Calmagite as a function of time ln C_0/C vs time) at different concentrations of H_2O_2 (Fig. 10). From the results, further increase in the initial H_2O_2 concentration above 100 mM causes inhibition in H_2O_2 process performance

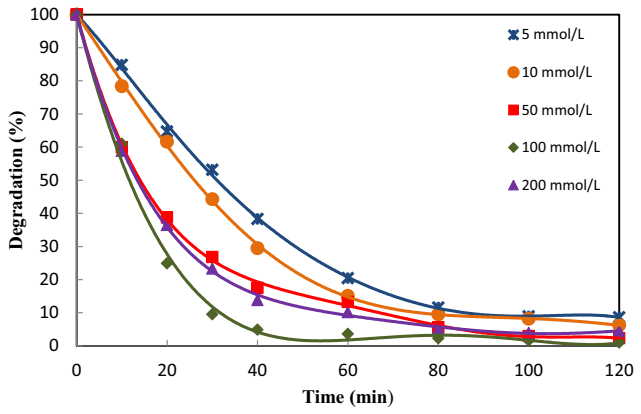


Fig. 9 Changes in the degredation percentage of the 2.1×10^{-5} M Calmagite solution at different concentrations of H_2O_2 in Britton Robinson buffer pH = 11.0.

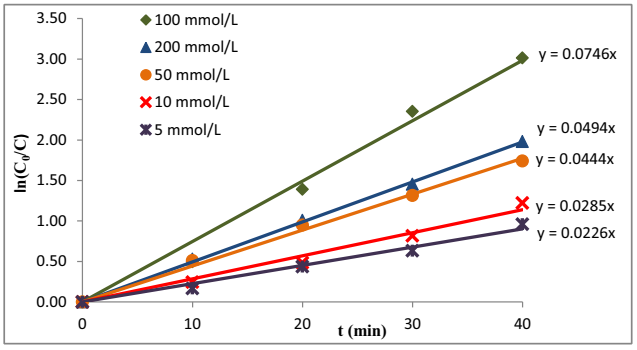


Fig. 10 The first-order representation of 2.1×10^{-5} M Calmagite degradation with time at different H_2O_2 concentrations and pH = 11.0.

because H_2O_2 itself acts as an OH scavenger. This situation is given Eq. (10):

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (10)$$

Therefore, it is very important to optimize the H_2O_2 concentration used for the efficiency of Calmagite degradation. Competitive reactions occur in high peroxide medium and high $^{\cdot}OH$ concentrations that produce an inhibitory effect for degradation of Calmagite. As shown in Eqs. (11-14), higher concentrations of hydroxyl radicals decrease their activity [15,24]:

$$HO^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (11)$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow HO^{\cdot} + H_2O + O_2 \quad (12)$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (13)$$

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \quad (14)$$

In reactions (11) and (14) $^{\cdot}OH$ decreases radicals and consequently reduces the probability of substrate oxidation. Therefore, in order to achieve optimum conditions of the process, it is necessary to determine a sufficient H_2O_2 concentration to avoid excess reagent to reduce degradation. At high H_2O_2 concentration (200 mM), H_2O_2 causes a reduction of hydroxyl radicals and, consequently the concentration of hydroxyl radical decreases. Thus, high concentrations of H_2O_2 cause a decrease in the degradation rate constant [15,24].

The effect of concentration of H_2O_2 (5–200 mM) on the degradation of 2.1×10^{-5} M Calmagite has been investigated in BR buffer media at pH = 11.0. Figs. 9 and 10 show the initial H_2O_2 concentration effects on the removal rate of Calmagite. By the addition of 5, 10, 50 to 200 mM H_2O_2, the degradation rate of the dye increased because of the enhanced H_2O_2 reaction. In the absence of H_2O_2 in the solution, the degradation percentage was estimated to reach 98% by the time of infinity, while after the addition of 100 mM H_2O_2, the degradation was achieved after only ~ 50 min. However, further increase of H_2O_2 dosage from 100 to 200 mM decreased the degradation rate and increased the 98% removal time from 50 to 80 min. Hence 100 mM H_2O_2 concentration appears to be the optimal concentration for the degradation of Calmagite. UV–Vis spectrums for degradation of Calmagite with H_2O_2 are given at optimum conditions in Fig. 11. This Figure shows the decrease in the absorbance at 605 nm, but no change of absorbance at 280 nm. According to Fig. 11, degradation of the Calmagite goes to aniline derivatives in UV media [8].Fig. 12

Experimental studies have been conducted at different initial H_2O_2 concentrations to investigate the kinetics of the degradation of Calmagite. From the experimental data, the initial degradation rate of Calmagite at different initial concentrations of H_2O_2 was fitted into Eq. (1) at times 0 and t. k is the first-order rate constant in min^{-1} and t is the time in min. For the plots of ln C/C_0 against time (Figs. 4, 7 and 10), a linear relationship with correlation coefficient > 0.99 was obtained, following pseudo-first-order kinetics considering all the H_2O_2 concentrations. The rate of degradation of the dyes by H_2O_2 was found to be first order with respect to dye concentration.

3.5. Effect of UV light

The solution of BR buffer at pH = 11.0, which contains 2.1×10^{-5} M Calmagite and 100 mM H_2O_2, is treated by 254 nm UV-lamp for different degradation times, and the changes of UV spectra of the solution is given in Figs. 13 and 14. At the same time the experimental data on the initial degradation of Calmagite at different times were fitted into Eq. (3) at time 0 and time t, as shown in Fig. 14. The reaction

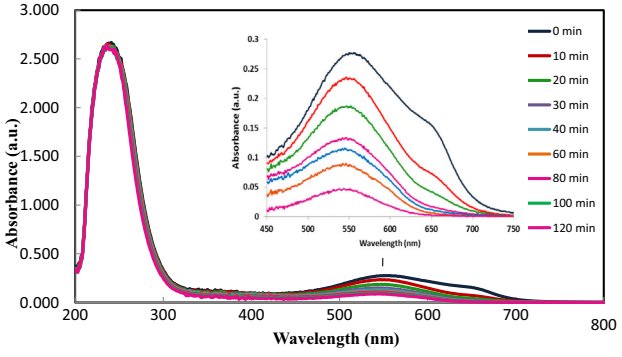


Fig. 11 UV–Vis spectra of 2.1×10^{-5} M Calmagite in BR buffer at pH = 11.0 for different degradation times by 100 mM H_2O_2.

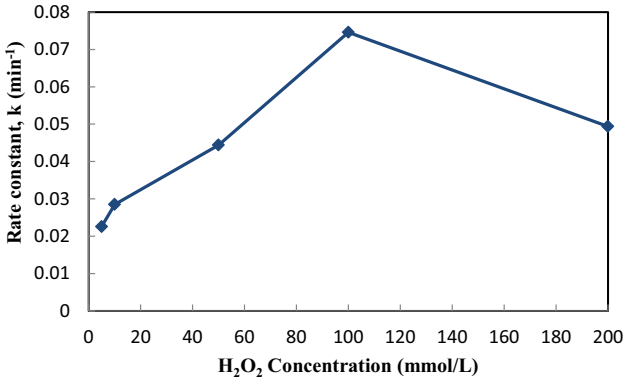


Fig. 12 The change of rate constants of Calmagite with H_2O_2 concentration at pH = 11.0 in H_2O_2/UV process.

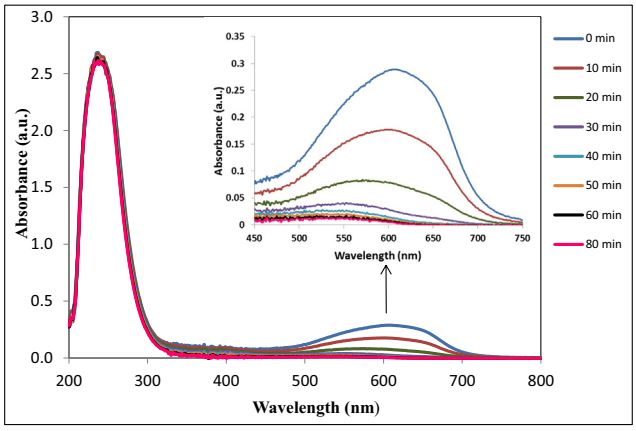


Fig. 13 UV–Vis spectra of Calmagite in BR buffer at pH = 11.0 treated by UV light at different times under the optimum conditions in H_2O_2/UV process.

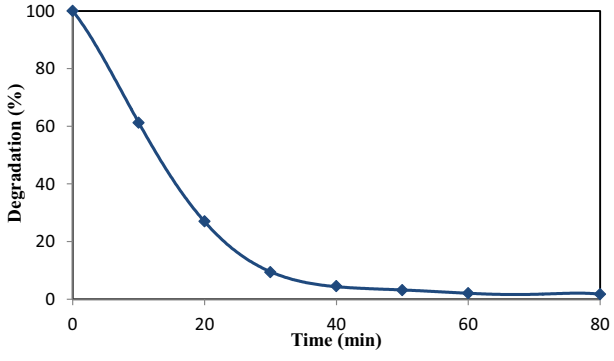


Fig. 14 Changes in the degradation percentage of the 2.1 × 10^{-5} M Calmagite solution in BR buffer pH = 11.0 in H_2O_2/UV process.

rate constant of degradation of Calmagite has been determined as 0.0727 min^{-1}.

Theoretically, in azo compounds, the breaking of the azo chemical bond can be achieved by photolysis by direct UV irradiation. According to Fig. 13, degradation of the Calmagite goes to aniline derivatives by UV light in H_2O_2 media. However, in the presence of H_2O_2 the degradation of the azo bond occurs more rapidly under short UV light, hydrogen peroxide is rapidly dissociated, producing ·OH, a non-selective and powerful oxidant, which decomposes the dye very quickly. The main reactions of this process are generating ·OH radicals and oxidizing of dye molecule as follows [25,26]:

$$H_2O_2 + UV \rightarrow 2HO^{\cdot} \quad (16)$$

$$HO^{\cdot} + dye \rightarrow H_2O_2 + dye^{\cdot} \rightarrow further oxidation \quad (17)$$

Degradation reaction of the Calmagite at the optimum condition is completed in 50 min for only H_2O_2 process and 30 min for H_2O_2/UV process. According to these results, degradation of the Calmagite in the H_2O_2/UV process is more effective than in the H_2O_2 process. This phenomenon can be explained by reaction (18) [27]. More radical formation of ·OH can make the UV process more efficient than the other.

$$HO^{-} + UV \rightarrow HO^{\cdot} \quad (18)$$

As shown in Fig. 13, at the optimum condition, two electronic transitions were observed at 280 nm at which π → π* belongs to the aromatic ring and 602 nm at which n → π* belongs to -N = N- , azo group in UV–Visible spectrum. According to the UV–Visible spectrum, are shown in Figs. 11 and 13, absorption of the Calmagite at 605 nm wavelength decreased with time in H_2O_2 and UV/H_2O_2 medium. After 120 min, the azo

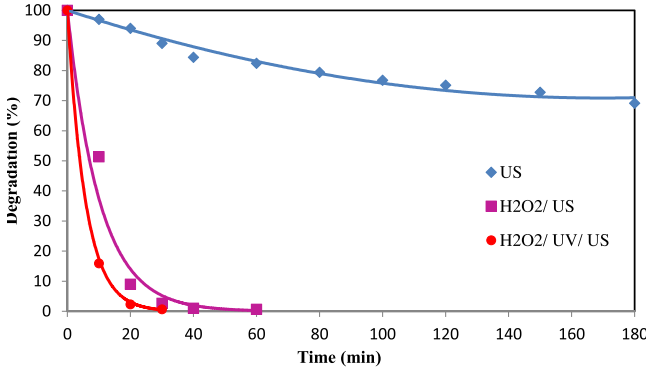


Fig. 15 Changes n the degradation of the 2.1x10^{-5} M Calmagite in Britton Robinson buffer at pH = 11.0 in H_2O_2/UV, H_2O_2/UV / US, and US processes.

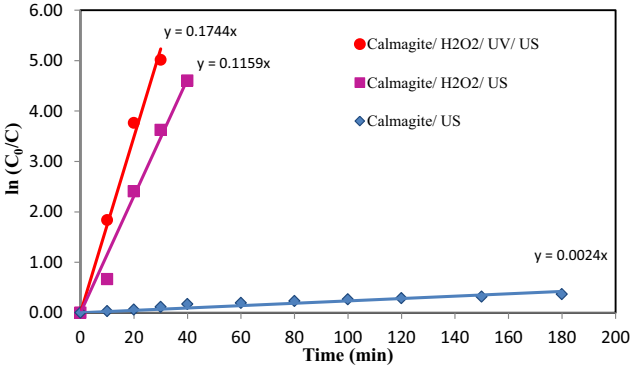


Fig. 16 The first-order rate representation of Calmagite 2.1x10^{-5} M in BR buffer at pH = 11.0 versus time, under H_2O_2/UV, H_2O_2/UV /US, and US processes.

group in Calmagite is cleavaged but the aromatic ring which corresponds to the absorbance value at 280 nm has not been changed at the optimum condition. The observed dependence of concentration, pH, and UV effect at 605 nm can be explained by a direct exchange of degradation reaction with the splitting of the azo group to form amines, while the aromatic rings at 280 nm are not exchanged at the optimum experimental condition [8,28–31].

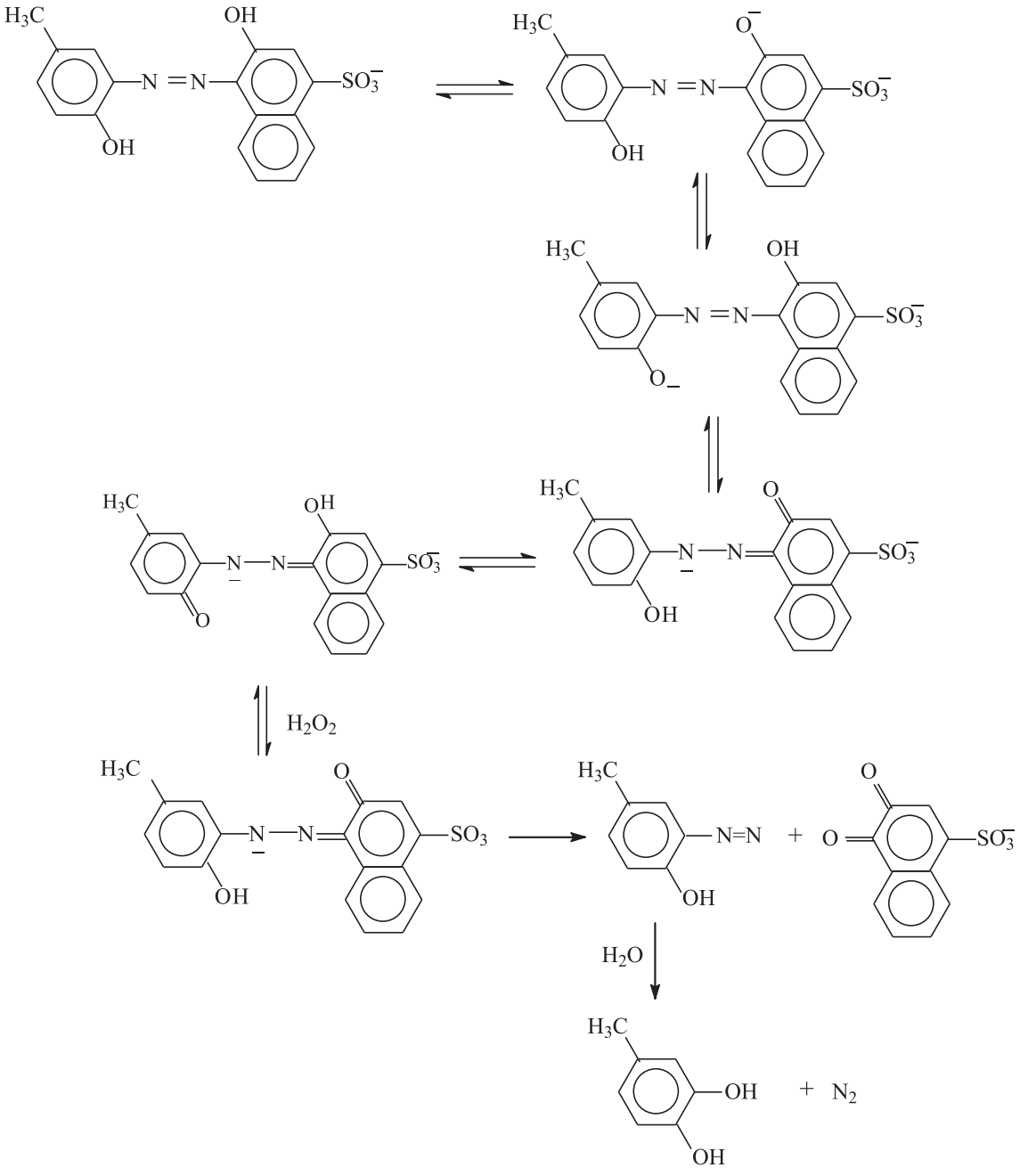
3.6. Effect of ultrasonic sound

In this study, both ultrasonic sound and the effect on H_2O_2/US and H_2O_2/UV/US processes have been studied. The solution in optimum conditions was treated with ultrasonic sound at different times and the experimental results are given in Figs. 15 and 16.

The degradation rate constant of Calmagite in H_2O_2/UV/US, H_2O_2/US, H_2O_2, and US processes have been calculated as 0.1744, 0.1159, 0.0816, and 0,0024 min^{-1}, respectively. Degradation of Calmagite by UV/H_2O_2/US process is significantly higher than the degradation by UV/H_2O_2 and H_2O_2 processes. According to the results, the order of the degradation rate of Calmagite has been determined as below:

"H_2O_2/UV/US" > "H_2O_2/US" > "H_2O_2" > "US"

The chemical effect of the ultrasonic method is based on the cavity formation phenomenon called "cavitation". Bubbles, caused by ultrasonic sound waves created in a liquid, form



Scheme 2 Chemical degradation of the Calmagite.

in very small time intervals, grow and collapse, releasing huge amounts of energy [32]. The underlying cause of chemical changes and transformations is the energy created by the collapse of these bubbles. At the bubble–liquid interface, ·OH radicals are concentrated and radical reactions are dominant in this region [33]. ·OH and ·H radicals appear as water is sonicated [34,35]. These reactions are given Eqs. (19)–(22).

$$H_2O \rightarrow))) HO^{\cdot} + H^{\cdot} \quad (19)$$

$$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2 \quad (20)$$

$$HO^{\cdot} + H^{\cdot} \rightarrow H_2O \quad (21)$$

$$H^{\cdot} + H^{\cdot} \rightarrow H_2 \quad (22)$$

The ·OH obtained with the help of the sonicator, increases the number of radicals and thus the reaction rate of the Calmagite decomposition by the ultrasonic sound method is faster than other methods.

In the UV / H_2O_2 and other systems in Scheme 2, it did not turn into complete decomposition under experimental conditions, and Calmagite's conversion reaction to CO_2, H_2O inorganic salts were not observed. [8,29–37].

4. Conclusions

Azo dyes have great importance as environmental and water pollutants. In this study, the degradation of Calmagite, which is an azo dye, by ·OH radical that obtained by H_2O_2, UV, and US process was investigated by spectrophotometric method. As seen from the UV–Vis spectrum of Calmagite, in H_2O_2/UV/US, H_2O_2/US, and US processes the degradation rate constants were determined as 0.1744, 0.1159, and 0.0024 min^{-1}, respectively. In this order, the rate of degradation of Calmagite and the amount of degradation increase with increasing concentration of ·OH radical. While generating the ·OH radical, the initial dye concentration, peroxide concentration, pH of media, effect time of UV light, and ultrasonic sound were optimized for degradation. The absorbance at 602 nm attributed to n → π* transition of azo (—N═N—) group decreased gradually and besides that, the absorbance at 280 nm representing the π → π* transition of the aromatic structure of dye was remained unchanged during the reaction time. That means degradation of the Calmagite has been converted amine derivatives. According to this phenomenon, the reaction mechanism has been proposed based on the literature.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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