Treatment of C.I Reactive Blue 160 by ozonation system

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Abstract. This study was carried out to assess the treatment ability of color, dye, and COD in the dyeing wastewater containing C.I Reactive Blue 160 by ozonation system. Both batch and continuous operating modes with concurrent and counter-current flows were investigated. The effects of the ozone gas flow rate, pH, temperature, Na₂CO₃ concentration, and initial dye concentration were evaluated. The decolorization, dye removal efficiencies, and mineralization ability of COD by ozonation were determined. The results indicated that ozonation had high efficiency in the treatment of dyeing wastewater containing C.I Reactive Blue 160. The treatment performance was affected by the ozone gas flow rate, pH, temperature, Na₂CO₃ concentration, and initial dye concentration. The removal efficiency of color, dye, and COD were 98.04%, 99.84%, and 87.31% for the treatment of 200 mg/L initial dye concentration in batch mode with 30 min ozonation time, respectively. In the continuous operation and counter-current flow, the color, dye, and COD removal efficiencies reached 97.24%, 99.76%, and 86.38% after 30 min HRT, respectively, and higher than concurrent flow. The reaction of ozone and C. I Reactive Blue 160 was the first-order reaction in both batch and continuous operation. The complete mineralization required 90 min ozonation time.

Keywords: C.I. Reactive Blue 160, reactive dye, ozonation, dyeing wastewater

1. Introduction
In the textile industry, dyeing wastewater is the most concerned problems due to it is not only a large volume but also containing wasted dyes. Untreated dyes in such wastewater can cause serious problem for the receiving water environment and surround land area because of the color and toxicity organic compounds including original and degradable intermediate substances. Thus, there were many studies carried out to find the feasible method for the dyeing wastewater treatment. Some methods that may be applied in the dyeing wastewater treatment were found such as adsorption, oxidation by chemical, photocatalyst, ozonation, membrane filtration, coagulation, electrocoagulation, and biological methods, etc [1, 2, 3, 4]. However, the brightly colored types of dye, water soluble reactive and acidic dyes cannot be effectively removed through conventional treatment system [5]. Ozonation is an impressed method in dyeing wastewater treatment. Ozone can decompose the aromatic rings of some textile dyes, azo dyes and other organic pollutants in wastewater [6, 7]. The advantages of this process are the absence of increasing volume of wastewater and no secondary waste solid production (sludge) [6, 7]. Some previous studies showed that ozonation had high reactive dye treatment efficiency such as Reactive dye...
Orange 13, Reactive dye Blue 19, Reactive Orange 16 [7, 8]. However, the application ability of ozonation method in the dyeing wastewater treatment depends on types of dye and operating conditions. It needs detailing research before applying it in the practical condition.

C.I Reactive Blue 160 belongs the Reactive dyes group that may become the most usage in the near future. It contains Azo group that is the most popular group of Reactive dye. It is difficult to degrade and cause problems for the health of human and animals. And the blue color is the loveliest color on the world [9, 10]. So, C.I Reactive Blue 160 was concerned in this study.

In case of the treatment of C.I Reactive Blue 160 in the dyeing wastewater, some methods were studied are biodegradation, photodegradation and ozonation. The photocatalytic degradation resulted on the treatment of C.I Reactive Blue 160 but the treated wastewater samples were too small, maximum volume of 180 mL, the initial C.I Reactive Blue 160 concentration was too low about 10 – 25 mg/L, whereas the real dyeing wastewater contains high dye concentration and large volume [11-14, 15-18]. So, this method is too difficult to apply in the practical treatment. The biological treatment was effective in the degradation of C.I Reactive Blue 160 as well. However, it still remains some disadvantages as long treatment time (4 hours – 4 days), selected and uncommon biological agent [19-23]. Ozonation was carried out with too low concentration from 5 mg/L – 15 mg/L, and small volume 1.2 L and 1.5 L, and batch operating mode. The effects of factors such as pH, ozone gas flow rate, temperature, Na₂CO₃, initial dye concentration have not investigated yet [24, 25]. In practical condition, the dyeing wastewater contains high dye concentration. Therefore, the treatment of C.I Reactive Blue 160 in dyeing wastewater by ozonation needs to be studied more with high dye concentration to find the effects of operating factor on treatment efficiency and assess its application ability in practical treatment condition. The feasible treatment method that can be effective, easily applied, and suit the trend of the development of wastewater treatment on the world.

For these reasons, ozonation was selected and carried out for the treatment of the dyeing wastewater containing C.I Reactive Blue 160.

2. Materials and methods

2.1. Materials

The synthetic dyeing wastewater was prepared by adding C.I Reactive Blue 160 powder (Oh Young Inc., South Korea) into the tap water. pH and conductivity of such wastewater were adjusted by Sodium hydroxide 99% or Sulfuric acid 99.9% (Samchun Pure Chemical Co., Ltd., South Korea) and sodium chloride 99.5% (Duksan Pure Chemicals Co., Ltd., South Korea), respectively. Its characteristics were presented in Table 1.

In addition, Sodium Carbonate Anhydrous (Na₂CO₃ 99%) was also added to synthetic wastewater in a range of 0.00% - 0.03% to determine its effect on the removal efficiency by ozonation.

Table 1. Characteristics of the synthetic wastewater

| Parameters     | Units | Range of value |
|----------------|-------|----------------|
| pH             |       | 3.00 ~ 10.76   |
| Dye concentration | mg/L | 100 ~ 400     |
| Color          | Pt-Co | 490 ~ 1900    |
| COD            | mg/L  | 25 ~ 80        |
| Conductivity   | µS/cm | 1500 ~ 2500   |
| Sodium chloride | %    | 0.05           |
| Sodium carbonate | %     | 0.00 ~ 0.03  |
| Temperature    | °C    | 15 ~ 35        |

A bench-scale system was set up as Figure 1, includes:

✓ A polyacrylic bubble column reactor (D x H = 100 x 1500 mm) installed with a ceramic diffuser (Ø60 mm) at the bottom has a total volume of 11.78 liters and a working volume of 10 liters.

✓ A mixing tank made of PVC and PE was used to store the synthetic wastewater with a stirrer to uniform the wastewater during the experimental procedure.
✓ An Ozone generator: Model PC-57 provided by Ozonetech Co., Ltd., South Korea. Gaseous ozone flow rate can be adjusted by a flowmeter. Generating Ozone concentration in gas flow was 64.17 mg/L measured by ozone analyzer (Aeroqual series 200, New Zealand).
✓ A magnet pump and a water flowmeter were used to supply wastewater into the bubble column reactor with the determined flows.

2.2. Experimental procedure

The experimental setup is presented in Figure. 1. Both batch and continuous operation modes were carried out in this study.

Determine the effect of operating factors on the treatment efficiency by ozonation system: 10 liters of the synthetic wastewater contained C.I Reactive Blue 160 was filled into the bubble column reactor. The effect of ozone gases flow rate, pH, temperature, sodium carbonate anhydrous concentration, and the initial dye concentration on the treatment performance of ozonation system were evaluated in the batch operation mode by sequent changing of ozone gases flow rate from 0.5 – 1.3 L/min, pH from 3 – 10, temperature from 15°C – 35°C, Na₂CO₃ concentration from 0.01 – 0.03%, and initial dye concentration from 100 – 400 mg/L.

Evaluate the treatment efficiency of dyeing wastewater by ozonation system: Color, CODcr, and dye removal efficiency by ozonation system with both batch and continuous operating modes were determined under the determined optimal operating condition.
All experiments were repeatedly carried out three times to ensure the reliability of the experimental results.

2.3. Analytical Methods

In this study, the maximum absorbance wavelength was carried out by HS 3300 UV-vis. The color of dyes is occurred by absorbing light in the visible spectrum in a range of 400 – 700nm. Namely, dyes have an absorbance wavelength in a range of 580 – 700nm observed in blue to green [26]. In the previous studies, the maximum absorbance wavelength of C.I. Reactive Blue 160 was 630nm, 618nm, 616nm, 610nm, and 604nm, depends on the purity of dye and spectrophotometer equipment [11-13, 18, 20, 23]. In this study, the maximum absorbance wavelength of C.I Blue 160 was carried out by HS 3300 UV-vis and was 611nm.

Dissolved C.I Blue 160 dye concentration was determined by the previous built calibration curve, Abs measured at the maximum wavelength, $R^2 = 0.9999$, as in Fig. 3.

There was relationship between dye concentration and color. In this study, with synthetic raw wastewater, the color was found to be linear with dye concentration follow: $y = 4.9964x +2.5$, $R^2 = 0.9996$. After ozonation, this relationship was changed to approximate the quadratic equation.

During the experiments, all samples were taken from column reactor with fixed reaction time and analyzed as follows:

- pH, conductivity, and temperature were measured by pH meter (Denver UltraBasic UB-10), conductivity meter (ATI Orion 130) and thermometer (Okaya Handy Thermo Pt-100 OH-IT), respectively.
- Color was analyzed by Spectrophotometer Hach DR 2800.
The COD was analyzed by titrimetric method, which according to the Standard Methods for The Examination of Water and Wastewater [27].

2.4. Calculation methods

2.4.1. Removal efficiency

The removal efficiency was determined as the followed function [28]

\[ E_{\text{tr}} \text{, } \% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \]  

(1)

Where:
- \( C_0 \): initial color (Pt-Co), or dye concentration (mg/L), or COD (mg/L).
- \( C_t \): color (Pt-Co), or dye concentration (mg/L), or COD (mg/L) respect to reaction time \( t \).

2.4.2. The energy consumption

The energy consumption of the ozonation process was determined as the energy required for the ozone generator to remove a specified quantity of pollutants, namely, COD, color, dye [28].

\[ E_{\text{O}_3} = \frac{P \times t}{V \times (C_0 - C_t) \times 60} \]  

(2)

Where:
- \( E_{\text{O}_3} \) is energy consumption, Wh/mg-COD, or Wh/mg-dye, or Wh/color unit.
- \( P \) is the power of Ozone generator, W
- \( t \) is the reaction time (min)
- \( V \) is the working volume of reactor column (L)
- \( C_0 \): initial color (Pt-Co), or dye concentration (mg/L), or COD (mg/L).
- \( C_t \): color (Pt-Co), or dye concentration (mg/L), or COD (mg/L) at reaction time \( t \).

All experiment was repeated 3 times and collected data was analyzed by using the ANOVA with \( \alpha = 0.05 \) in Microsoft Excel.

3. Results and discussion

3.1. The effects of operating factors

The treatment efficiency of dyeing wastewater by ozonation system depends on the amount of dissolved ozone in wastewater and dye concentration. The ozone solubility is the function of some elements including the inter-surface area between gas phase and liquid phase, retention time, temperature, pressure, pH, and the appearance of ozone decomposition inhibitor.

All experiments were carried out under atmospheric pressure. Most the wastewater treatment systems are operated under atmospheric pressure in practical conditions, and controlling pressure in the practical conditions is infeasible, especially in the large wastewater treatment systems so the effect of pressure on the removal efficiency was neglected.

In this study, the effects of ozone gas flow rate, pH, temperature, Na\(_2\)CO\(_3\) concentration (the inhibitor of ozone decomposition), and the initial dye concentration on the removal efficiency were investigated and alternately presented as follows:

3.1.1. The effect of ozone gas flow rate:

The ozone gas flow rate is one of factors affecting on treatment performance by ozonation because of its effect on the gas holdup and gas bubble velocity (contact retention time between ozone bubble and pollutants). The gas holdup is proportional function of gas flow rate [28].

In this study, the effect of ozone gas flow rate were determined by decolorization and dye treatment ability with the ozone gas flow rate changed in a range of 0.5 L/min - 1.3 L/min, reaction time from 0 –
10 min (2 min interval), initial dye concentration of 200 mg/L. The results of ANOVA analysis showed that both the ozone gas flow rate and reaction time had significant effects on the color and dye removal efficiencies. The interaction between the ozone gas flow rate and reaction time significantly affected on the color and dye treatment ability by ozonation as well (both P-values << 0.05).

As seen in Fig.4, at the gas flow rate of 0.9 L/min, the color and dye treatment efficiency were higher than others. When the gas flow rate increased in ranges of 0.5 L/min – 0.9 L/min, the color and dye concentration efficiencies increased due to increasing the gas holdup led to rise the contact surface area between pollutants and ozone bubbles.

![Figure 4. Color and dye treatment efficiency versus different flowrate and reaction time](image)

When ozone gas was diffused into the wastewater, many bubbles were formed and caused the gas holdup. However, increasing the gas flow rate also leads to increasing the bubble size. Because the bubbles can be combined to form the bigger bubbles lead to decrease surface area. This study clearly indicated that the bubbles not only increased the amount and their size but also changed their shape from sphere shape to more oval shape when the gas flow rate increased from 0.5 L/min to 1.3 L/min, respectively, Fig.5.

According to George Gabriel Stokes (1819-1903), the velocity of sphere matter increases following the exponential function of its diameter, expressed by the Stokes equation:

$$v = \frac{d^2 \times (\rho - \rho_l) \times g}{18 \mu}$$  \hspace{1cm} (3)

Where:
- $v$ is velocity of sphere matter
- $g$ is gravitational acceleration
- $d$ is diameter of sphere matter
- $\rho$ is density of environment (gas or liquid)
- $\mu$ is viscosity of environment (gas or liquid)
Those were all reasons for the gas flow rate increased over 0.9 L/min, the removal efficiency decreased. These results were the same trend in previous study [28]. It may be explained as: Although the gas holdup was higher in 1.1 L/min gas flow rate case, the formed bubbles size was bigger and the ozone bubbles velocity were faster led to reducing the contacting time and contact surface area between the ozone bubbles with pollutants. So the removal efficiency reduced. The gas flow rate of 0.9 L/min was suitable for the ozonation treatment in this system.

3.1.2. The effect of pH:

pH is the important factor in the ozonation process because it decides the reaction mechanism: the direct reaction mechanism occurred in an acidic solution whereas the indirect reaction mechanism occurred in the high alkaline condition.

According to Erdal Kusvuran et. al. (2010 and 2011), pH of direct and indirect mechanisms was 3 and 10, respectively [29, 30]. Especially, both of these mechanisms occurred contemporary when pH at neutral and slightly basic [30, 24]. Ozone (O₃) was dominated reactant in acidic and the radical species (OH•, HO₂, O₂⁻…) were dominated reactants in alkaline. In a neutral and slightly basic solution, both of them occurred together.

Although the oxidation potential of hydroxyl radical (2.8 V) is higher than ozone (2.42 V), the attack of hydroxyl radical with hydroxyl radical is not always stronger than ozone [31, 32]. It depends on type of dye. According to Erdal Kusvuran et al., cationic dyes were destroyed better than anionic dyes by ozone reagent in acidic. Reversely, the anionic dyes were destroyed better than the cationic dyes by hydroxyl radical in basic [30].

In the case of C.I. Reactive Blue 160, the obtained data presented that the removal efficiencies of color and dye were reduced when increasing pH from 3 to 10. The color removal efficiency reached up 79% after 10 min ozonation in pH 3 whereas these were 68% and 61% at pH 7 and pH 10, respectively. The color removal efficiencies at all pH values were gradually converging when increasing reaction time and the color removal efficiency of pH 3 samples were still higher than others (Fig.6).

The dye removal efficiencies had a little different trend compare to the color treatment between different pH values. The dye removal efficiencies at pH 10 were significantly lower than others during the first 15 min reaction time and then they were slowly increased and evenly approaching 99.9% (Fig. 6).
These results proved that the decomposition reaction of C.I. Reactive Blue 160 molecules by ozone was more selective than by hydroxyl radical. According to Chedly Tizaoui and Naser Grima (2011), the hydroxyl radicals were interested in reaction with the intermediates products rather than parent molecules [7]. Thus, the removal efficiencies of color and dye were decreased at high pH conditions.

The results of ANOVA analysis also showed that pH, the interaction between pH, and reaction time were significant effects on the color and dye removal by ozonation. P values were 3.0 x10^{-24} – 5.76 x 10^{-24} and 2.5 x10^{-17} – 9.8 x 10^{-12}, respectively.

3.1.3. The effect of temperature:
Temperature is a very important factor in a chemical reaction. It accelerates reaction rate lead to shortening reaction time. Besides accelerating reaction rate, the temperature is also the important factor that affect the ozone dissolving from the gaseous phase into the aqueous phase. Unfortunately, dissolved ozone will be decreased when temperature increases because of increasing bubble size. More detailed, high temperature leads to reduce the surface tension of water. Thus, bubble size will be increase. Therefore, the retention time of bubbles in wastewater was shortened [28]. Moreover, the increasing temperature makes to reducing ozone life in solution. The half-life values of ozone in neutral water are 30 min, 15 min, and 8 min respect to 15°C, 25°C, and 35°C.

Thus, temperature may have a positive or a negative effect on the treatment efficiency of ozonation. Therefore, the dependence of treatment efficiency on temperature needs to be concerned, especially in temperate and frigid countries, temperature changes so much between seasons, even in the day.

In this study, the effects of temperature on the removal efficiencies were surveyed at 15°C, 25°C, and 35°C. The surveying results were presented in Fig. 7.

![Figure 6. Effect of pH on the color and dye removal efficiency](image)

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ozone and ozone decomposition by increasing temperature. Therefore, when the temperature of wastewater rose from 15°C to 35°C, the average color and dye removal efficiencies decreased.

In addition, the results of ANOVA analysis indicated that temperature and reaction time had a significant effect on the treatment efficiency, both of dye and color removal. However, the interaction between temperature and reaction time only had an effect on dye removal.

3.1.4. The effect of Na$_2$CO$_3$ concentration:

Sodium carbonates anhydrous is an inhibitor in the decomposition of ozone. So, they help maintain the ozone domination reagents.

In this study, the experiments were carried out with 4 samples: without Na$_2$CO$_3$, 0.01% Na$_2$CO$_3$, 0.02% Na$_2$CO$_3$, and 0.03% Na$_2$CO$_3$. The without Na$_2$CO$_3$ samples were adjusted pH up to 10, similarly pH conditions of samples containing Na$_2$CO$_3$. The results of ANOVA analysis showed that Na$_2$CO$_3$ significantly affected the color, dye, and COD removal efficiencies (P-value were $9.03 \times 10^{-6}$, $3.95 \times 10^{-6}$, and $1.98 \times 10^{-37} << 0.05$, respectively). The interaction between Na$_2$CO$_3$ and reaction time significantly affected on the color, dye, and COD removal efficiencies as well (P-value are $4.54 \times 10^{-37}$, $7.15 \times 10^{-28}$ and $3.31 \times 10^{-46} << 0.05$, respectively).

As results in the effect of pH, the decomposition reaction between C.I. Reactive Blue 160 and ozone was more selective than hydroxyl radical. Thus, the removal efficiencies of samples containing Na$_2$CO$_3$ were better than samples without containing Na$_2$CO$_3$. That was proved by the results presented in the Fig.6, the removal efficiencies increased at higher sodium carbonate anhydrous concentration. In particular, the removal efficiencies of sample containing 0.03% Na$_2$CO$_3$ were impressive. With only 2 min ozonation, the dye removal efficiency of this sample was 47.3% whereas it was 34.49%, 31.58%, and 30.52% for 0.02% Na$_2$CO$_3$ sample, 0.01% Na$_2$CO$_3$ sample, and without Na$_2$CO$_3$ sample, respectively.

![Figure 8. Effect of sodium carbonate anhydrous on the color and dye removal efficiency at the first 15 min ozonation](image)

However, this trends is only true for the first 15 min ozonation. The longer ozonation, the better removal efficiencies in without Na$_2$CO$_3$ sample. Reversely, the removal efficiencies of samples containing Na$_2$CO$_3$ decreased when increasing Na$_2$CO$_3$ concentration. This result may be explained by precipitation of CaCO$_3$ formed by Ca$^{2+}$ in water and CO$_3^{2-}$ released by ozonation of organic components. Because pH of wastewater is around 10, the dominant alkaline agents are CO$_3^{2-}$. This results was consistent with the previous study of Nelson Saksono et al. (2009), the precipitation of calcium carbonate occurs immediately when initial pH $\geq 8.5$ [33]. Thus, maybe the precipitation of calcium carbonate occurs parallel with the decomposition C.I. RB 160.

3.1.5. The effect of initial dye concentration

The initial dye was also an important factor markedly affect the removal efficiencies [11-14, 15-18]. It was proved by the results of ANOVA analysis. The dye concentration had significant effect on the
color, and dye removal efficiencies (P-value are $2.88 \times 10^{-87}$, and $9.8 \times 10^{-125} << 0.05$, respectively). The interaction between dye concentration and reaction time also significantly affected the color and dye removal efficiencies (P-value are $1.44 \times 10^{-81}$, and $3.31 \times 10^{-127} << 0.05$, respectively). Namely, the color and dye removal efficiencies decreased when increasing initial dye concentration. Three samples, have initial dye concentrations of 100 mg/L, 200 mg/L and 400 mg/L, were treated under the same conditions: without pH adjustment, ozone gas flow rate 0.9 L/m. The results were showed in Fig. 9.

![Image](image_url)

**Figure 9.** Effect of initial dye concentration on the color and dye removal efficiency

During the first 10 min ozonation, the color removal efficiency of sample 100 mg/L rose very fast and reached up 89% whereas it was only 61.63% and 31.86% for sample containing 200 mg/L and 400 mg/L initial dye concentration. Moreover, the dye removal efficiencies were more impressive than color removal efficiencies. Only during the first 10 min ozonation, the dye removal efficiency of sample 100 mg/L, 200 mg/L, and 400 mg/L are 99.49%, 94.81%, and 75.55%, respectively. Specially, after 30 min ozonation, the dye and color removal of sample 100 mg/L and 200 mg/L were nearly complete. These results occurred due to a larger amount of dye molecules and the generated intermediate products in the solution in higher initial dye concentration sample. So, ozone consumption requirement was higher than others. And supplied ozone in the first 20 min ozonation was not enough for the degradation of 200 mg/L and 400 mg/L dye concentration. Thus, the removal efficiencies decreased. These results agreed to the previous study on dye treatment by ozonation [28].

### 3.2. The C.I Reactive Blue 160 treatment efficiency by ozonation system with operating batch mode

The experiments were performed with ozone gas flow rate of 0.9L/min, no adjusted pH, temperature of 15-16°C, the obtained data indicated that the effluent of the dyeing wastewater containing 200 mg/L C.I. RB 160 was satisfy the strictest discharge standard after 25 min ozonation. Output parameters were as follows: pH = 6.47, Color = 40 Pt-Co, COD = 24.09 mg/L, and dye residual concentration = 0.53 mg/L. The removal efficiency of color, dye, and COD are 96.05%, 99.62%, and 76.44%, respectively (Fig. 10). The effluents can be satisfying to the discharge standard in Vietnam, Korea. The reaction between ozone and C.I. RB 160 was found as the first-order reaction and the reaction rate coefficients were 0.1402 min⁻¹, 0.8119 min⁻¹, and 0.0605 min⁻¹ corresponding to the color, dye, and COD removals (Fig.11). These results were same with the previous research on treatment Acid Red 114 dye by ozonation [28]. The maximum energy consumption was 1.744 kWh/m³ treated water.

In fact, the dyeing wastewater usually contains sodium carbonate. According to Dieter Sedlak [34], sodium carbonate anhydrous was usually used with concentration 0.02%. From the results in determination of the effects of sodium carbonate on the removal efficiencies in ozonation, the presence of Na₂CO₃ in the dyeing wastewater enhanced the removal efficiencies of color, dye, and COD. Therefore, in case of the real dyeing wastewater that contains Na₂CO₃, the removal efficiencies will be higher and the energy consumption will be lower than the results obtained in this study.
Legend:
(a2) : Reaction order of color removal
(b2) : Reaction order of dye removal
(c2) : Reaction order of COD removal

Figure 10. Characteristics of treatment process of sample 200 mg/L without Na₂CO₃
To determine the reaction time for completely mineralize COD, the experiments were extended reaction times. The results showed that 90 min ozonation time was enough to mineralize 100% COD in the wastewater without Na$_2$CO$_3$. In this study, the wastewater containing 0.02% Na$_2$CO$_3$ was investigated as well. The results indicated that the mineralization was complete with only 70 min. Thus, the ozonation had ability to treat the dyeing wastewater containing C.I Reactive Blue 160 approach to reuse purpose. Energy consumption were 4.8 kWh/m$^3$ and 3.733 kWh/m$^3$ for the wastewater containing 0.00% and 0.02% Na$_2$CO$_3$, respectively.

3.3. The C.I Reactive Blue 160 treatment efficiency by ozonation system with continuous operating mode

The removal efficiencies of C.I Reactive Blue 160 by ozonation in continuous operating mode were investigated with both concurrent and counter current. The synthetic wastewater containing 200 mg/L initial dye concentration was treated under the operation conditions as ozone gas flow rate 0.9 L/min, without pH adjustment (pH in range of 7.48 – 7.58). HRT was sequentially changed 10 min, 20 min, 25 min and 30 min by adjusting of wastewater flow rate of 1 L/min, 0.5 L/min, 0.4 L/min and 0.33 L/min, respectively.

With counter current flow, ozonation also had effective results in treatment of C.I RB 160. The color, dye and COD residuals after 30 min HRT were 28 Pt-Co, 0.48 mg/L and 13.83 mg/L, respectively. The removal efficiency of color, dye and COD achieved 97.24%, 99.76% and 86.38%, Fig. 11. The color, dye and COD removals followed the first-order rate law as well, with the reaction rates were 0.1224 min$^{-1}$, 0.2027 min$^{-1}$ and 0.0632 min$^{-1}$, respectively.

In case of concurrent flow, HRT = 30 min, the removal efficiency of COD, color, and dye reached 85.61%, 97.24%, and 99.76%, respectively. Both of them were lower than counter current flow because in concurrent, there was velocity resonance of wastewater and ozone gas bubbles led to reduce reaction time of ozone and pollutants. Remaining of color, dye and COD after 30 min HRT were 35 Pt-Co, 0.59 mg/L and 14.6 mg/L, respectively. The reaction of C.I RB 160 with ozone in concurrent flow was also the first-order reactions. The reaction rates were 0.1164 min$^{-1}$, 0.1959 min$^{-1}$ and 0.0618 min$^{-1}$ in the color, dye and COD removals, respectively.

Compare with the previous studies on the degradation of C.I RB 160, this study showed that ozonation was a more effective method and had higher application ability. It not only had high removal efficiency but also could treat a larger amount of wastewater containing higher pollutant concentration with shorter reaction time, easier operation, and without generated secondary solid waste [11-23].
4. Conclusions
The removal efficiency of color, dye and COD in the dyeing wastewater containing C.I Reactive Blue 160 by ozonation were significantly affected by the ozone gas flow rate, temperature, pH, Na₂CO₃ concentration, and initial dye concentration. Ozonation was performed in the bubble column reactor with both the batch and continuous modes with concurrent and counter current flow. Ozonation had high efficiency in the treatment of dyeing wastewater containing C.I RB 160. The effluent of the dyeing wastewater containing 200 mg/L C.I. RB 160 was satisfy the strictest discharge standard after 25 min ozonation with both operating modes systems. Ozonation time was required longer, approximately 90 min to remove completely COD, mineralized 100%. The presence of Na₂CO₃ in wastewater reduced reaction time and saved energy. The impressive advantages of ozonation were high degradation ability of refractory organic contaminants, short HRT, no sludge production and complete mineralization ability.

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