Thermal-pressure-mediated hydrolysis of Reactive Blue 19 dye

Maria Siddique [a], Robina Farooq [b,*], Abda Khalid [a], Ather Farooq [b], Qaisar Mahmood [a], Umar Farooq [b], Iftikhar Ahmad Raja [a], Saleem Farooq Shaukat [c]

[a] Department of Environmental Sciences, COMSATS Institute of Information Technology, Abbottabad 22060, Pakistan
[b] Department of Chemistry, COMSATS Institute of Information Technology, Abbottabad 22060, Pakistan
[c] Department of Electrical Engineering, COMSATS Institute of Information Technology, Abbottabad 22060, Pakistan

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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.

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

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.

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

where, C_t and C_o 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 ($\lambda_{max} = 256$) from the spectrum. Changes in concentration in the solution were calculated by Beer–Lambert law.

$$A = l\varepsilon C \qquad (2)$$

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/dm^3) [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].

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

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 than 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^{TM} 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
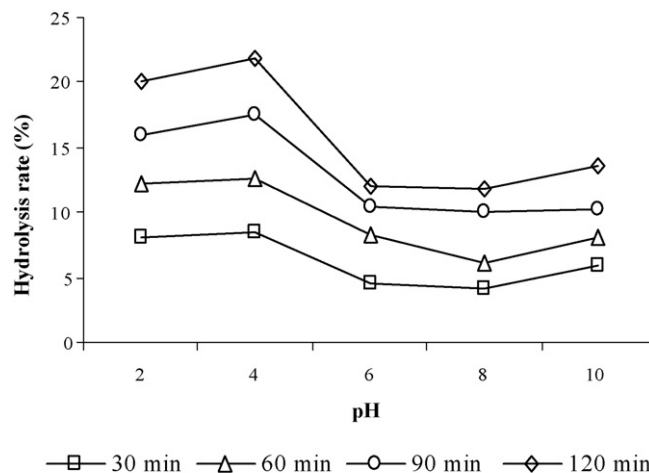

Fig. 1. Effect of pH on the hydrolysis of RB 19 dye at 120 °C and 2 atm pressure.