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# Ultrasound-assisted Fenton's treatment of Reactive Black 5 dye: effect of system parameters, kinetics and mechanism

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#### ABSTRACT

This study deals with the sonochemical decolourization of aqueous Reactive Black 5 dye solution. The production of highly reactive radicals can be intensified through the addition of various substitutes. The decolourization study of Reactive Black 5 at different experimental conditions, such as the change in pH, bubbling gases (oxygen, argon, nitrogen and air), hydrogen peroxide dosage, sodium chloride dosage, Fenton's reagent and ultrasound probe tip diameter were performed. The maximum decolourization occurs at acidic pH of 3.0, Argon gas bubbling, 8.82 mmol/L hydrogen peroxide, 10 g/L NaCl addition and the colour removal are the highest for Fenton's reagent-treated Reactive Black 5 dye solution which followed pseudo-first-order rate kinetics. For the entire conditions studied, larger probe tip diameter has shown higher colour removal. Degradation intermediates were identified through GC-MS study. This study shows that decolourization is dominated through the hydroxylation reaction and can suitably be used as a promising method for the decolourization of Reactive black 5 dye.

Keywords: Ultrasound; Decolourization; RB5 dye; Fenton's reagent; Hydroxylation reaction

## 1. Introduction

The coloured wastewater dicharged by the textile, dyeing, pulp and paper industries causes severe water pollution problem to the surface waters mainly river water all over the world. This coloured wastewater contains many dyes depending upon the use by the textile industries. The major classifications of dyes are acid, basic, azo, reactive, etc. Azo dyes are the largest group of colourants used in industry. Azo dye is a kind of dye which contains at least one -N=N- bond in its molecular structure, these dyes are coloured because of complex molecular structure with very

high molecular weight. The azo dyes are nonbiodegradable and when it is discharged from the industry after its use, the wastewater containing the azo dye causes a severe water pollution problem affecting the health of the human being. Azo dyes degradation product produces colourless aromatic amines, which are toxic and carcinogenic [1]. In the case of dyes which imparts colour to the wastewater, the cleavage of -C=C- and -N=N- bonds would reduce the colour of the wastewater [2]. Depending upon the dye concentration and reaction time, dyes can have their influence on the environment. To avoid these consequences, it is essential and necessary to decolourize and degrade them before discharging into the environment.

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There are three major types of commonly practiced wastewater treatment namely, physical, chemical and biological methods. There are some of the newly emerging methods for treating wastewater containing the dye. Among them, the recent, effective and emerging technology is the Advanced Oxidation Process (AOP's). AOPs were defined as the water treatment process which operates at near ambient temperature and pressure producing highly reactive radicals sufficient enough to break recalcitrant organic pollutants [2]. Among the radicals produced, hydroxyl radicals has high oxidation potential (2.33 eV) which can react/attack the organic molecules to undergo cleavage [3]. Some of the oxidation processes which operates at ambient conditions, such as photo-catalytic oxidation, Fenton's chemistry, ozonation, hydrogen peroxide, ultrasound, ultrasound/H<sub>2</sub>O<sub>2</sub> or ozone, UV/H<sub>2</sub>O<sub>2</sub> or ozone, Ozone/H<sub>2</sub>O<sub>2</sub>, sonophotochemical oxidation, Photo-Fenton processes, catalytic AOPs, use of AOPs in conjunction with biological oxidation, sonochemical degradation followed by wet air oxidation and CAV-OX [3,4] are used to study for the treatment of dye wastewater.

Sonochemical Engineering is one such process which can disintegrate the molecular structure of the dyes present in wastewater. It is a process of inducing ultrasound wave having frequency above the hearing range of the human ear i.e. greater than 20 kHz and up to 10 MHz [5]. Sonochemical reactions are induced by high-intensity acoustic irradiation of liquids at frequencies that produce cavitation. Cavitation is a phenomenon of formation of micro bubbles, the growth and implosion in the irradiated liquid. The dynamics of cavity growth and collapse are strikingly dependent on the local environment [6]. Extreme temperature (2,000-5,000 K) and pressure (up to 1,800 atm) released during the adiabatic bubble collapse causes the fragmentation of those gas molecules, trapped in the micro bubbles into radical species. These radical species recombine or react with other gaseous molecules within the cavity or in the surrounding liquid, after their migration [7-9]. There are three different theories about cavitation namely, the hot-spot theory, the electrical and the plasma theories. The most understandable theory is the hot-spot approach, in which each cavitation bubble acts as a localized micro reactor, which generates instantaneous temperatures of several thousand degrees and pressures in excess of 1,000 atmospheres [10,11]. Sonication improves mass transfer and chemical reaction and it reduces or eliminates chemical usage, resulting in minimum sludge and disposal problems. The coupling of ultrasound with hydrogen peroxide enhances the efficiency of free radical generation through cavitation. Sonochemistry

offers the potential for shorter reaction cycles, cheaper reagents and less extreme physical conditions, leading to less expensive and smaller plants [12–22].

The hydrophilic and nonvolatile compounds mainly degrade through hydroxyl radical-mediated reactions in the solution, while hydrophobic and volatile species degrade thermally inside or in the vicinity of the bubble. Reactive azo dves are nonvolatile, water-soluble compounds and their passage into the gas cavity is unlikely. So, oxidative radical reactions in the bulk solution are expected to be the major route for their destruction. Destruction or mineralization of organic compounds by these processes is based on the oxidative degradation by free-radical attack, particularly by hydroxyl radical, which is a far more powerful oxidizing agent than all commonly known oxidants. One of the simplest ways to increase the free radical in the liquid medium is through Fenton's reagent addition. Recent studies with modified/Fenton's process in assistance with ultrasound have proven to effectively decolour dye solution. Zero-valent iron aggregates along with ultrasound had decolourized the Reactive Black 5, Direct Blue 15 and real textile wastewater rapidly when treated under acidic conditions and hydrogen peroxide addition [23-25]. The synergy factors have proven to be higher when compared to individual ultrasound and Fenton's processes. This type of Fenton's process has an advantage of reuse of zero-valent iron aggregates for further treatment when compared to homogeneous Fenton's process.

Application of ultrasound for the colour removal of textile azo dye Reactive Black 5 is taken for this study. To aid complete decolourization of the RB5 aqueous dye solution, parametric variations such as pH of the aqueous solution, dosage of hydrogen peroxide, bubbling the gases like Oxygen, Argon, Nitrogen and Air, the addition of ferrous sulphate, Fenton's reagent and addition of sodium chloride were performed. Initial RB5 concentration and ultrasound probe tip diameter study were also performed in order to make the process feasible for field application. GC-MS analysis was performed to identify the degradation intermediates.

## 2. Experimental procedure

## 2.1. Chemicals

Reactive Black 5 was obtained from Sigma–Aldrich (306452) and was used as supplied. High-purity reagents, sulphuric acid (Merck), sodium hydroxide (Merck), sodium chloride (Merck), hydrogen peroxide solution (30% w/w, Merck) and ferrous sulphate



Fig. 1. Spectrum of Reactive Black 5.

(Merck) were used for the solution preparation. All the solutions were prepared using double distilled water.

#### 2.2. Methods

#### 2.2.1. Experimental set-up

The system consists of a 100 mL glass reactor with a cooling water jacket to keep the reactor contents at constant temperature  $(27 \pm 0.5 \,^{\circ}\text{C})$ . Sonication probe (SONICS Vibra-cell, VCX 500 model) with a titanium tip of 13 mm diameter and 25 mm diameter, which emits ultrasound waves at 20 kHz and delivers a net power output of 500 W, is used for all the experiments. All the experiments were performed with 100 W set power.

#### 2.2.2. Experimental procedure

1,000 ppm of Reactive Black 5 stock solution was prepared by dissolving 1 gm of dye in 1,000 mL of distilled water. The prepared solution is stored in the dark and used for further solution preparation. From the stock solution, 10 ppm Reactive Black 5 dye solution was prepared for this study. The pH of the Reactive Black 5 solution was altered either by adding drops of 0.05 N sulphuric acid solution or 0.05 N sodium hydroxide solution. A small dosage in steps of 4.41, 8.82, 17.64, 26.46, 35.28 and 44.1 mmol/L of hydrogen peroxide was added to study its effect on RB5 dye colour removal. To study the effect of cavitation nuclei, the RB5 solution was purged with different gases such as Oxygen, Argon, Nitrogen and Air, respectively, for duration of 5 min, at the rate of 5 LPM which is sufficient enough to make the aqueous solution saturated with the respective gas nuclei. A minimal concentration of 0.5 mM ferrous sulphate was

taken for this study and its effect on colour removal of RB5 was done under different conditions, such as solution pH with ultrasound, pH 3 with ultrasound and with an optimized concentration of hydrogen peroxide, pH and ultrasound (Fenton's reagent). The salt, sodium chloride, was added to the RB5 aqueous solution to study the effect of it on the colour removal with different dosages, such as 5, 10, 20 and 30 g/L. All these experiments were also performed with a larger probe tip diameter of 25 mm to study the effect of it on the decolourization of RB5 solution. For all the experiments, the ultrasound was irradiated for an hour and the decolourization of RB5 was monitored using UV–vis spectrophotometer for every 15 min with intermittent sampling.

### 2.2.3. Analytical procedure

The optical absorption spectra of the Reactive Black 5 dye solutions were recorded by JASCO UV–Visible spectrophotometer with a quartz cuvette of 10 mm path length. The maximum peak in the absorption spectra for Reactive Black 5 is 597 nm. The UV–vis spectrum and the chemical structure of RB5 are shown in Fig. 1. Degradation intermediates were analysed using GC-MS (Perkin–Elmer Clarus 500).

## 3. Results and discussion

In this study, the suitability of ultrasound to decolourize the synthetically prepared Reactive Black 5 dye solution and its extent of decolourization with parametric variation like aqueous solution pH, H<sub>2</sub>O<sub>2</sub> concentration, gas bubbling (Oxygen, Argon, Nitrogen and Air), ferrous sulphate, Fenton's reagent, Probe tip diameter, initial dye concentration and sodium chloride were analysed and presented in the following section.

#### 3.1. Aqueous solution pH variation

Ultrasonic irradiation of 10 ppm dye solution was carried out at various pH (3.0, 5.0, 7.0, and 9.0). Fig. 2 shows the effect of initial pH on the decolourization efficiency. The variation in aqueous solution pH has significant influences on the colour removal of RB5. From the figure, it was obvious that acidic condition favours colour removal. The colour removal of the dye is highest when the pH of the aqueous dye solution is 3.0. This is due to the fact that in acidic conditions the RB5 molecule would attain more hydrophobic character resulting in higher availability of the RB5 molecule for ultrasound treatment [17]. There is a gradual decrease in the decolourization rate of RB5 solution under alkaline conditions. This is due to the loss of hydrogen molecule which makes the RB5 molecule more hydrophilic and it becomes difficult for the OH radicals produced out of the cavitation bubble to reach the RB5 molecules. The per cent colour removal of the dye is minimum when the pH is 7. The decolourization value increases for pH 9.0 because of the fact that the hydroxyl ions are more at base pH than at neutral pH. When compared with ultrasound (US) treatment alone, the aqueous solution pH variation study showed higher colour removal. The degradation of RB5 has followed pseudo-firstorder kinetics and the rate constant for ultrasound treatment alone is found to be  $3.44 \times 10^{-3} \text{ min}^{-1}$ . The rate constant for RB5 aqueous solution at pH 3 is found to be  $7.36 \times 10^{-3} \text{ min}^{-1}$ .

#### 3.2. Hydrogen peroxide dosage variation

Fig. 3 shows the colour removal efficiency of the RB5 dye solution for different dosage of hydrogen



Fig. 2. Decolourization of RB5 dye solution with the variation of initial pH [US Irradiation time—1 h, RB5 conc. 10 ppm].



Fig. 3. Decolourization of RB5 dye solution with the variation of  $H_2O_2$  [US Irradiation time—1 h, RB5 conc. 10 ppm, Solution pH].

peroxide. The dosage of hydrogen peroxide for 100 mL of 10 ppm of Reactive Black 5 solution was 4.41, 8.82, 17.64, 26.46, 35.28 and 44.1 mmol/L. It was observed that for 8.82 mmol/L H<sub>2</sub>O<sub>2</sub> dosage, the colour removal percentage is highest (35%) and it was lowest for 44.1 mmol/L H<sub>2</sub>O<sub>2</sub> (11.85%). This can be explained by the scavenging of OH<sup>•</sup> radicals with excess production of H<sup>•</sup> radicals and OH<sup>•</sup> radicals to form H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> again without undergoing oxidation reaction after a certain concentration of H<sub>2</sub>O<sub>2</sub> (26]. The rate constant for 8.82 mmol/L H<sub>2</sub>O<sub>2</sub> ultrasound treated RB5 aqueous solution is  $7.03 \times 10^{-3} \text{ min}^{-1}$ .

## 3.3. Bubbling gas variation

The gases Oxygen, Argon, Nitrogen and Air are bubbled one at a time for about 5 min in the aqueous solution of RB5 to make the respective gases saturated. The study of gas bubbling was done to understand the mechanism of degradation of RB5 dye by ultrasound process and again this would pave a way to intensify the colour removal rate of dye solution. Since inducing ultrasound into any solution undergo cavitation reaction (which is purely a bubble dynamics phenomena), the content of the nuclei has greater influence on the net result (i.e. production of OH • radicals). In this case, as mentioned earlier, four gases were considered to understand the behaviour of RB5 dye colour removal and with which the mechanism/ location of degradation could be deduced. Fig. 4 shows the decolourization of the azo dye Reactive Black 5 with various gas nuclei. The experimental results clearly indicate that the variation in the bubble



Fig. 4. Decolourization of RB5 dye solution with purging of gases [US Irradiation time—1 h, RB5 conc. 10 ppm, Solution pH].

content has greater influence on the colour removal rate. The maximum decolourization of 28% occurs for argon-bubbled RB5 solution followed by oxygen (20%), air (18%) and nitrogen (16%). This is due to the inert nature of argon gas and apart from this argon is having a higher heat capacity ratio leading to higher temperatures and pressures than other gases during the cavitation event producing higher OH<sup>•</sup> radicals required for oxidation [11,27]. In general, mono-atomic gases like helium, argon, krypton, etc. have the highest specific heat ratio ( $\gamma = 1.67$ ), and final collapse temperature for a monatomic gas could be two times higher than that of a triatomic gas. Another factor which needs to be considered in the case of gas bubbling is the solubility. More soluble is the gas, more availability of nuclei for cavitation event [28]. Though the presence of oxygen enhances the colour removal rate, it acts as a scavenger of hydrogen atom and hydroperoxyl radical causing a number of other reactions to occur in the form of  $H_2O_2$ ,  $O_2$ , O and  $H_2$  [29]. Lower decolourization with nitrogen-bubbled RB5 solution can be explained as the nitrogen molecules may react with hydroxyl radicals and oxygen atoms to form oxides of nitrogen reducing the activity of OH<sup>•</sup> radicals with RB5 molecules [28]. The rate constants for argon and nitrogen-bubbled ultrasound-treated RB5 aqueous solution are 5.44 and  $3.12 \times 10^{-3} \text{ min}^{-1}$ , respectively. The gas bubbling experiments provide an indication that the higher availability of OH<sup>•</sup> radicals in the bulk liquid medium is more significant and enhances the colour removal rate of RB5 dye solution.

## 3.4. Combined effect of pH and the bubble content

It was known from the pH variation study and gas bubbling study (Sections 3.1 and 3.3) that for achieving efficient colour removal, RB5 molecules should prevail in hydrophobic form and higher OH<sup>•</sup> radicals should be available sufficient enough to interact with RB molecule. Hence, with an aqueous solution in an acidic medium and bubbling of gas would provide good interaction between OH<sup>•</sup> radicals and RB5 molecules. The experimental results further show a good improvement in the colour removal efficiency of RB5 aqueous solution with the conditions of pH 3 and gas bubbling. Although the colour removal efficiency trend followed is the same for gas bubbling as like in section 3.3, but there is significant improvement in the efficiencies for all gases as shown in Fig. 5. For argon, it is 53% colour removal followed by oxygen (44%), air (29%) and nitrogen (27%). Their respective rate constants were 12.16, 10, 5.64 and  $4.99 \times 10^{-3}$  $\min^{-1}$ , respectively. This study gives evidence that the RB5 molecules would be having very good interaction with the produced OH • radicals efficiently if it is in hydrophobic form which is favoured at acidic pH.

### 3.5. Effect of electrolyte (Sodium chloride)

The degradation of dyes was highly influenced by the amount of dissolved salts that are present in the aqueous solution and the dissolved salts were one major integral part of textile wastewater. The addition of sodium chloride increases ionic strength of the aqueous solution phase, which drives the organic compounds to the bulk-bubble interface [30]. Apart from these changes, the properties of the solution such as viscosity, vapour pressure and heat capacity will also be changed accordingly with the addition of



Fig. 5. Decolourization of RB5 dye solution with purging of gases at pH 3 [US Irradiation time—1 h, RB5 conc. 10 ppm].

sodium chloride. These changes to the dye could provide a good interaction between OH radicals produced out of the cavitation bubble and the dye molecule which are brought near to the bulk-bubble interface. RB5 dye is highly soluble in water and has relatively lower vapour pressure. With these properties, it is expected that the degradation of RB5 dye could occur through hydroxylation in the bulk liquid medium [31]. Fig. 6 shows that with the addition of NaCl there was increased colour removal till 1g of NaCl addition to 10 ppm of RB5 aqueous solution when compared with ultrasound treatment alone. These results give an indication that the RB5 could be treated effectively when they are brought near to the surface of the bubble-bulk interface. The decreased colour removal rate of RB5 aqueous solution after 1 g NaCl addition could be explained with the increased number of NaCl molecules which suppress the interaction of RB5 molecule with OH<sup>•</sup> radicals.

## 3.6. Effect of Fenton's reagent

The Fenton's reagent is a homogeneous catalytic oxidation process which is the combination of an oxidizing reagent (Hydrogen Peroxide) and the catalyst (an oxide or metal salt, usually iron) to produce hydroxyl radicals (OH<sup>•</sup>) capable of destroying a wide range of organic pollutants in water and wastewater [10,32]. The hydroxyl radicals are generally referred to as primary oxidizing chemical species generated in accordance with the fundamental equation. In an acidic environment, upon ultrasound irradiation, the ferrous ion initiates and catalyses the decomposition of  $H_2O_2$ , resulting in the generation of OH<sup>•</sup> [33–35]. The overall reaction is:



Fig. 6. Sonication of RB5 dye solution with the dosage of electrolyte sodium chloride [US Irradiation time—1 h, RB5 conc. 10 ppm].

$$Fe^{2+} + H_2O_2 \to Fe^{3+} + HO^- + OH^{\bullet}$$
 (1)

Hydroxyl radicals are powerful oxidation agents that have an oxidation potential of 2.8 eV [12,36]. They are capable of rapidly attacking organic substrates (RH) and cause chemical decomposition of these compounds by H-abstraction and addition to C–C unsaturated bonds [13]:

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

$$R^{\bullet} + Fe^{3+} \rightarrow R^+ + Fe^{2+}$$
(3)

Numerous competing reactions which involve Fe<sup>2+</sup>, Fe<sup>3+</sup>, H<sub>2</sub>O<sub>2</sub>, hydroxyl radicals, hydroperoxyl radicals and radicals derived from the substrate, may also be involved. The influence of Fe<sup>2+</sup> for the ultrasonic decolourization of 10 ppm RB5 aqueous solution was studied in conditions of 0.5 mM  $\text{Fe}^{2+}$ , pH 3 + 0.5 mM $Fe^{2+}$  and Fenton's reagent (pH 3 + 0.5 mM  $Fe^{2+}$  +  $8.82 \text{ mmol/L H}_2O_2$ ), respectively. The results as shown in Fig. 7 clearly indicate that there is a drastic increase in the decolourization rate of RB5 aqueous solution with Fenton's reagent-assisted ultrasound treatment. The colour removal observed was ~94% when treated with Fenton's reagent, and it was only ~18 and ~35% with  $0.5 \text{ mM Fe}^{2+}$  treatment and pH  $3 + 0.5 \text{ mM Fe}^{2+}$ , respectively. It should also be noted that ~94% colour removal was observed within 15 min of treatment time. Hence, Fenton's reagent-assisted ultrasound treatment of RB5 dye proved not only as an effective treatment but also a faster treatment among the treatment methods studied (rate constant is  $39.59 \times 10^{-3} \text{ min}^{-1}$ ). The reason could be the effective OH<sup>•</sup> radical production, better interaction of OH radicals with RB5 molecule and continuous regeneration of  $Fe^{2+}$  [37] which leads to



Fig. 7. Effects of Fenton's reagent.

continued production of OH<sup>•</sup> radicals to react with RB5 molecules.

#### 3.7. Effect of initial concentration variation

The effect of initial dye concentration on the colour removal of Reactive Black 5 were performed with concentrations of 10, 50, 100, 500 and 1,000 ppm to evaluate the effectiveness of the Fenton's reagent at pH 3,  $0.5 \text{ mM Fe}^{2+}$  and  $8.82 \text{ mmol/L H}_2O_2$ . Fig. 8 indicates that the reaction conditions help in colour removal at a faster rate for lower dye concentration and as the initial dye concentration increases the colour removal rate



Fig. 8. Effect of initial RB5 concentration.

decreases [38]. With the condition studied, 10, 50, 100 and 500 ppm RB5-treated solutions resulted in the complete colour removal whereas for 1,000 ppm, 61% colour removal was attained. For 100 and 500 ppm, the colour removal rate was faster than 10 and 50 ppm RB5 solution. As the number of the RB5 molecules increases to a very large extent, there would be no sufficient OH<sup>•</sup> radicals available to react with RB5 molecules and hence there is a reduction in colour removal rate of the RB5 at very high RB5 concentration (1,000 ppm).

#### 3.8. Effect of probe tip diameter

The experiments are carried out for 25 mm probe with various operating conditions as done for 13 mm probe and the results are shown in Fig. 9. For all the conditions, it was found that the colour removal was greater for 25 mm probe than 13 mm probe. It is obvious that this happens due to the larger areas of irradiating surface in 25 mm probe compared with 13 mm probe for the same power input, and the ultrasound intensity produced was higher in 25 mm probe than with 13 mm probe [3,39]. Larger areas of irradiating surface lead to the increased cavitation event and increased OH<sup>•</sup> radical production for the same conditions studied as with 13 mm probe. In the case of Fenton's reagent study, for 25 mm probe treatment complete colour removal (~99%) of RB5 was observed. The rate constants were 5.4, 10.69, 10.22, 10.87 and  $65.12 \times 10^{-3} \text{ min}^{-1}$  for the conditions studied (Ultrasound alone, pH 3, Argon bubbling, 1g NaCl and Fenton's reagent treatment). This study gives evidence



Fig. 9. Effect of ultrasound probe tip diameter.



Fig. 10. Gas chromatogram of the ultrasound-assisted Fenton's-treated RB5 dye.

Table 1 List of fragmented compounds from GC-MS through ultrasound-assisted Fenton's-treated RB5 dye

S.no.	Retention time (min)	Chemical name	Molecular formula
1.	16.63	3-Hexadecene	C <sub>16</sub> H <sub>32</sub>
2.	18.90	2,4-bis(1,1-dimethylethyl)-Phenol	C <sub>14</sub> H <sub>22</sub> O
3.	19.79	E-15-Heptadecenal	C <sub>17</sub> H <sub>32</sub> O
4.	20.73	2-(methylthio)-Benzothiazole	$C_8H_7NS_2$
5.	23.03	1-Octadecene	$C_{18}H_{36}$
6.	25.15	Heneicosane	$C_{21}H_{44}$
7.	29.40	Heneicosane	$C_{21}H_{44}$
8.	31.53	1-Nonadecanol	$C_{19}H_{40}O$
9.	34.36	1-Tetracosanol	$C_{24}H_{50}O$

that higher probe tip diameter can relatively reduce the pollutant treatment time. treatment which would further mineralize the listed compounds into  $CO_2$  and  $H_2O$ .

## 3.9. GC-MS analysis

All the above experimental studies were quantified with colour removal of RB5 dye. As colour removal doesn't provide evidence of complete pollutant removal, GC-MS experiments were performed to identify the intermediates formed upon the degradation of RB5 dye. The GC spectra and the list of compounds fragmented out of the treated RB5 (10 ppm) dye aqueous solution under ultrasound-assisted Fenton's treatment is shown in Fig. 10 and Table 1. The OH\* radicals undergo oxidation reaction by attacking the RB5 dye through the cleavage of -N=N- (azo group) resulting in several other compounds as listed in Table 1. The compounds listed prove that the RB5 molecule had undergone complete colour removal but produced several organic compounds as from GC-MS analysis. Hence, the RB5 dye requires further

## 4. Conclusions

In this experimental study, the colour removal of Reactive Black 5 dye was investigated by varying several parameters with the application of ultrasound. The pH variation study showed acidic pH of 5 is favourable for RB5 dye degradation. The reaction kinetics had followed pseudo-first-order rate reaction. Addition of the strong oxidant had enhanced the colour removal rate of RB5 dye than with mere ultrasound treatment. Cavitation bubble variation study, combined pH (3) and cavitation variation study and NaCl addition studies showed strong evidence that good interaction between the RB5 molecule and produced OH radicals would result in the efficient treatment of RB5 dye. It can be understood that the degradation of RB5 would occur in the bulk liquid medium through hydrolysis of OH<sup>•</sup> radicals. Fenton's treatment (which produces  $OH^{\bullet}$  radicals in the bulk liquid medium) of RB5 dye aqueous solution with the best experimental conditions such as pH 3, 8.82 mmol/L H<sub>2</sub>O<sub>2</sub>, a minimal of 0.5 mM Fe<sup>2+</sup> concentration and 25 mm probe tip diameter leads to complete colour removal. GC-MS analysis provided an indication that the ultrasound-treated Fenton's treatment of RB5 dye had resulted in the complete colour removal and the intermediates identified indicates the need for further treatment for complete pollutant removal. Further, the initial concentration variation study with ultrasound-assisted Fenton's treatment appears that the present methodology is viable for textile wastewater treatment.

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