



Thermal-pressure-mediated hydrolysis of Reactive Blue 19 dye

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ABSTRACT

The thermal-pressure-mediated hydrolysis rates and the degradation kinetics of environmentally persistent Reactive Blue (RB) 19 dye were studied. The dye decomposition was studied at 40–120 °C, pH 2–10, and atmospheric pressure range of 1–2 atm. The intermediates and end products formed during the degradation were identified using gas chromatography/mass spectrometry and a possible degradation pathway of RB 19 was proposed. The stability of the dye in aqueous solution was influenced by changes in pH. At pH 4, half-life was 2247.5 min at 40 °C and it reduced to 339.4 min when the temperature was increased to 120 °C. Acidic conditions were more conducive to enhance hydrolysis rate than basic ones as the decomposition was optimum at pH 4. The kinetic studies indicated that the rate of hydrolysis apparently followed first order reaction. A linear relationship was observed between hydrolysis rate of RB 19 dye and increasing temperatures and pressures. Overall, 23% dye decomposition occurred in 120 minutes at pH 4, 120 °C and pressure of 2 atm. Along with thermal-pressure, a combination of techniques like physico-chemical, biological, enzymatic etc. may be more suitable choice for the effective treatment of RB19 dye.

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1. Introduction

Dyes are used in a number of industries such as textile, leather, food, pharmaceutical, plastics, cosmetics and paper printing [1,2]. There exist various classes of dyes, like azo, anthraquinone, reactive, acidic, basic, neutral, disperse and direct dyes. But the most commonly used dyes are azo and anthraquinone dyes [3–5]. They constitute more than 60% of reactive dyes. Wastewater discharged from Textile industries contains high concentrations of reactive dyes and other contaminants that pose serious threats to sustainability of natural ecosystems [6]. Further, dyes disturb aquatic ecosystems by obstructing light penetration and oxygen transfer into water bodies [7]. Moreover, the contamination of reactive dyes may present a risk to the aquatic living organisms through bioaccumulation thus entering into food chain [8,9]. Toxicity of reactive dyes has been reported at concentrations as low as 5.2 mg L⁻¹ [10].

Recently, different methods dealing with treatment of textile wastewater like conventional methods including physico-chemical treatment [6], biological oxidation [11], adsorption and advanced oxidation processes (AOPs), e.g. ozonation, photolysis, electrochemical, sonolysis [12,13] etc., have been investigated. Usually, these processes lead to the release of more toxic products than

the parent compound that prove fatal for the living creatures [14]. Hydrolysis is one of the principal detoxification mechanisms for organic compounds. At high temperature and pressure, pure liquid water becomes surprisingly effective medium for the degradation of organic compounds. By increasing pressure the rate of chemical reaction increases due to increase in dissociation constant of water. Rapid conversions are observed for the majority of organic compounds [15]. Also hydrolysis by-products are normally less toxic to the environment than parent compound [16].

Water at high temperature and pressure simultaneously acts as a solvent, catalyst and reagent for reactions that are typically catalyzed by acids or bases. By using this process very selective transformations are accessible by reactions in pure, hot water without using toxic and environmentally destructive materials [15].

The objective of the present study was to investigate the rate of hydrolysis at different pH, pressure and temperature conditions and its kinetics to comprehend the degradation of RB 19 dye. The intermediates and end products were identified and a possible degradation pathway was proposed.

2. Experimental

2.1. Synthetic dye solution

The commercial color index (CI) Reactive dye (Reactive Blue (RB) 19, molecular weight = 626.54) was generously provided by Arzoo

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Textile Mills, Faisalabad, Pakistan which was used without further purification. The stock solution of RB19 was prepared at lab scale by dissolving 1000 mg in a liter of distilled water. For the hydrolysis studies the stock solution was further diluted as per requirements of the experiment.

2.2. Experimental procedure

Synthetic dye solution was distributed into different flasks (1 L capacity) and then pH was adjusted as per requirements of the experiment with the help of pH meter (HANNA of model HI 99003). The initial pH of the sample was set by using dilute sodium hydroxide (1 M) or hydrochloric acid (1 M). The initial dye concentration in each sample was 100 mg L⁻¹ after dilution contained in 200 mL of the sample. The hydrolysis experiments were conducted in autoclave under different conditions of temperatures (40, 60, 80, 100, 120 °C) and pressures (1 and at 2 atm pressure). Various pH conditions used were 2, 4, 6, 8 and 10. Each experiment was conducted for 2 h and samples were drawn at time intervals of 30, 60, 90 and 120 minutes to measure the dye decomposition. Each experiment was performed in duplicates.

2.3. Analytical procedures

The color and concentration of dye in the treated effluents were determined by using UV Spectrophotometer (IRMECO of Model U2020) at scanning spectrum of 200–800 nm [17]. In order to determine the percentage decolorization, following formula was used.

$$\text{Dye decolorization(\%)} = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

where, C_t and C_0 are the concentrations (mg L⁻¹) of dye at reaction time t and 0, respectively [17]. Residual dye concentrations were determined by using the value of absorbance at the characteristic wavelength ($\lambda_{\text{max}} = 256$) from the spectrum. Changes in concentration in the solution were calculated by Beer–Lambert law.

$$A = \epsilon l C \quad (2)$$

where A is the absorbance, l , the path length (cm), ϵ , the molar extinction coefficient (mol⁻¹ cm⁻¹) and C , the dye concentration at time t (mol/dm³) [18,19].

The total organic carbon (TOC) of the samples was determined using TOC analyzer (Shimadzu, model TOC-V CSH). The instrument was operated at 680 °C furnace temperature and 20 mL sample injection. Reduction in percentage total organic carbon content was measured using following equation [19,20].

$$\text{TOC(\%)} = \frac{(\text{TOC}_{\text{initial}} - \text{TOC}_{\text{final}})}{\text{TOC}_{\text{initial}}} \times 100 \quad (3)$$

The degradation products were identified using gas chromatography/mass spectrometry (GC–MS) (PerkinElmer Clarus 600). The samples were collected at different time intervals and were extracted according to the procedure reported in the literature [21]. The GC was equipped with an Elite-xlb column (30 m × 0.25 mm) and 0.25 μm film thickness and connected directly to MS. The GC column was operated at 40 °C for 1.50 min which was then increased to 300 °C at the rate of 20 °C/min. The other experimental conditions were: helium as a carrier gas with the flow rate of 1 mL, sample volume 1 μL, injection temperature 200 °C, injection mode split, and split ratio is 50.

2.4. Statistical analysis and graphical work

All determinations were performed in duplicate and mean values are presented in the results. Statistical comparisons of the mean values were performed by analysis of variance (ANOVA), followed

by Duncan's multiple range test ($p < 0.05$), using SAS 8.3 software (SAS Ins. Inc., Cary, USA). Graphical work was carried out using computer program Sigma Plot™ v.10.

3. Results and discussions

3.1. Effect of pH

The decomposition rate of the dye under investigation was highly influenced by the reaction pH as shown in Fig. 1. A significant increase ($p < 0.05$) in the percentage decomposition of dye was observed with the decreasing pH and the highest value was obtained in acidic conditions. It seemed that the hydrolytic reaction might have been catalyzed by hydronium ions in acidic medium. Since hydrogen ions (H⁺) are not consumed during hydrolysis and just act as a catalyst, so they acts as a better catalyst as compared to OH⁻ for the conversion of RB 19 dye in to inorganic compounds [22].

Moreover, the H⁺ ions not only act as catalysts but also enhance the electro negativity of the leaving group in acidic conditions, which helps in breaking of the bonds in the RB 19 dye. Thus, the rate of hydrolysis continues to increase with increasing H⁺ ion concentrations [15]. The present experiment had an interesting observation that hydrolytic rate did not increase further when pH was lowered below 4. Insignificant difference for dye degradation was observed for pH 2 and 4, but we considered pH 4 as optimum experiment due to convenience. Our results are in agreement with Rajkumar et al. [21].

3.2. Effect of temperature and pressure

As the temperature and pressure were increased from 40 to 120 °C and atmospheric pressure to high pressure, the rates of decomposition were also significantly ($p < 0.05$) increased Fig. 2. Water provides more suitable and favorable reaction medium at high temperature than boiling water at atmospheric pressure for organics. With the increase in temperature from 40 to 120 °C, the ionic product (dissociation constant) of water increases and the dielectric constant of water falls rapidly. These changes in the physical properties alter the solvent properties of water [15].

At high temperature and pressure, water acts simultaneously as a convenient solvent, catalyst and reagent for reactions that are typically catalyzed by the acid or base. High temperature and pressure makes the water as the most effective medium for reactions of the organic compounds. Moreover, the chances of pollution are

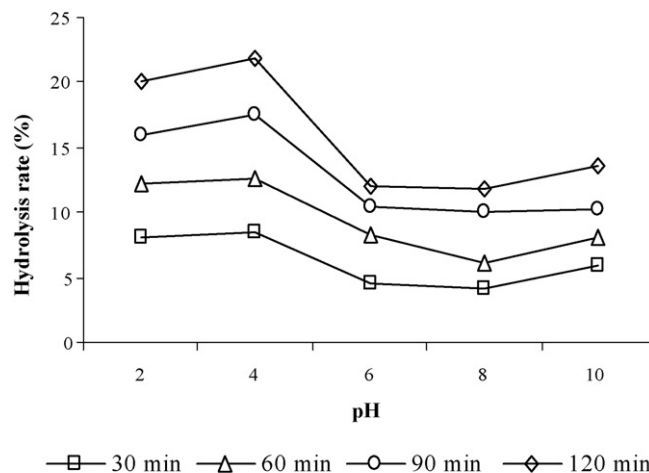


Fig. 1. Effect of pH on the hydrolysis of RB 19 dye at 120 °C and 2 atm pressure.

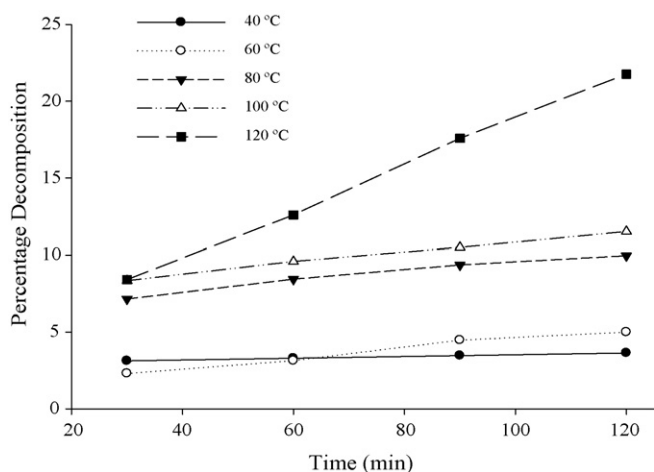


Fig. 2. Effect of different temperatures on the percentage decomposition of RB 19 dye.

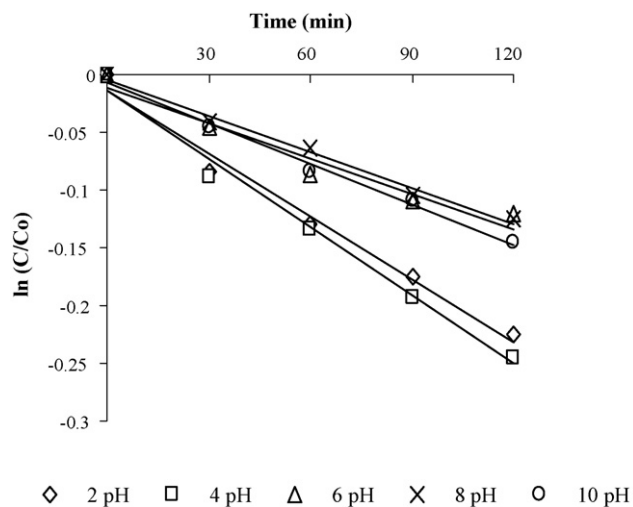


Fig. 4. Determination of order of reaction at 120 °C.

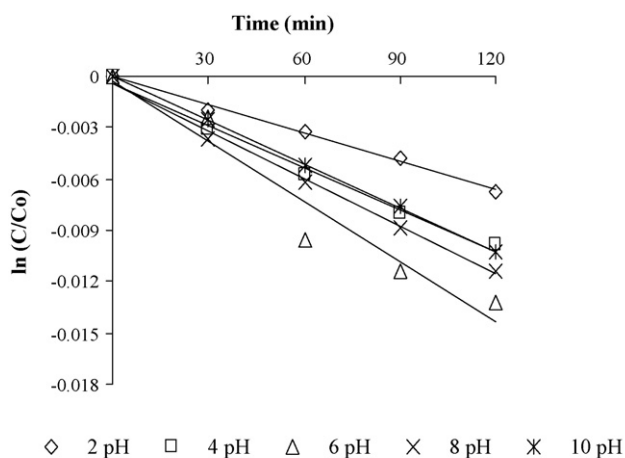


Fig. 3. Determination of order of reaction at 40 °C.

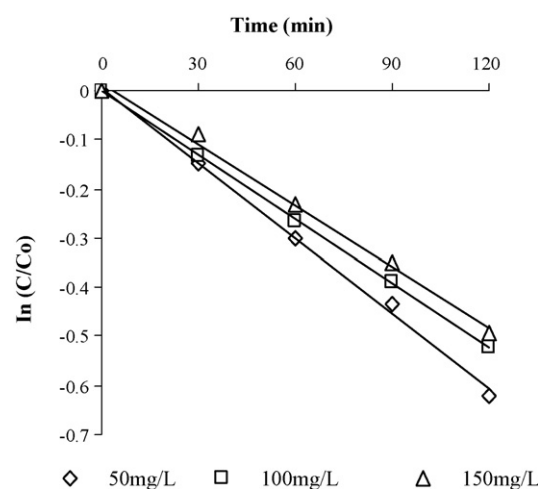


Fig. 5. First order kinetic plot of RB19 dye degradation by hydrolysis process at different concentrations at 120 °C.

also less and it is an environmental friendly process of treating the organic compounds.

3.3. Decomposition kinetics of RB 19 dye

Under different conditions of temperatures (40, 60, 80, 100 and 120 °C) and pressures (1 and 2 atm) the reaction order was determined as a function of pH by plotting a graph between the reciprocal of remaining dye concentrations against time at pH values 2–10. The dye decomposition followed 1st order of kinetics as shown previously [23] (Figs. 3 and 4).

The decomposition kinetics were determined for different RB 19 dye concentrations for various time intervals, temperatures and pressures (Table 1). Values of rate constant (*k*) for first, second and third order showed that the reaction followed first order for various experimental conditions under investigation.

The order of reaction was confirmed by plotting the graph between the $\ln(C_t/C_0)$ against time (Fig. 5) at different initial con-

Table 1
Determination of rate constant (*k*) for 1st, 2nd and 3rd order of reaction at pH 4.

Concentrations (mg L ⁻¹)	Reaction time (min)	1st order kinetics $k = 2.303/t \log a/a - x$	2nd order kinetics $k = 1/at \cdot x/a(a - x)$	3rd order kinetics $k = 1/t \cdot x(2a - x)/2a^2(a - x)^2$
50	30	0.04	0.1×10^{-3}	0.3×10^{-5}
	60	0.04	0.1×10^{-3}	0.2×10^{-5}
	90	0.04	0.1×10^{-3}	0.2×10^{-7}
	120	0.04	0.1×10^{-3}	0.2×10^{-5}
100	30	0.04	0.7×10^{-4}	0.5×10^{-3}
	60	0.39	0.6×10^{-4}	0.5×10^{-6}
	90	0.04	0.5×10^{-4}	0.5×10^{-6}
	120	0.04	0.6×10^{-4}	0.3×10^{-4}

Note: temperature: 120 °C, pressure: 2 atm.

Table 2
Integrated rate law and regression coefficient for first order reaction at different concentrations of RB19.

c mg ⁻¹	First order $\ln C = -k_1t + C'$	R ²
50	$\ln C = -0.1528t + 0.1574$	0.99
100	$\ln C = -0.1304t + 0.1294$	0.99
150	$\ln C = -0.125t + 0.1418$	0.99

Note: temperature: 120 °C, pressure: 2 atm.

centrations, by employing first order rate equation.

$$\ln \left(\frac{C_t}{C_0} \right) = -kt \quad (3')$$

where, C is the dye concentration at time *t* and *o* is the concentration (mg L⁻¹), *k* is first order rate constant (min⁻¹) and *T* is reaction time in minutes [24].

The correlation between $\ln(C_t/C_0)$ and treatment time was linear (straight line). This was a typical first order reaction plot (Fig. 5). The slopes of the lines gave the apparent rate constant (*k*). The regression coefficient *R*² obtained (Fig. 5) for first order reaction at different concentrations of RB 19 is shown in (Table 2). The *R*² values ranged from 0.9998 to 0.995, confirming that hydrolysis of RB 19 followed the first order reaction.

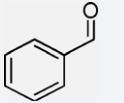
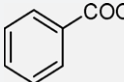
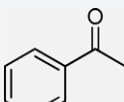
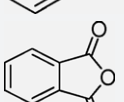
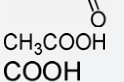
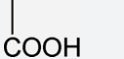
Carneiro et al. [19,20] evaluated the dependence of initial decomposition rate on the RB 4 dye concentration from slopes of the curves $\ln(A - A_\infty)$ as a function of time. The results obtained from his study showed that the curves of $\ln(A - A_\infty)$ vs. time are linear and the degradation followed a first order kinetic with a rate constant. The results described in Fig. 5 are in good agreement with those reported in literature [25].

Table 3
Effect of different conditions of temperature on half-life reduction.

	Temperature °C				
	40	60	80	100	120
<i>k</i> (min ⁻¹)	0.31×10^{-3}	0.42×10^{-3}	0.87×10^{-3}	1.02×10^{-3}	2.04×10^{-3}
<i>t</i> _{1/2} (min)	2247.5	1630.5	792	681.6	339.4

Note: dye concentration = 50 mg L⁻¹, time = 20 min, pH 4.

Table 4
Intermediates identified by GC–MS analysis.

Compounds	Structure	Time (min)					
		10	20	30	45	60	120
Benzaldehyde		P	P	P	A	A	A
Benzoic acid		P	A	A	P	P	A
Acetophenone		P	A	A	A	A	A
Isobenzofuran-1,3-dione		P	A	A	A	A	A
Acetic acid		A	P	P	P	P	P
Oxalic acid		A	A	P	P	P	P

P: present, A: absent. Note: dye concentration = 500 mg L⁻¹, temperature: 120 °C and pressure: 2 atm, pH 4.

The reaction kinetics describes the reaction rates while the reaction order defines the dependence of the reaction rate on the concentrations of reacting species. The reaction order is determined experimentally and not necessarily related to the stoichiometry of the reaction. However, it is governed by the mechanism of the reaction, that is, by the number of chemical species that must collide for the reaction to occur [26]. The reaction rate for first order kinetics depends on one species. Thus the mechanism involved in the thermal-pressure hydrolysis of RB 19 was the first order reaction.

3.4. Half-life reduction

Increasing temperature from 40 to 120 °C resulted in the significant (*p* < 0.05) decrease of half-life. At pH 4, half-life was 2247.5 min at 40 °C which reduced to 339.4 min when the temperature was increased to 120 °C. The values of rate constant and half-life at different temperatures and pH 4 are shown in (Table 3). Because the reaction order for the RB 19 decomposition was first order, therefore following equation was used to determine the half-life.

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

Half-life has been calculated for the degradation of organophosphorous pesticides, under natural conditions and under high temperatures and pressures. It was found that half-life decreased with increasing temperatures and pressures [15–22].

3.5. Total organic carbon (TOC) reduction

The most common way of estimating the dye degradation in its intermediates and end products is to monitor the reduction in TOC. In our experiment, almost 32.8% TOC reduction was attained from the treated samples under following optimized conditions: dye concentration 100 mg L^{-1} , initial pH 4, temperature 120°C , pressure 2 atm and reaction time 120 min. The reduction in TOC indicated the loss of reactive group during the reduction process. Although we obtained considerable reduction of TOC (32%) which was comparable to previous studies [21,27,28]; however, it was also noted that dye oxidation takes longer time compared with previous studies.

3.6. GC–MS analysis of degradation products

The products which were formed during the degradation of RB 19 were identified by GC–MS as shown in Table 4. Samples at different intervals were collected during the hydrolysis of 500 mg L^{-1} RB 19 at pH 4.0. The degradation pathway was proposed and illustrated in Fig. 6. In this process of oxidation the C(5)–C(6), C(13)–C(14), C(6)–C(7), C(12)–C(13), C(8)–N, C(9)–S, C(11)–N, C(17)–S, C(15)–N bonds were prone to cleave. The treatment of dye after 10 min showed the formation of benzaldehyde, acetophenone, benzoic acid and isoindoline-1,3-dione. Benzaldehyde was formed through the cleavage of C(6)–C(7) and C(13)–C(14), whereas

benzoic acid was formed after the oxidation of benzaldehyde. The isoindoline-1,3-dione may be formed after the cleavage of C(6)–C(7) and C(12)–C(13) bonds. The compounds identified after 20 min treatment were similar except the appearance of acetic acid peak and disappearance of isoindoline-1,3-dione. The samples at 30 min showed the presence of benzaldehyde, acetic acid, and newly appeared oxalic acid peak. The formation of oxalic acid and acetic acid resulted from the ring cleavage and its further oxidation was also evident by the products determined after the final treatment for 120 min.

3.7. Correlation of decolorization with GC–MS degradation products

It was observed that a maximum of 31% decolorization took place with first 30 minutes of treatment (Table 5). GC–MS results showed that RB19 dye broke into benzaldehyde, benzoic acid, acetophenone, isoindoline-1,3-dione by the cleavage of its chromophores within first 30 minutes which might have caused a maximum decolorization within this time period. Moreover, the benzoic acid, acetophenone and isoindoline-1,3-dione were decomposed into either acetic acid or oxalic acid that might have resulted in decolorization. However, ultimate decolorization occurred was 74% due to RB19 decomposition after 120 minutes as indicated by GC–MS results.

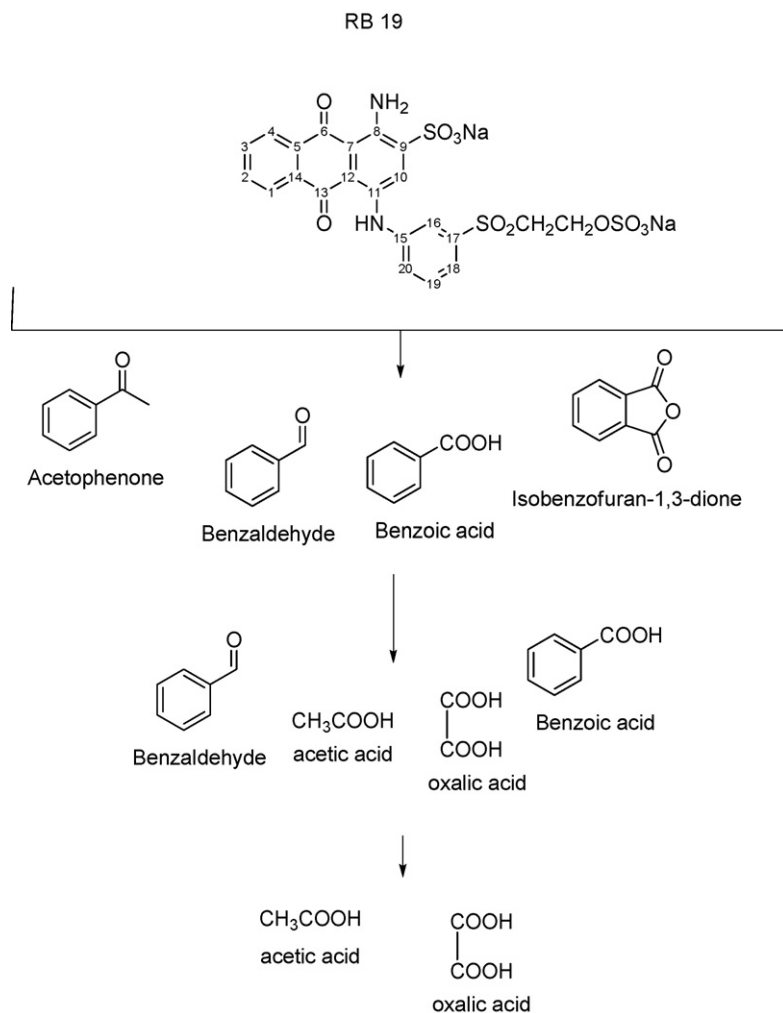


Fig. 6. Proposed degradation pathway of RB 19 dye by thermal pressure-mediated hydrolysis at pH 4, conc: 500 mg L^{-1} , temp: 120°C , pressure: 2 atm.

Table 5
Percentage decolorization (%) of Reactive Blue 19 dye at pH 4.

Time (min)	Percentage decolorization
30	31.05
60	48.28
90	61.47
120	74.39

Note: dye concentration = 100 mg L⁻¹, temperature: 120 °C and pressure, 2 atm.

4. Conclusions

1. The rate of hydrolysis of RB 19 dye increased with increasing temperatures and pressures. Decomposition of dye was optimum at pH 4. Kinetics studies indicated that the rate of hydrolysis apparently followed the 1st order reaction. At pH 4, half-life was 2247.5 min at 40 °C and it reduced to 339.4 min when the temperature was increased to 120 °C.
2. The major intermediate and end products formed during the degradation were identified through GC–MS as benzaldehyde, acetophenone, benzoic acid and isoindoline-1,3-dione, acetic acid and oxalic acid. The degradation pathways was proposed after careful examination of degradation products, further research is required to find out the precise mechanism of the degradation pathways of RB19 dye through thermal-pressure-mediated hydrolysis.
3. Overall, 23% dye decomposition occurred in 120 minutes at pH 4, 120 °C and pressure of 2 atm. It implies that this technique alone is not sufficient to deal with the treatment of RB19 dye containing wastewaters. A combination of techniques like physico-chemical, biological, enzymatic, etc. is required for the effective treatment of RB19 dye.

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