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Original Research

Ultrasound-Assisted Hydrogen Peroxide and Iron Sulfate Mediated Fenton Process as an Efficient Advanced Oxidation Process for the Removal of Congo Red Dye

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Abstract

In the present study the ultrasound (US) and ultrasound-assisted hydrogen peroxide, and iron sulfate mediated Fenton process (sono-Fenton) was carried out for the degradation of the Congo red (CR) dye. Degradation rate, COD removal, and degradation mechanism of dye in the combined process were studied and the factors affecting the system performance i.e., pH, initial dye concentration, ultrasonic power, time, and effect of variations in concentrations of hydrogen peroxide and iron sulfate were also investigated. The results showed that the dye degradation and COD removal in the sono-Fenton process was 83% and 89% after 60 min of contact time and the coupling process was more efficient and synergistic compared to the respective individual processes. The extent of CR removal increased with increasing the US power and concentration of $FeSO_4$, and H_2O_2, to an optimum level but decreased with increasing dye concentration, and the optimum conditions were found as pH = 3.5, dye conc. = 25 mg L^{-1}, US power = 80 W, time = 60 min, H_2O_2 conc. = 5 mM, $FeSO_4$ conc. = 25 mg L^{-1}. As revealed by GC–MS results, the sono-Fenton treatment of CR, for 30 min resulted in the formation of byproducts that were finally degraded to small molecules within 60 min of contact time. The synergy of the sono-Fenton process in comparison to respective individual processes is attributed to the increased generation of $^{\bullet}H$ and $^{\bullet}OH$ radicals. The study demonstrated the potential use of the combination process ‘sono-Fenton’ for the efficient decontamination of water from dye pollutants.

Keywords: sonolysis, fenton, sono-Fenton process, synergy, Congo Red

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Introduction

The production of different essential goods and services generates toxic materials into environmental media like water, soil, and air. The textile industry is one of the major sources of severe water contamination due to the production and utilization of different dyes for the coloring of different products [1]. The dyes or coloring agents are commonly utilized in an aqueous form, which can change the physical appearance of a matter after its application [2]. Untreated textile dyes when released into the environment, in open water bodies, are hazardous and resistant for photodegradation under the sunlight due to their chemical stability and strong bonding [3-5]. Most of the dyes and their metabolites are toxic and have carcinogenicity and teratogenicity to aquatic biota [6] and human life [7-10].

Congo red (CR), a Sodium salt of 3,3′-([1,1′-biphenyl]-4,4′-diyl)bis(4-aminonaphthalene-1-sulfonic acid [11] is a diazo dye. It was selected as a model dye in this study due to its high solubility in an aqueous solution and its persistence once it is discharged into the natural environment. It is mainly used in textile industries due to its strong affinity with the fibers during the fabrication process. CR is a subordinate of napthoic acid and benzidine and is metabolized to cancer-causing byproducts [12] that can cause severe impacts on the environment as well as on human beings if exposed. Most of the dyes are non-biodegradable or their biodegradation rate is too slow, and the existing techniques i.e., photocatalysis, precipitation, membrane, and adsorption, etc used to diminish dyes are not pondered to be suitable now [13-16]. For these reasons, advancement in promoting other treatment techniques like advanced oxidation processes/techniques (AOPs) in which hydroxyl radicals are used as an oxidant in the aqueous-phase oxidation for the pollutant degradation as it has built up its place in a very short time in the treatment technologies [17]. The application of the Fenton process for the degradation of pollutants is one of the most promising AOPs and has gained a lot of attention in recent years [18] In this technique, ferrous ions (Fe^{2+}) act as a catalyst and result in the formation of •OH radicals from H_2O_2 [19].

The primary demerit of the Fenton process is the continuous loss of catalyst and the need for acidic pH. The use of ultrasonic cavitation for the destruction of different dyes in the wastewater [20-22] is an AOP and the cavitational bubbles (produced by sonolysis) are vigorously collapsed with the formation of momentary hydroxyl radical groups [23, 24]. These radicals can then disperse outside of the cavitational bubble into the model solution medium and decompose the pollutant. The unstable compounds of the solute may vaporize into the bubble and achromatize by the hard situations produced by the cavitational collapse. The degradation of an organic contaminant, which has very low vapor pressure and is in the solution, is largely due to the action of reactive species produced by Fenton's reagents i.e., hydroxyl radicals which have strong oxidizing power. The general form of chemical reaction in the Fenton process can be expressed as follows:

$$\mathrm{Fe}^{+2} + H_2O_2 \quad \rightarrow \quad \mathrm{Fe}^{+3} + \mathrm{HO}^{-} + \cdot\mathrm{OH} \qquad (1)$$

Many research studies concluded that sonolysis alone cannot completely remove or degrade the dyes in a solution [25]. Therefore, this has been applied in conjugation with other advanced oxidation processes to know the synergistic effects of these processes in the removal of pesticides, coloring agents, and phenols [26, 27]. The present study aimed at the degradation of a Congo red (CR) as a model dye in a hybrid system i.e., Sono- Fenton process, which is a commonly used dye in industrial processes. The novelty of the work is in terms of investigating the efficacies of combined advanced oxidation processes based on the use of cavitation and Fenton chemistry at pilot scale operation. The effects of the operational factors such as pH, concentration of ferrous ions, hydrogen peroxide, initial dye conc., and US (ultrasonic) power on the removal of CR dye were investigated. Moreover, the % dye degradation, COD removal, and the possible degradation mechanism of CR have been explored.

Materials and Methods

Materials

Congo Red (CR) was generously provided by Arzoo Textile industries, Faisalabad, Pakistan, and was used without further purification, as shown in Fig 1. All reagents, iron sulfate, hydrogen peroxide (35% v/v, analytical grade) HCl, NaOH, and H_3PO_4 were purchased from Merck (Germany) and used as received without any further purification. All solutions were prepared in distilled water.

Experimental Setup

Stock solution (500 mg L^{-1}) of the CR dye was prepared to use for each experiment by diluting it up to 25 mg L^{-1}. 100 mL from the stock solution was placed in the reaction vessel, and the appropriate amount of hydrogen peroxide and iron sulfate was added to the solution. Sulphuric acid and sodium hydroxide were used for pH adjustment. The pH meter (PHS-3BW Benchtop obtained from Shanghai Total Industries Co, Ltd) was used to check the pH of the solutions. The reaction temperature was maintained at 30±1ºC within a glass reactor equipped with a water circulation jacket. Sonolysis experiments were carried out by using the Digital Ultrasonic Bath Cleaner Model (UTECH Products INC). Calibration of the ultrasound system was performed using calorimetric measurements and oxidative species monitoring using the Fricke dosimeter [28]. Samples were taken after 15 min time intervals

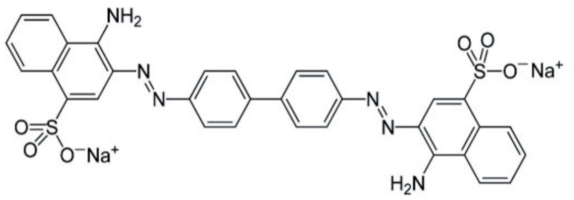

Fig. 1. Chemical structure of CR dye.

and analyzed on UV/Visible Spectrophotometer (T80+UV/VIS Spectrophotometer double beam) using the specific wavelength of 496 nm. Experiments were performed in duplicate. The percent removal of CR dye from the model solution was calculated by the following equation.

$$\%R = \left(\frac{X - Y}{X}\right) \times 100 \tag{2}$$

Where X and Y are the concentrations of dye before and after reaction time.

Experimental Procedure

Different experimental procedures and techniques were used to investigate the individual and synergistic effects of different parameters for dye removal i.e., sonolysis, hydrogen peroxide (H_2O_2), and iron sulfate ($FeSO_4$) alone and in combinations of ultrasound/hydrogen peroxide (US/H_2O_2), ultrasound/iron sulfate (US/H_2O_2), hydrogen peroxide/iron sulfate (H_2O_2/$FeSO_4$) and ultrasound combined with $H_2O_{2,}$/$FeSO_4$. Samples were placed in the Ultrasonic bath under different reaction conditions and were immediately analyzed for CR (%) removal through UV/Vis Spectrophotometer after being collected from the experimental system. Effects of pH, initial concentrations of CR, variable concentrations of ferrous sulfate and hydrogen peroxide, ultrasonic power, and contact time, on the degradation of CR, dye were investigated.

Analysis Methods

For COD analysis, 1.5 mL of digestion solution, and 3 mL of H_2SO_4 solution were added into 2.5 mL of the CR sample. The solutions were digested for 120 min at 150°C in a COD digester (Spectroquant TR 320, Merck D-64217) and analyzed to determine the chemical oxygen demand of the sample using a COD meter (Aqua Lytic AL100). COD (mg L^{-1}) removal from the model solution for each specific time interval (15, 30, 45, and 60 min) was calculated using the following equation.

$$\text{COD} \quad \text{Removal}\,(mg/L) = \quad R_i - R_f/Ri \tag{3}$$

Where $R_{i\,=}$ the initial reading and $R_{f\,=}$the final reading. To calculate the percent removal of COD from the solution through the sono-Fenton process, the following equation was used:

$$\%C = \left(\frac{X \quad - Y}{X}\right) \times 100 \tag{4}$$

Where % C = the percent removal of COD, X = the initial con centration (mg L^{-1}) and Y = the final concentration (mg L^{-1}).

GC–MS Analysis

The degradation products were identified using a gas chromatograph-mass spectrometer (GC–MS) (Perkin Elmer Clarus 600). The samples were collected at different time intervals and were extracted according to the procedure reported in the literature [29]. The GC was equipped with an Elite-xlb column (30 m x 0.25 mm) and 0.25 µm film thickness and connected directly to MS. The GC column was operated at 40ºC for 1.50 min which was then increased to 300ºC at the rate of 20ºC/min. The other experimental conditions were, helium as a carrier gas with a flow rate of 1 mL, sample volume 1 µl, injection temperature 200ºC, injection mode split, and the split ratio are 50 [30].

Results and Discussion

Degradation of Congo Red in Different Systems

The degradation experiments were performed by employing different techniques (alone and in combination) i.e., Sonolysis, $H_2O_{2,}$ $FeSO_4$, US/H_2O_2, US/$FeSO_4$, H_2O_2/$FeSO_{4,}$ and ultrasound combined with $H_2O_{2,}$/$FeSO_4$ to observe the effects of different parameters on CR removal. The degradation efficiency of 13, 15, and 24% were found when alone ultrasound, $FeSO_4$, and H_2O_2, were used at a contact time of 60 min (Fig 2). Non-volatile organic compounds present in the liquid phase undergo degradation mainly by reaction with $^{\bullet}$OH radicals. In the combined system the degradation was increased due to the cavitational effect [31] and 47, 56, and 64 % dye removal was observed respectively when US/$FeSO_4$, $FeSO_4$/H_2O_2, and US/$FeSO_4$ were used. Further, the combined ultrasound/H_2O_2/$FeSO_4$ system showed 83% removal after 60 min of treatment (Fig 2, Table 1) indicates an accelerating effect due to cavitational phenomena. A detailed comparison with other published systems is complicated using different conditions but these results indicate that using ultrasound can enhance the action of the H_2O_2/$FeSO_4$ system so that each experimental parameter was further studied to determine the origin of the effects.

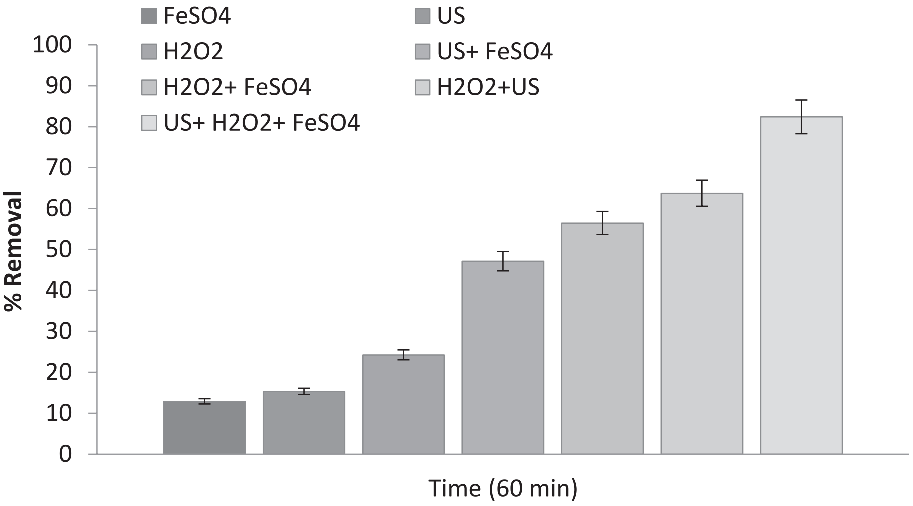

Fig. 2. Comparison of different techniques in CR degradation with/without H_2O_2, $FeSO_4$ by Sonolysis (Dye conc. = 25 mg L^{-1}, $FeSO_4$ conc.= 25 mg L^{-1}, H_2O_2 = 5mM, pH = 3.5, contact time = 60 min, US power = 80 W).

Effect of H_2O_2 Concentration on the Degradation of CR

Various concentrations of hydrogen peroxide (H_2O_2) were tested for the degradation of CR dye under the reaction conditions (i.e., dye concentration of 25 mg L^{-1}, working volume of 100 ml, $FeSO_4$ addition of 25 mg L^{-1} (coupled techniques only), US power of 80 W with 35 kHz frequency (coupled techniques only), a contact time of 60 min and pH of 3.5. H_2O_2 concentrations were 0.5, 1, 3, 5, 7, 9 and 15 mM. The maximum degradation was observed by the addition of 5 mM with other optimized parameters in all the techniques used, as shown in Fig. 3. It was observed that the addition of hydrogen peroxide significantly increased the degradation efficiency of the system. The degradation of CR dye increased from 62% to 83 % with the increasing concentration of H_2O_2 from 0.5 mM to 5 mM in the Ultrasound-assisted Fenton process. However, a further increase in the H_2O_2 concentration from 5 mM to 15 mM caused a reduced degradation rate. A lower and negligible decolorization efficiency of H_2O_2 was observed and this behavior might be due to the limited oxidation ability of lower H_2O_2 concentration as compared to hydroxyl radical [32]. At low concentrations, H_2O_2 cannot generate enough $^{\bullet}OH$ radical and the oxidation rate is logically slow. At higher oxidant (H_2O_2) concentrations, once radicals have been formed, they are disabled through scavenging reaction mechanisms by H_2O_2 itself to form hydroperoxyl radicals (Eq. 5), which have lower oxidizing power in comparison, and the latter can also scavenge hydroxyl radicals according to Eq. (6):

Table 1. Comparison of the effectiveness of different techniques in the degradation of CR dye.

S. No.	Technique	Removal (%)
1	$FeSO_4$	13
2	US	15
3	H_2O_2	24
4	US + $FeSO_4$	47
5	$FeSO_4$ + H_2O_2	56
6	US + H_2O_2	64
7	Sono-Fenton (US + H_2O_2 + $FeSO_4$)	83

$$H_2O_2 + {}^{\bullet}HO \rightarrow H_2O + HOO\bullet \tag{5}$$

$$HOO\bullet + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{6}$$

The major consideration of continuous H_2O_2 dosing mode in the sono-Fenton process is to avoid excess H_2O_2 addition resulting in the •OH self-competition (Eq. 7) during the oxidation reaction (Eq.8 and 9) as:

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + {}^{\bullet}HO_2 \tag{7}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{8}$$

$${}^{\bullet}OH + {}^{\bullet}OOH \rightarrow O_2 + H_2O \tag{9}$$

It was observed that increased H_2O_2 concentration effectively enhanced decolorization. However, an additional amount of H_2O_2 in solution would react with the $^{\bullet}OH$ leading to a decrease in decolorization efficiency [32, 33]. A similar trend was observed for the degradation of a toxic dye by the catalytic system varying the initial concentration of H_2O_2 from 0.006 to 0.1 mM [34, 35] and also for the degradation of phenol by advanced Fenton process by changing H_2O_2 concentration in the range of 10-50 mM [36]. Our results

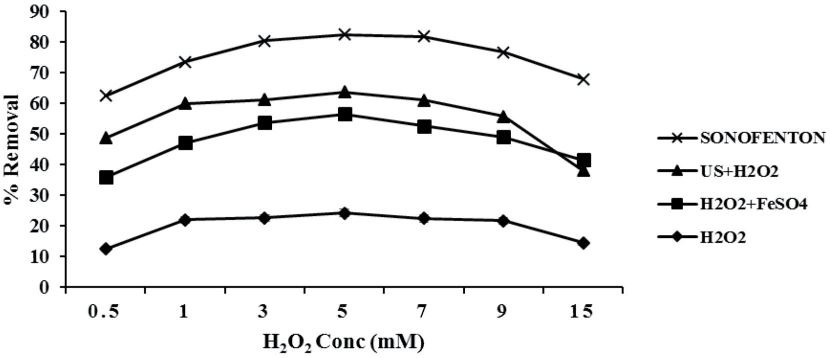

Fig. 3. Effect of hydrogen peroxide concentration on percent removal of CR (Dye conc. = 25 mg L^{-1}, FeSO4 conc. = 25 mg L^{-1}, pH = 3.5, US power = 80 W).

also propose that the optimum levels concentration of hydrogen peroxide must be retained to get high degradation efficiency of the pollutant, it is noticed that the Congo red decolorization efficiency drops when the concentration of H_2O_2 exceeds a threshold value [37].

Effect of Iron Sulfate concentration on the degradation of CR

Different concentrations of $FeSO_4$ (2, 5, 10, 15, 20, 25, and 50 mg L^{-1}) were investigated in the degradation studies of CR dye. Other optimized parameters were fixed as dye concentration of 25 mg L^{-1}, working volume of 100 mL having a pH of 3.5 with the contact time of 0 to 60 min at a temperature of 30 ± 1°C, Ultrasonic power of 80 W, and US frequency of 35 kHz with the addition of 5 mM H_2O_2 (coupled techniques only). Experimental results showed that the most efficient degradation was obtained by adding 25 mg L^{-1} of iron sulfate into the model solution with other optimized parameters as compared to the other iron sulfate concentrations i.e., 2, 5, 10, 15, 20, 50, and 100 mg L^{-1} (Fig. 4). The reactions of hydrogen peroxide with Iron Sulfate are given below:

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \quad (10)$$

In this reaction, ${}^{\bullet}OH$ radicals can also react with ferrous ions (Fe^{2+}) to form ferric ions (Fe^{3+}) or may react with organic compounds:

$$ {}^{\bullet}OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (11)$$

$$ {}^{\bullet}OH + \text{organics} \rightarrow \text{products} \quad (12)$$

Also, •OH can react with H_2O_2 to produce other radicals and may also react with each other to give hydrogen peroxide (Eq. 7 and 8). The Fenton reactions give ferrous ions and radicals during the process and the reactions are given as:

$$H_2O_2 + Fe^{3+} \leftrightarrow H^+ + FeOOH^{2+} \quad (13)$$

$$FeOOH^{2+} \rightarrow HO_2\bullet + Fe^{2+} \quad (14)$$

$$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+} \quad (15)$$

$$HO_2\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+ \quad (16)$$

Different concentrations of Iron sulfate were added to the model solutions in different experiments

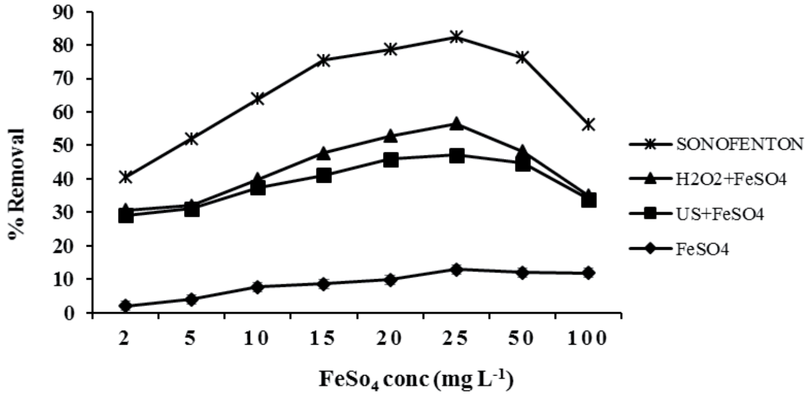

Fig. 4. Effect of hydrogen peroxide concentration on percent removal of CR (Dye conc. = 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, pH = 3.5, US power = 80 W).

to observe its effects on the removal of the dye from the solution through the Ultrasound-assisted Fenton experiments. The reactions equations of the three processes are given below:

$$Fe^{2+} + H_2O_2 +))) \rightarrow Fe^{3+} + {}^{\bullet}OH + OH- \quad (17)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+ \quad (18)$$

$$FeOOH^{2+} +))) \rightarrow Fe^{2+} + HO_2 \text{ (fast)} \quad (19)$$

$$Fe^{3+} + H_2O +))) \rightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \quad (20)$$

Where: [ ))) means ultrasound]

The experimental results showed that the most efficient degradation was obtained by adding 25 mg L^{-1} of iron sulfate into the model solution with other optimized parameters in all the techniques as compared to the other iron sulfate concentrations, as shown in Fig. 4. The results of Sono-Fenton experiments showed that 2, 5, 10, 15, 20, 25, 50 and 100 mg L^{-1} of $FeSO_4$ addition resulted in 41%, 52%, 64%, 75%, 79%, 83%, 76% and 56% removal of CR dye respectively (Fig. 4). The degradation rate increased with increasing Iron sulfate concentration and maximum degradation reached 25 mg L^{-1} concentration, but further increased in iron sulfate concentration negatively affect the Congo red degradation efficiency [37]. By using the Sono-Fenton process, it was observed that the rate of dye degradation was significantly enhanced by the addition of Fe^{2+}, which produced highly $^{\bullet}OH$ and that further increased in iron sulfate concentration from an optimized concentration of 25 mg L^{-1} to 50 mg L^{-1}. It could be the fact that at high Fe^{2+} concentrations, the solution undergoes the self-quenching of $^{\bullet}OH$ by the added amounts of Fe^{2+} to produce Fe^{3+} [38, 39]. In contrast, other researchers revealed that excess addition of Fe^{2+} would react with the •OH and decrease the amount of $^{\bullet}OH$ in the system. Even the excessive addition of Fe^{2+} led to the decrease in degradation efficiency, reasonably higher iron dosages only would be beneficial under certain conditions [40, 41]. After the ideal (Fe^{2+}) concentration, the further increase in the concentration of Fe^{2+} resulted in brown turbidity of the solution that causes a reduction in degradation efficiency due to the reaction of excessive hydroxyl radicals and ferrous ions react with hydroxyl radicals i.e., the scavenging effects due to the excessive hydroxyl radicals. Therefore, the degradation rate leads to a rapid fall in pollutant removal [42]. Also, such decreased degradation efficiency could be demonstrated by the redox reactions since hydroxyl radicals are scavenged by this reaction or with another ferrous ion molecule. The ferric ions (Fe^{3+}) generated can react with hydrogen peroxide as well as with hydroperoxy radicals that give ferrous ions in the solution which results in decreasing degradation efficiency. Considering optimum Fe(II) concentration was chosen as 25 mg/L for the decolorization of 25 mg L^{-1} Congo red dye [43].

Effect of Initial pH on the Degradation of CR

The pH range plays an important role in the elimination of organic compounds through advanced oxidation processes. The selection of optimized parameters like $FeSO_4$ 25 mg L^{-1}, acoustic power 80 W, contact time 60 min, H_2O_2 5 mM, and a working volume of 100 mL, the effect of pH (range 3.5-8.5) was investigated in the present study. As presented in Fig. 5, the maximum removal of CR was observed at pH 3.5 for all the applied techniques. The highest CR removal (83%) was obtained for the ultrasound-assisted Fenton process at pH 3.5. The degradation efficiencies of the sonolysis alone in the degradation of CR were higher under acidic pH conditions. Several studies found that pH is acidic condition has higher oxidation ability for the Fenton oxidation process [44, 45] as they suggested that maximum removal efficiencies of ultrasound at low pH. It was also observed that acidic pH is better

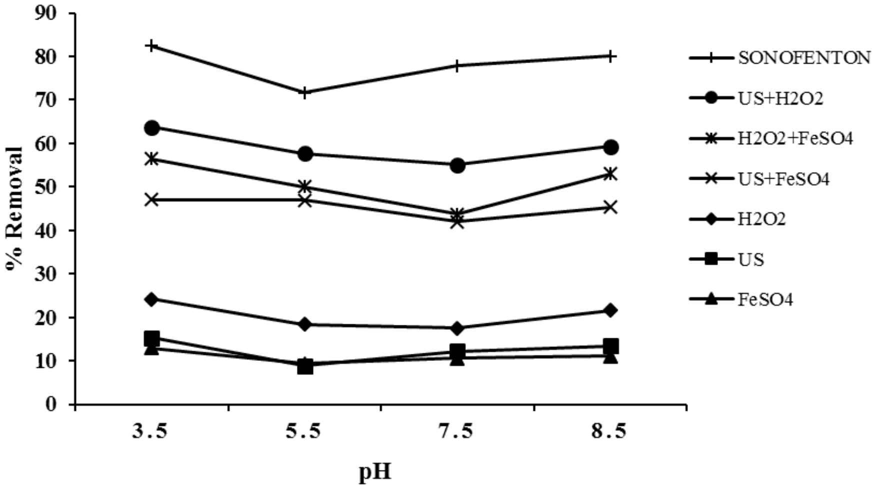

Fig. 5. Effect of pH on percent removal of CR (Dye conc. = 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc. = 5 mM, US power = 80 W).

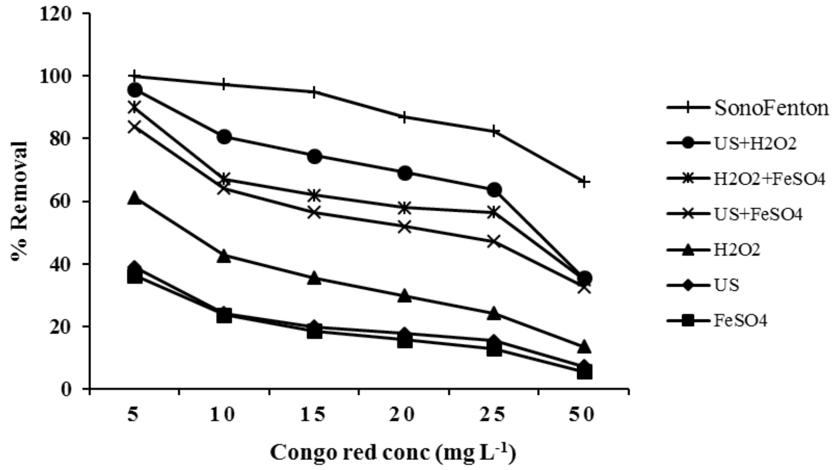

Fig. 6. Effect of initial dye concentration on percent removal of CR (Dye conc. = 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc. = 5 mM, pH = 3.5, US power = 80 W).

as compared to alkaline pH for pollutant removal [46-48] reported that CR degradation was higher at acidic pH (3.5) and lower in basic solutions (8.5). At pH 8.5, the degradation efficiency was lower due to the presence of Na^+ ions in the dye mixture. The degradation rate and efficiency constant were highest at a pH of 3.5 [49]. In the current study, the degradation of CR dye was highest at pH 3.5. It is because the lower pH favors the formation of iron complex and at higher (>4), then Fe^{3+} (Ferric ions) precipitates which causes a decrease in the soluble iron species fractions. Another possibility is the formation of complexes may reason decrease in the reactions with H_2O_2 [50]. In the ultrasound-assisted Fenton process, maximum removal was obtained at 3.5 pH as compared to another pH of 5.5, 7.5 and, 8.5, as shown in Fig. 5. A similar trend was reported using iron-alumina catalyst in the diverse Fenton process in the oxidation of dye solutions [51] It is due to the compilation of the increasing pH effects in the solo systems of ultrasound, hydrogen peroxide, and iron sulfate.

Effect of Initial dye Concentration on the Degradation of CR

In Fig. 6, it is shown that the degradation of the dye increased with the decrease in dye concentration in the solution while decreased with the increased CR concentration (range 5-50 mg L^{-1}) in the model solution during different processes adopted to study the CR degradation. In 60 min of sono-Fenton process, 100% removal was obtained for 5 mg L^{-1} of dye concentration, 97% for 10 mg L^{-1}, 95% for 15 mg L^{-1}, 87% for 20 mg L^{-1}, 83% for 25 mg L^{-1}, and 66% for 50 mg L^{-1} dye concentration (Fig. 6). The reason for the obtained trends maybe because that the increasing concentration of dye in the solution needs more $^{\bullet}OH$ radicals to be degraded [51–53] and the reason for this is that concentrations of hydrogen peroxide and iron sulfate and US power was optimized for the specific concentration (25 mg L^{-1}) of the CR dye. In other words, as the concentration of hydroxyl radicals produced by the fixed H_2O_2 and Fe(II) concentrations

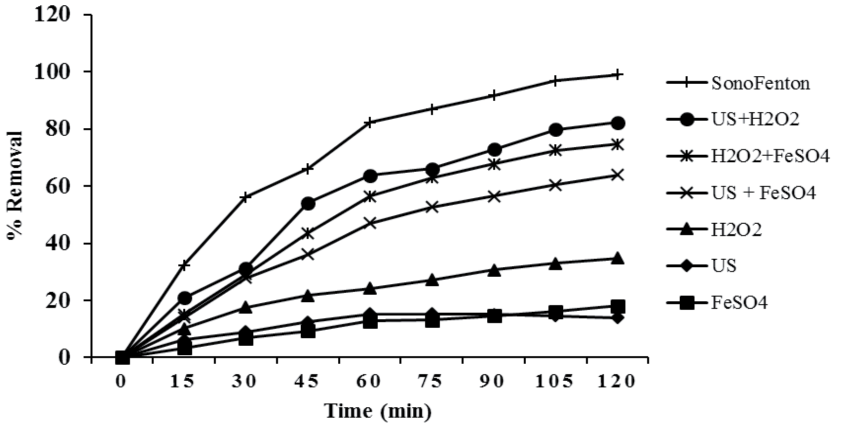

Fig. 7. Effect of contact time on percent removal of CR (Dye conc. = 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc.= 5 mM, pH = 3.5, US power = 80 W).

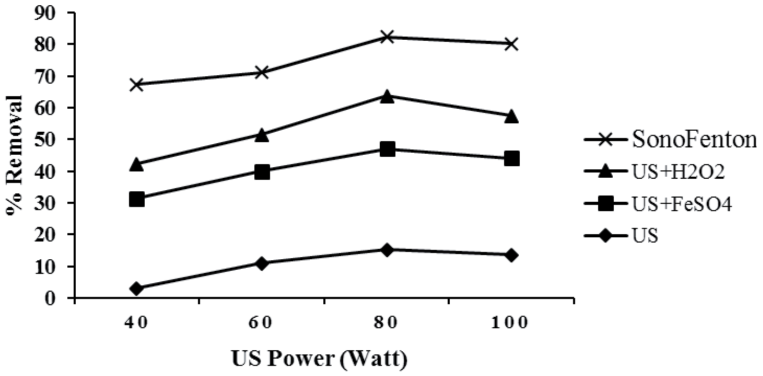

Fig. 8. Effect of Ultrasonic power on percent removal of CR (Dye conc.= 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc. = 5 mM, pH = 3.5, US power = 80 W).

was the same, decolorization reduced with the increase in CR concentration [54], and as the concentrations of hydrogen peroxide and iron sulfate and US power was optimized for the specific concentration (25 mg L^{-1}) of the CR dye. Therefore, a further increase in CR concentration may need more hydrogen peroxide and iron sulfate concentrations additions and it may need high Ultrasonic power [55].

Effect of Contact Time on the Degradation of CR

The effects of contact time (0-60 min) on the degradation of different concentrations of CR dye in the model solution were investigated. The results demonstrated that with an increase in contact time, the degradation of the Congo red dye increases [56, 57] as shown in Fig. 7. However, a further increase in contact time had a significant effect on the % removal of the CR dye [58]. In 60 min of contact time for the sono-Fenton process, 100% removal was achieved for 5 mg L^{-1} CR concentration, while a decreasing trend in the % removal efficiency was observed with 97%, 95%, 87%, 83%, and 66% for 10 mg L^{-1}, 15 mg L^{-1}, 20 mg L^{-1}, 25 mg L^{-1} and for 50 mg L^{-1} respectively.

Effect of Ultrasonic Power on the Degradation of CR

Different ultrasonic powers (40, 60, 80, and 100 W) settings were applied to get the maximum removal efficiency at a specific power range. In all the applied systems including Sono-Fenton ($US/FeSO_4/H_2O_2$), maximum removal was achieved at 80 W with other optimum reaction conditions. The results showed that at 40 W, 67% removal was achieved, and at 60 W, 80 W, and 100 W, the CR removal efficiency was 71%, 83%, and 80% respectively (Fig. 8).

From the results, it is found that the removal efficiency of ultrasound increased with the increased capacity of ultrasonic power, and maximum degradation of the dye was obtained by applying 80 W. The increase in the power capacity causes a shorter lifetime of the cavitational bubble and cavitational bubbles collapse occurs very rapidly, which results in more production of $^{\bullet}H$ and $^{\bullet}OH$ radicals and it enhanced the opportunity of the radicals to attack the CR molecules [59, 60]. Increase the generation of free radicals, the combination of ultrasound with hydrogen peroxide looks to be a promising option. The concentration of hydrogen peroxide plays a crucial role in deciding the extent of

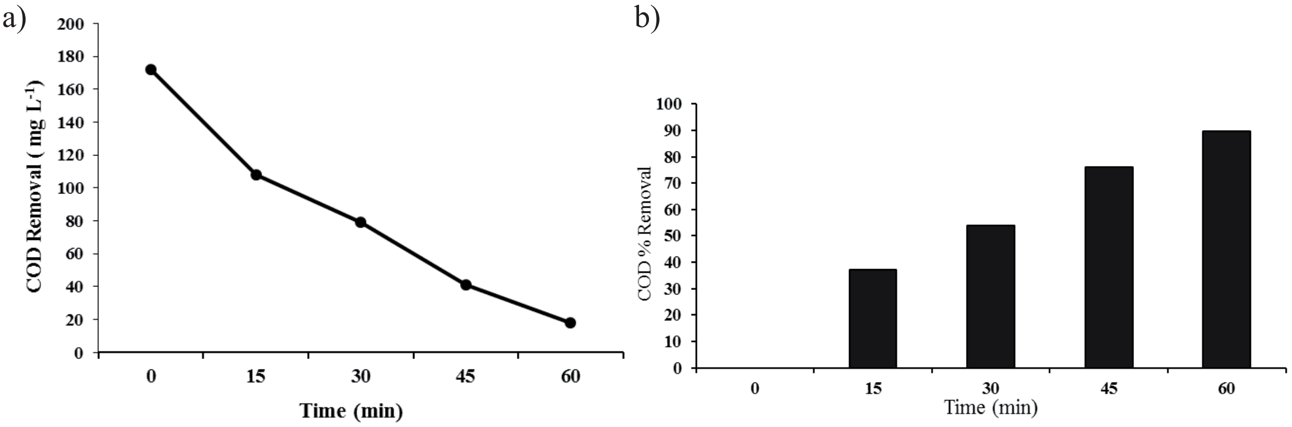

Fig. 9 a) Change of COD during the sono-Fenton degradation of CR, b) COD removal efficiency during sono-Fenton degradation of CR (Dye conc.= 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc. = 5 mM, pH = 3.5, US power = 80.

degradation obtained for the combined process. On one side, it also acts as a source of producing more and more free radicals by the dissociation process but on the other hand, it also acts as a scavenger for the generated free radicals when excessive free hydroxyl radicals are produced as given by the following equation scheme:

$$H_2O_2 \rightarrow 2^{\bullet}OH- \tag{21}$$

$$\bullet OH + H_2O_2 \rightarrow H_2O + O_2H^{\bullet} \tag{22}$$

Thus, the effect of the combined process will be very much dependent on the utilization of free radicals by the organic pollutant molecules and the degradation efficiency may increase with an increase in contact time and life of the generated free radicals. This adverse effect after optimum concentration is due to the scavenging effect. H_2O_2 in the presence of sonication from hydroxyl radicals. The increase in the concentration of H_2O_2 hydroxyl radicals also increases but beyond certain concentrations, some of H_2O_2

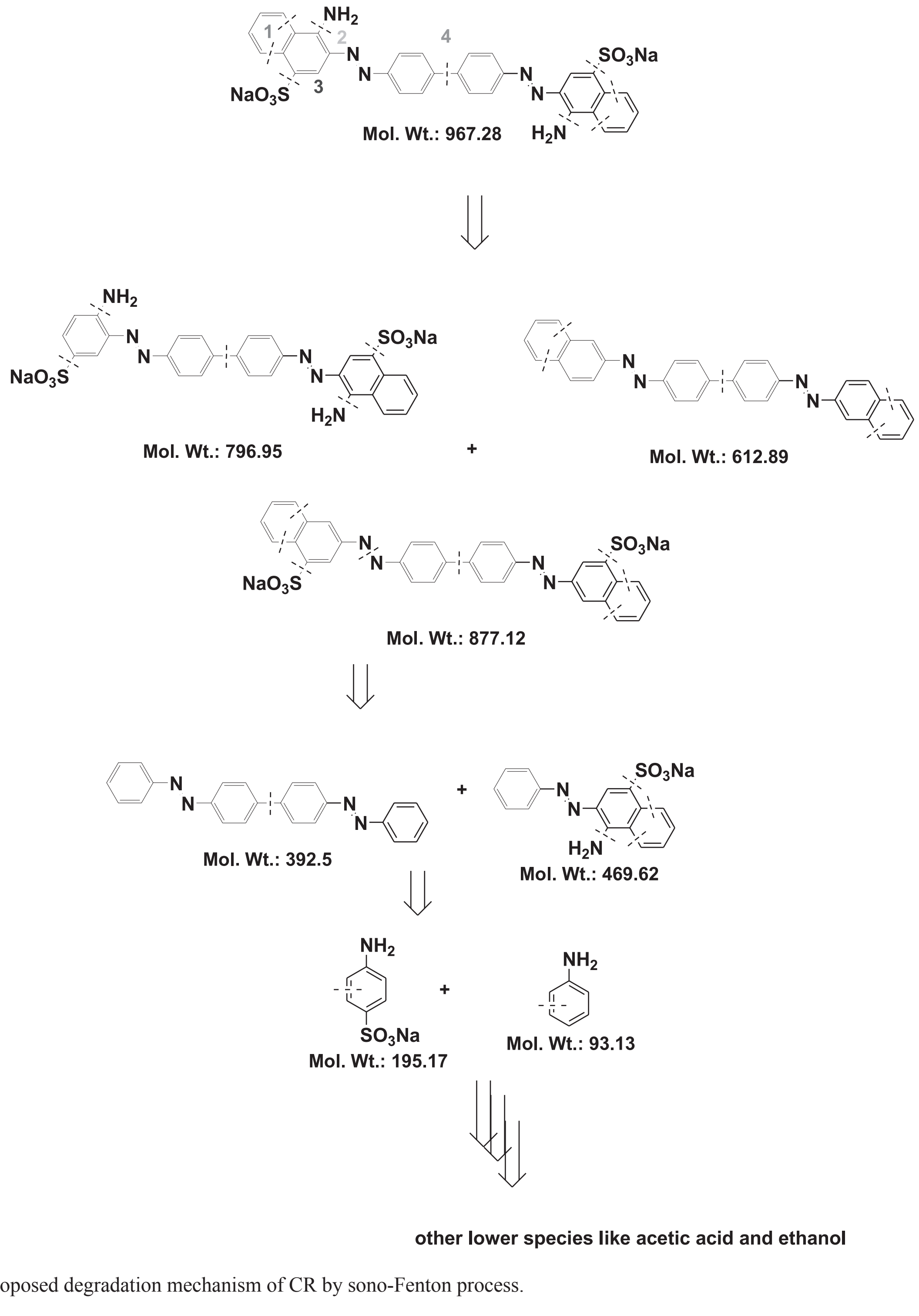

Fig. 10. Proposed degradation mechanism of CR by sono-Fenton process.

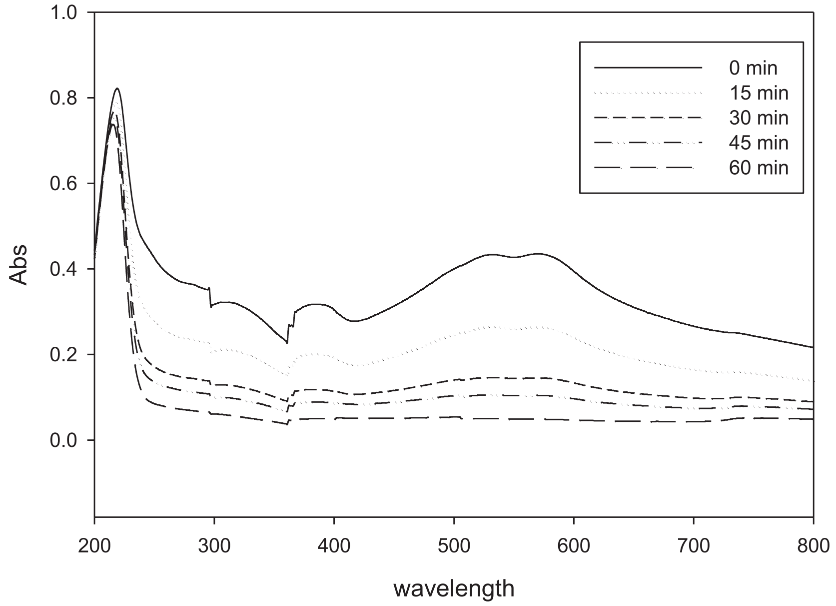

Fig. 11. UV/Visible spectral changes during sono-Fenton degradation of CR (Dye conc.= 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc. = 5 mM, pH = 3.5, US power = 80 W).

remains in excess. This excess H_2O_2 recombines with •OH radicals and form H_2O and O_2H radical that has low oxidation potential compared to that of •OH radical, which results in a decrease in the rate of degradation.

Mineralization of CR and Its Proposed Intermediate Byproducts

Mineralization involves the formation and subsequent breakdown of intermediate by-products, as a result of the hydroxylation and rupturing of the aromatic rings [61]. In the present study, the mineralization of CR was monitored by measuring the change in COD and confirmed using GC-MS. Fig. 9 (a, b). showed a decrease in COD concentration and an increase in percent removal that correspond to the sono-Fenton degradation of CR under optimum operating conditions i.e., dye conc. = 25 mg L^{-1}, $FeSO_4$ conc. = 25 mg L^{-1}, H_2O_2 conc. = 5 mM, pH = 3.5, US power = 80 W. During the sono-Fenton degradation of CR, the synergy of the combined system is evident [62] in the decrease in COD concentration (172-18 mg L^{-1}) and increase in percent removal (up to 89%) at 0-60 min. This was hypothesized to be the evolvement of intermediate and byproducts with lower molecular weight from the rupturing and hydroxylation reaction of •OH with the principal CR structure [61, 62].

The products which were formed after the sono-Fenton treatment were identified using GC–MS. Samples at different intervals were collected during the sono-Fenton process of CR at optimum conditions. The degradation pathway of the CR structure and the mechanism of its breakdown is illustrated in Fig. 10. The bonds highlighted as 1-4 are the bonds that were prone to cleave and was resulted in 4 different types of species in the treatment time of 30 min [62]. Further treatment of up to 60 min resulted in the disappearance of dye where the byproducts were finally degraded to small molecules, which are harmless and not toxic to the environment [63].

Change in UV/Visible Absorption Spectra

The degradation of CR by the sono-Fenton process was confirmed by a change in spectra from 0-60 min at λ_{max} = 496. From the spectral results, it was found that the initial absorbance peak of the CR is maximum as compared to the other absorbance peaks obtained at different time intervals i.e., 15, 30, 45, and 60 min [63]. The reduction in absorbance peaks means that the degradation of CR occurs with the increasing time interval by applying the sono-Fenton process [63] as shown in Fig. 11.

Conclusions

The results obtained from this study revealed that the ultrasound-assisted hydrogen peroxide and iron sulfate mediated Fenton process (sono-Fenton) is more efficient as compared to individual processes. The synergy of the sono-Fenton process in comparison to respective individual processes is attributed to the increased generation of $^{\bullet}H$ and $^{\bullet}OH$ radicals. The maximum 83% of CR degradation and 89 % of COD removal was attained by the sono-Fenton process under optimized reaction conditions i.e., 25 mg L^{-1} dye concentration, the addition of 5 mM H_2O_2, 25 mg L^{-1} $FeSO_4$, and pH of 3.5 at room temperature of 30±1°C with the contact time of 60 min. GC–MS analysis showed that the sono-Fenton treatment of CR for 30 min resulted in the formation of some byproducts but further increase in time from 30 to 60 min showed that the byproducts were degraded to small molecules. The initial GC-MS results could not assist to propose the degradation mechanism of dye, therefore; further research will be required to determine the low molecular weight compounds. The study demonstrated the potential use of the combination process 'sono-Fenton' for the efficient decontamination of water from dye pollutants.

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Conflict of Interest

The authors declare no conflict of interest.

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