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Original Research Article

Sonochemical degradation of malachite green in the presence of persulphate, Co (II) and Fe (II) as catalyst

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ARTICLE INFORMATION

ABSTRACT

Nowadays, one of the most important global concerns is water pollution which showed increasing trends during the recent decades. The aim of this study was to develop a new method, based on the increment of degradation rate by using immobilized Co and Fe ions and activated persulphate to form highly reactive sulphate radicals, to degrade MG in aqueous solution. An ultrasonic bath with a frequency of 35 kHz was used to investigate the effect of different methods such as the only US, ultrasonication coupled with persulphate (US+PS), ultrasonication+Co (US+Co), ultrasonication+Fe (US+Fe), ultrasonication+Co resin (US+Co$_{resin}$), ultrasonication+Fe resin (US+Fe$_{resin}$), ultrasonication+Co activated persulphate (US+Co+PS), ultrasonication+Fe activated persulphate (US+Fe+PS) to find the best and efficient approach for treating the wastewater. The other parameters such as the effect of pH, dosage of persulphate, Co and Fe as catalyst and contact time were investigated. The FT-IR spectra were utilized to find out which bands shifted during the sonication. The outcomes illustrated that, the US system coupled with PS and Co was the best way among the others.

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Graphical Abstract
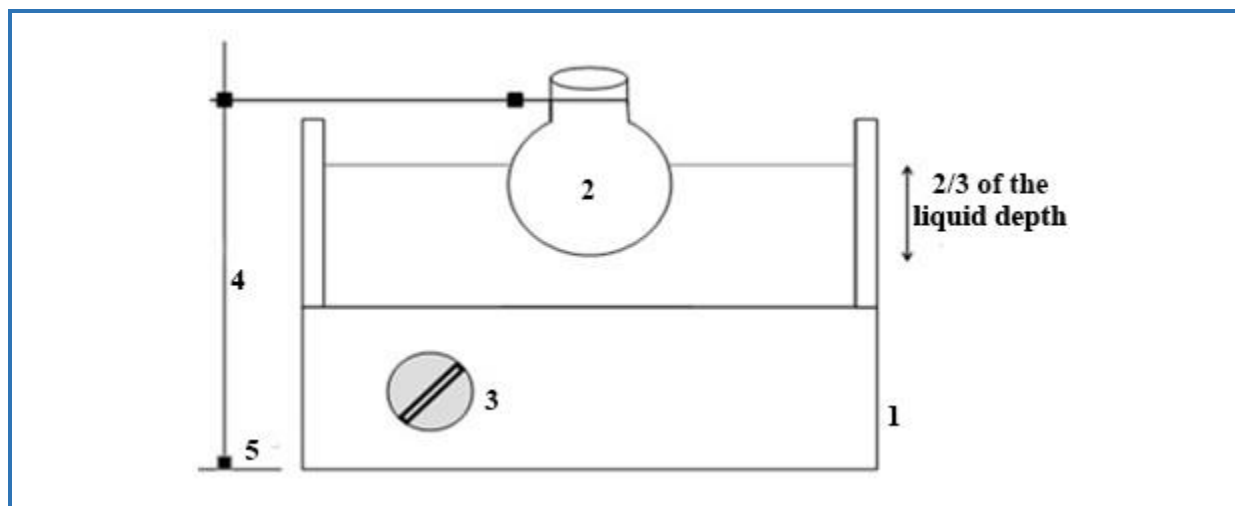
Introduction

Malachite green carbinol hydrochloride ($C_{23}H_{26}N_2O \cdot HCl$) is a water soluble, non-volatile and organic compound which can be used as a bactericide, food coloring agent, medical disinfectant, food additive and anthelminthic as well as a dye in the silk, wool, leather, jute, cotton, paper, and acrylic industry. However, it is a toxic chemical primarily used as a dye [1, 2]. It was also determined that there is a significant health risk to humans who eat fish contaminated with MG [3]. This chemical compound was classified as class II health hazard as it was found to be toxic to human cells and might cause liver tumor formation. So its usage has been banned in several countries including the USA. But it has been used in many countries yet due to its low price, availability, and high efficiency [4]. The disposal of these colored wastewaters poses the main problem for the industry as well as a threat to the environment [5]. Nearly 70–80% of wastewater coming out from silk dyeing industries is from the rinse operation [6–8]. Methods capable for waste-waters purification of malachite green are the USA alone [9] and this in combination with a catalyst like Co, tea leaves and even ozone [10–12]. Persulphate anion just has an oxidation potential of 2.1 V so it has less efficiency. Persulphate activation will be needed to improve the degradation capacity and it can be done by heat or adding catalyst (such as Co (II) and Fe (II)) and then sulphate radicals are produced. Sulphate radical reacting with one electron oxidation has an oxidation of potential of 2.6 V and it generates the dye radicals [13, 14]. Generation of the sulphate radical is shown in the following Equations:

$$e^-_{aq} + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^- \tag{1}$$

Generation of dye radical

$$Dye + SO_4^- \rightarrow Dye^- + SO_4^{2-} \tag{2}$$
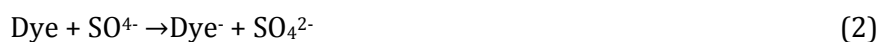
Sonochemistry has been widely researched in recent decades for the degradation of steady organic pollutants in aqueous solutions [15–17]. The generation of highly reactive hydroxyl radicals during sonolysis from the following Equation 3 by acoustic cavitation moreover direct pyrolytic degradation of the organic pollutants enhances the degradation efficiency [18]. Dyestuff in aqueous media was degraded by ultrasonication within 3 h and also followed the first-order kinetics [19].

$$H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}H \tag{3}$$

Ultrasound catalysis produces sulphate radical by activating the persulphate and has faster kinetics. Equations 4 and 5 reveal formation of the sulphate and hydroxyl radicals by ultrasonication.

$$S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^- \tag{4}$$

$$H_2O + SO_4^- \rightarrow {}^{\bullet}OH + {}^{\bullet}H + SO_4^{2-} \tag{5}$$
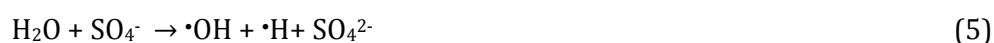
The dye was declined by the extensive production of hydroxyl and sulphate radicals as well as its intermediates at a faster rate [20]. Several recent investigations reported successful removal of a wide range of organic pollutants from aqueous solutions and it appears that the pollution prevention and application of this novel means of reaction in environmental remediation are unlimited [21–23]. Vinodgopal and co-workers [24] demonstrated that 65% of the remazol black B (a reactive textile azo dye) was mineralized by a 640 kHz ultrasonic system during 6 h sonolysis. Also, some researchers determined the reaction order in ultrasound degradation of dyes [25–27] and some others investigated the combined method on degradation of some water soluble polymers [28–30]. Recently, some new methods have been employed to determine the effect of the catalysis in ultrasound degradation of dyes [31–33]. The objective of this research study was to investigate the effects of ultrasound irradiation coupled persulphate, Co and Fe on the sonochemical degradation of MG in aqueous solutions.
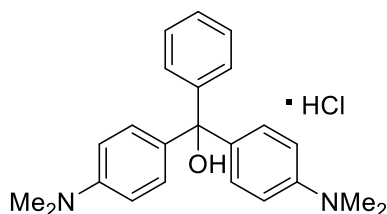
Experimental

Materials and methods

Malachite green carbinol hydrochloride was obtained from the Sigma-Aldrich and used without further purification. Its chemical structure is given in Scheme 1 potassium persulphate, sodium hydroxide, nitric acid, cobalt nitrate, and ferrous chloride were purchased from the Merck (Germany). Cationic resin (Amberlite IR120), distilled water was used to make aqueous solutions.

Ultrasonic bath (T 460/H)

The ultrasonic bath was purchased from the Elma (GmbH) with the operating frequency of 35 kHz and with a rated output power of 170 W. The bath had the dimension of 240×137×100 mm³. The total internal body was made from the stainless steel. The reaction temperature was kept constant at 25±0.5 °C by using a cooling coil inside the reactor and water was pumped at the required pressure during the sonication. A 50 mL standard flask was used as a reactor vessel. The reactor volume of the dye solution with known concentration was 15 mL. The liquid depth in the tub was maintained at $\frac{2}{3}$ rd of its total depth. The vessel was completely immersed into the reactant solution in the middle of the bath. At regular intervals, the samples were drawn out and the color intensity was measured spectrophotometrically. Figure 1 shows the experimental setup for the study.

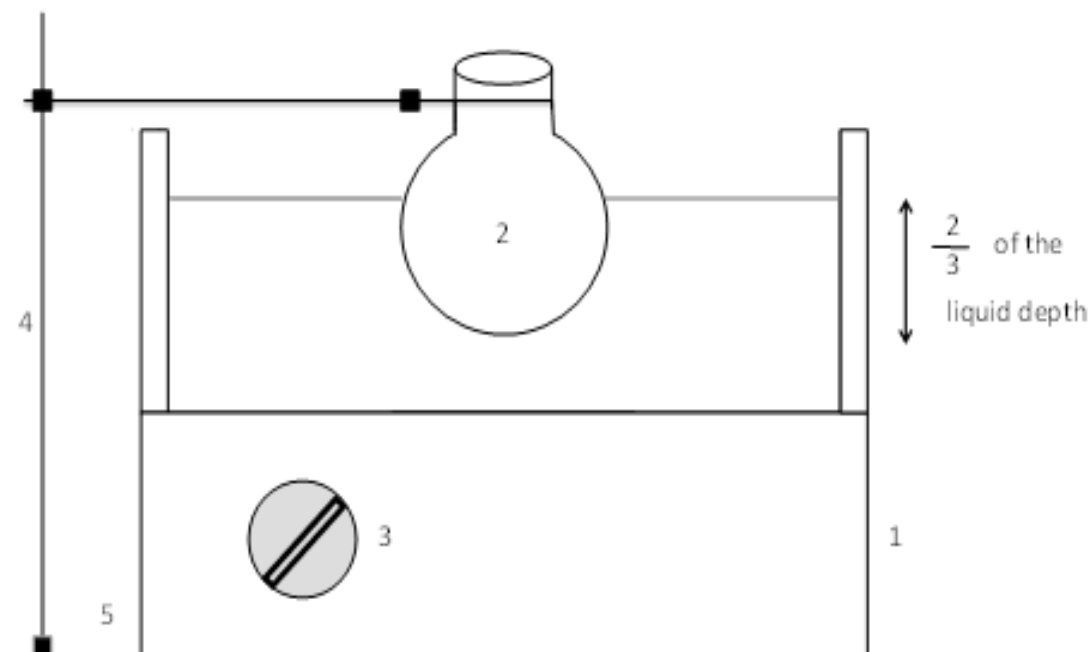**Scheme 1.** Chemical structure of malachite green carbinol hydrochloride

Figure 1. Schematic representation of the 35 kHz bath type sonicator and reactor vessel employed in sonolysis experiments where 1) Ultrasonic bath, 2) A 50 mL standard flask, 30 Time adjustment knob, 4) Steel stand, 5) To power supply

Preparation of catalysis

For this research study, persulphate anion was activated by using the immobilized Co and Fe ions and also ultrasonication. The Co and Fe that impregnated by cationic resin were prepared by mixing the resin (25 g) with 10% cobalt nitrate solution and 10% ferrous chloride solution separately. They were left overnight. To remove the humidity, they were located in an oven at 105 °C for 1 h and then they were heated again with the help of Whatman filter paper in the oven at 50 °C for one night so that they become dry. The rapid degradation of the MG increased due to more production of hydroxyl and sulphate radicals. However, in this case, Co and Fe cannot be recovered and remained in treated water as a pollutant. These studies were conducted to select a suitable support material to immobilize the catalyst. Therefore, in this work, Co and Fe resins as catalysis supporting media were used.

Analytical method

The λ_{max} of dye solution was identified with the help of UV-vis spectrophotometer, (Ultrospec 2000, Biotech Pharmacia, England) at 617 nm. A calibration plot based on Beer–Lambert's law related the absorbance to concentration.

The decolorization efficiency was calculated using the Equation 6 [34].

$$D= [(A_i – A_f) \times 100] / A_{in} \qquad (6)$$

Where D is the percentage of decolorization efficiency, A_i the initial absorbance for sample before treatment, and A_f is the final absorbance for sample after treatment.

Characterization

Fourier transform infrared spectroscopy, FT-IR, (Tensor 27, Bruker) was employed to determine the effects of ultrasound irradiation, persulphate, Co and Fe ions on the sonochemical degradation of MG. For spectating liquid samples, one drop of each sample was put between KBr cells then spectra were measured.

Results and Discussion

Effect of catalysis

In this study, persulphate ($S_2O_8^{2-}$) which can be activated by H_2O_2, was used to increase destroying kinetics of a wide range of contaminants [35]. Recent work indicated that, the sulphate radical was used to oxidize the lindane. Sulphate radical was activated using the ferrous sulphate and

persulphate anion, prepared from sodium persulphate. The oxidation power of the persulphate can sustain over weeks [36]. 2,4-dichlorophenol, atrazine, and naphthalene were degraded by cobalt/peroxymonosulfate [37]. In this experience, the amount of MG and persulphate (PS) were taken 30 mg/L and 1.1 g/100 mL, respectively. Then ultrasonic irradiation was done and ultrasonic waves were used as a stirrer. The optimum decolorization efficiency was 98%. 0.01 g/100 mL of Co was used in solution form added to MG (30 mg/L) solution. The result showed that the best percentage of decolorization was 60%. In MG+Fe method, 0.01 g/100 mL of Fe was used in solution form added to MG (30 mg/L) solution. Decolorization efficiency for MG+Fe system was 51%. The amount of Co was taken 0.01 g/100 mL to increase the efficiency of decolorization of MG at a shorter time period. The plot of percentage decolorization versus sonication time is presented in Figure 2.

Figure 2. Effect of PS, Co, Co+PS on MG sonochemical degradation. [MG]$_0$ = 30 mg/ L, T = 25 ± 0.5 °C

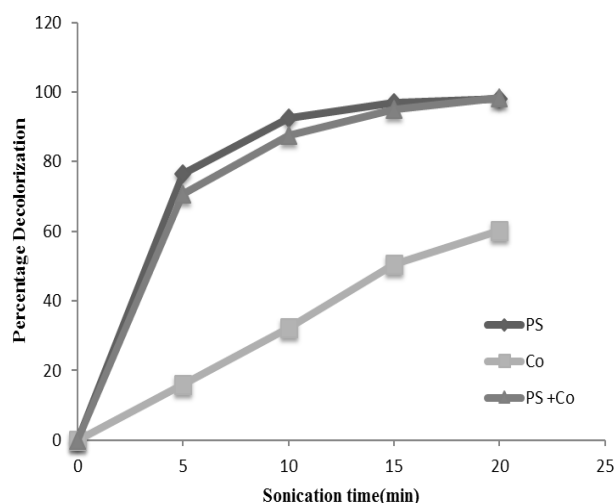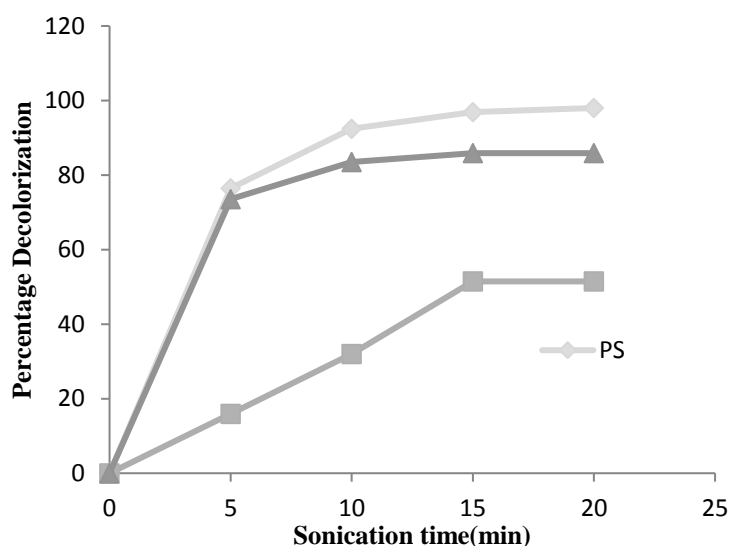**Figure 3.** Effect of PS, Fe, PS+Fe on MG sonochemical degradation. [MG]$_0$ = 30 mg/ L, T = 25 ± 0.5 °C

The outcome illustrates that the percentage of decolorization was 99%. In this section of studies, ultrasonic combined PS and Fe ions in order to degrade MG and the amount of Fe was taken 0.01 g/100 mL. The highest percentage of decolorization was 89%. The results are demonstrated in Figure 3. The time duration taken for maximum decolorization efficiency in the presence of Co and Fe was 20 min.

Effect of pH at presence of Co and Fe

One of the parameters that has been affected the degradation of wastewater was pH. The influence of pH on the ultrasonic degradation of MG (30 mg/L) in the presence of PS (1.1 g/100 mL), Co and Fe ions impregnated resin separately (1 g/100 mL) was studied in the range of pH from 1 to 11. pH value was adjusted with the dilute nitric acid and sodium hydroxide. Table 1 demonstrates that in the MG+PS+Co$_{resin}$ system, the initial pH is 3.18 and the optimum decolorization happened in the pH=4 and components were degraded after pH=6, which is basically due to formation of the cobalt oxide. So there was no influence of pH on this method of treatment, which might be due to the pH independence of the ultrasound and persulphate activated by Co at a wide range of pH. In the MG+PS+Fe$_{resin}$ system, the initial pH was 2.31 and the optimum decolorization happened at the pH=1 and the data in Table 2, indicated that in the range of 1-3, the pH the decolorization of MG were effective. However, by increasing the pH from 4 to 10, the components were destroyed by formation of the iron oxide.

Table 1. Effect of pH on MG sonochemical degradation, [MG]$_0$=30 mg/L, T=25±0.5 °C, sonication time 20 min

pH	Decolorization (%) before US	Decolorization (%) after US
2	88	88
4	57	91
6	64	89

Table 2. Effect of pH on MG sonochemical degradation. [MG]$_0$=30 mg/ L, T=25±0.5 °C, sonication time 15 min

pH	Decolorization (%) before US	Decolorization (%) after US
1	90	90
2	80	87
3	63	77

Effect of persulphate dosage

For optimizing this parameter, the persulphate dosage of 0.1, 0.5, 1.0, 1.3, and 1.6 g/100 mL was taken up for the study with constant resin dose of 1 g/100 mL and MG concentration was 30 mg/L under ultrasound irradiation. Results showed in Table 3 for Co resin and Table 4 for Fe resin. Therefore, the best amounts of PS at the presence of Co and Fe were chosen 1.3 mg/L and 1 mg/L, respectively.

Effect of Co and Fe dosage

To evaluate the effect of Co and Fe resins dosages, five experiments were performed for each of them. The different concentrations of Co and Fe resins (0.05, 0.1, 0.2, 0.5, 1 g/100 mL) coupled with MG (30 mg/L) and PS (1.3 g/100 mL) were taken. All of them were carried out under ultrasound irradiation. Table 5 and Table 6 present the best amount of Co and Fe resins.

Table 3. Effect of PS dosage for MG degradation in the presence of Co resin (experimental condition: pH – actual pH, T=25±0.5 °C, sonication time 20 min)

PS dosage (g/100 mL)	Decolorization (%)
0.1	83
0.5	89
1.0	90
1.3	92
1.6	89

Table 4. Effect of PS dosage for MG degradation in the presence of Fe resin (experimental condition: pH – actual pH, T=25±0.5 °C, sonication time 15 min)

PS dosage (g/100 mL)	Decolorization (%)
0.1	86
0.5	87
1.0	89
1.1	81
1.3	80

Table 5. Effect of Co impregnated resin dosage on MG degradation (experimental condition: pH – actual pH, T=25±0.5 °C, sonication time 20 min)

Co dosage (g/100 mL)	Decolorization (%)
0.05	89
0.1	88
0.2	89

0.5	87
1.0	91

Table 6. Effect of Fe impregnated resin dosage on MG degradation (experimental condition: pH – actual pH, T=25±0.5 °C, sonication time 15 min)

Fe dosage (g/100 mL)	Decolorization (%)
0.05	89
0.1	90
0.2	90
0.5	92
1.0	88

Effect of Co and Fe resins

According to previous experiments that provided the best amount for Co resin (1 g/100 mL) and Fe resin (0.5 gr/100 mL), in this section Co and Fe resins added to MG (30 mg/L) individually and they were kept under ultrasound irradiation for 20 min and 15 min, respectively. As seen in Figure 4 and Figure 5, the of decolorization percentage were 43% for Co resin and 38% for Fe resin.

Effect of contact time

In this part, the effective contact time were studied by keeping the other parameters at the optimum level. The maximum decolorization efficiency at the presence of Co as catalyst was achieved within 20 min. So the optimum time duration was taken 20 min. In the case of Fe as catalyst, the best contact time was 15 min.

FT-IR spectra of degraded MG

The FT-IR spectra of the degraded MG that are sampled at the end of 20 min for MG, MG+PS, MG+PS+Co, MG+PS+Co$_{resin}$ are illustrated in Figure 6 and for other system, contain MG, MG+PS, MG+PS+Fe, MG+PS+Fe$_{resin}$ the FT-IR spectra of the ultrasonic degradation at the end of 15 min are depicted in Figure 7. To achieve the best result in this section, the optimum amount of the MG, PS, Co, Co resin, Fe and Fe resin were selected and the concentration of each system contains: (a) MG (30 mg/L), (b) MG+PS (1.1 g/100 mL), (c) MG+PS (1.1 g/100 mL)+Co (0.01 g/100 mL), (d) MG+PS (1.3 g/100 mL) +Co resin (1 g/100 mL); under US at T=25±0.5 °C, sonication time 20 min and in Figure 7: (a) MG (30 mg/L), (b) MG+PS (1.1 g/100 mL), (c) MG+PS (1.1 g/100 mL)+Fe (0.01 g/100 mL), (d)
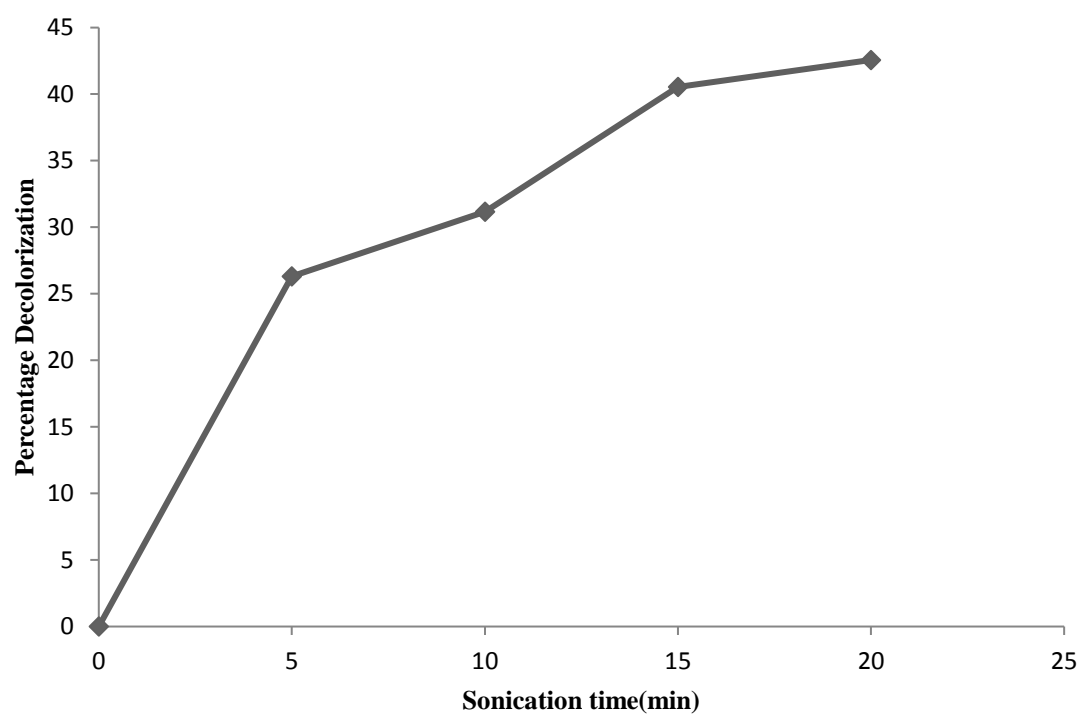
Figure 4. Effect of Co resin on MG sonochemical degradation. $[MG]_0$ =30 mg/ L, T=25±0.5 °C
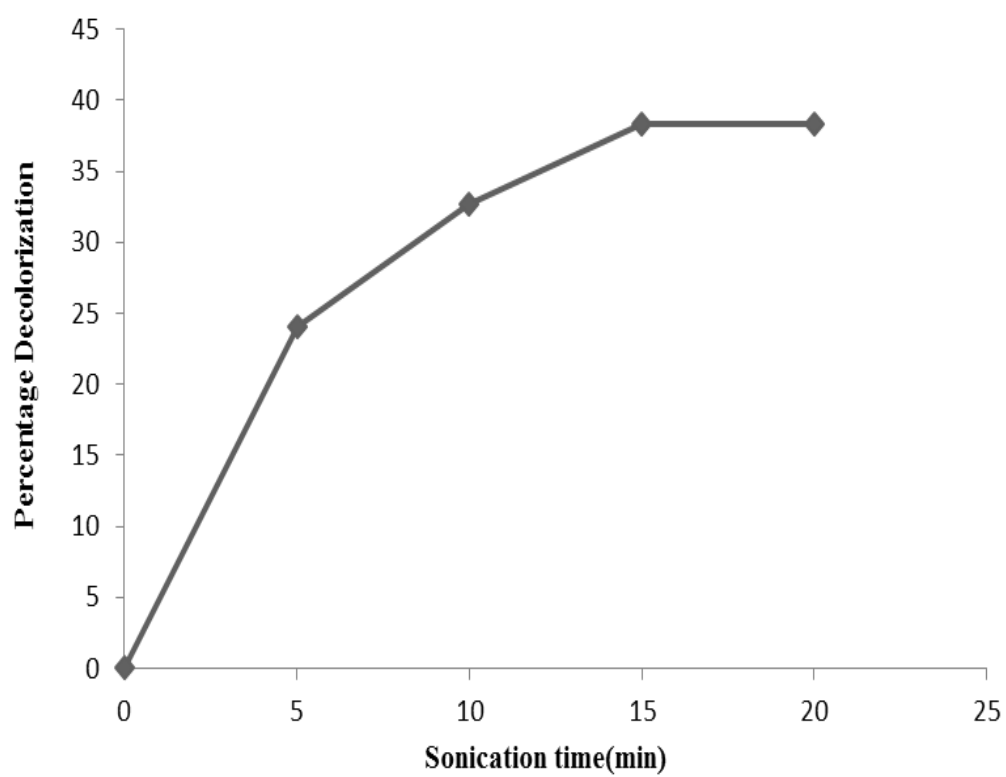
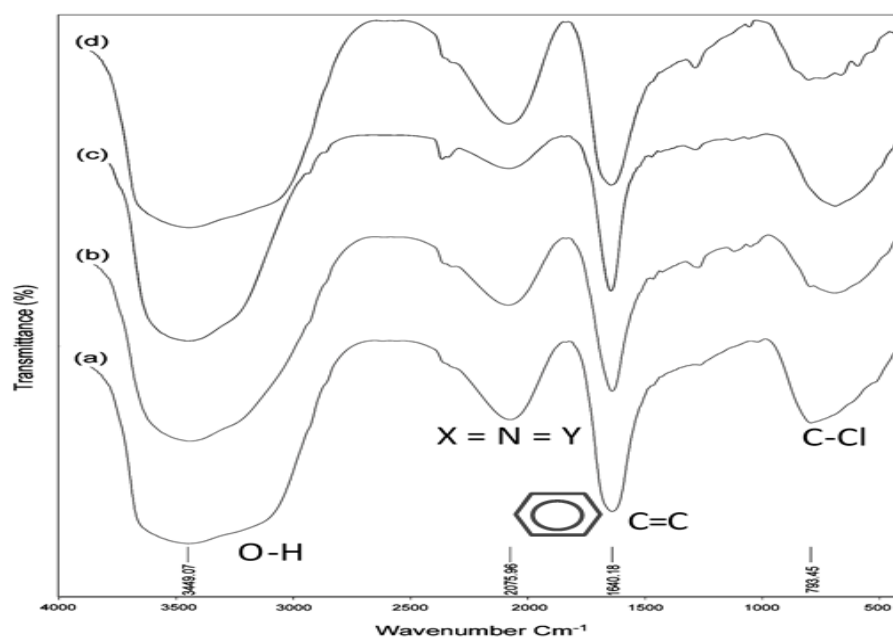**Figure 5.** Effect of Fe resin on MG sonochemical degradation. $[MG]_0$ =30 mg/ L, T=25±0.5 °C

Figure 6. FT-IR spectra of MG: a) MG, b) MG+PS, c) MG+PS+Co, d) MG+PS+Co$_{resin}$; under US at T=25±0.5 °C, which sonicated for 20 min
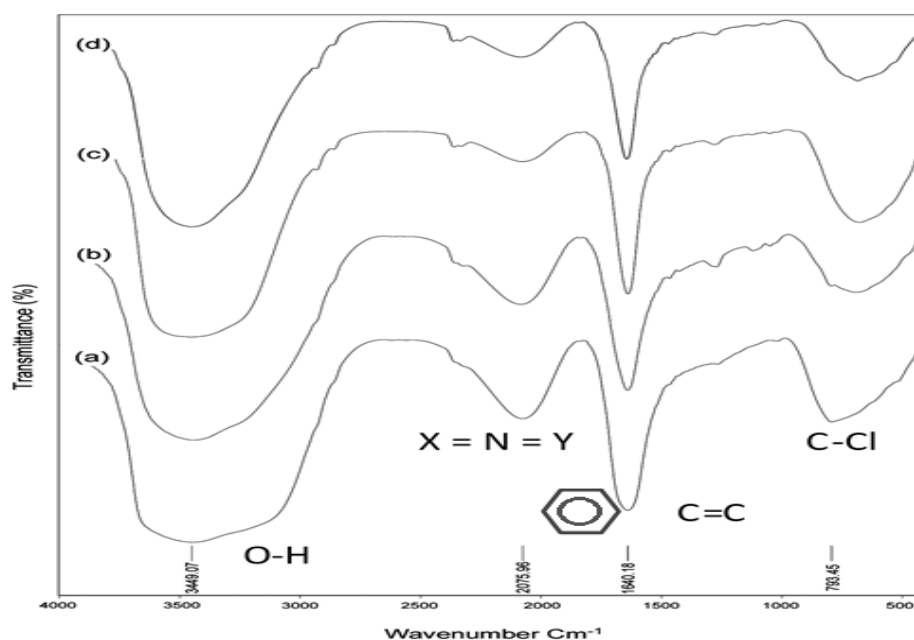

Figure 7. FT-IR spectra of MG: a) MG, b) MG+PS, c) MG+PS+Fe, d) MG+PS+Fe$_{resin}$; under US at T=25±0.5 °C that sonicated for 15 min

MG+PS (1 g/100 mL) + Fe resin (0.5 g/100 mL); under US at T=25±0.5 °C. The FT-IR spectra of the degradation for two catalysts were similar but the intensity of peaks in each system was different. The transmittance peaks which appear at 3450, 2075, 1640, and 700 cm^{-1} can describe the hydroxyl, X=N=Y, C=C (or aromatic chain) and C–Cl groups, respectively. The IR spectra suggested that, there

was no significant difference between the chemical structure of the single degraded MG and other systems.

Conclusions

In this work, degradation of MG by using sulphate radical activated by ultrasonication, Co and Fe ions separately were found to be feasible. The decolorization percentage of the MG, MG+PS, MG+Co, MG+Co$_{resin}$, MG+PS+Co$_{resin}$, MG+Fe, MG+Fe$_{resin}$ and MG+PS+Fe$_{resin}$ were 33%, 98%, 60%, 43%, 99%, 51%, 38%, and 89%, respectively. Results showed that, MG+PS+Co system performed better than the others. pH showed no influence on the degradation. The optimum dose of persulphate, Co resin, and Fe resin were found to be 1.1 g/100 mL, 1 g/100 mL, and 0.05 g/100 mL, respectively, which contain 10% cobalt nitrate and 10% ferrous chloride and reaction times were 20 min and 15 min at the presence of Co and Fe, respectively. The results of the FT-IR spectroscopy indicated that the chemical structure of the MG was not alerted by sonochemical degradation and additional of catalysis considerably.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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