

## Degradation of Blue KN-R Dye in Batik Effluent by an Advanced Oxidation Process Using a Combination of Ozonation and Hydrodynamic Cavitation

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**Abstract:** The popularity of batik has been increasing since it was declared as a world cultural heritage by UNESCO in 2009. Correspondingly, the content of textile dyes in textile industry wastewater is also increased. These dyes contain functional groups which make them quite stable in the environment and causes pollution. In this work, degradation of 100 ppm Blue KN-R has been investigated using ozonation, hydrodynamic cavitation, and a combination of the two for 60 min. The three configuration methods were optimized in terms of different operating parameters, namely flowrate, initial pH and dosage of ozone, to obtain the maximum degradation of Blue KN-R. It was found that the highest decolorization level for a single method was 70.16% for the single ozonation process at pH 11 and 156.48 mg/h of ozone and 1.79% for the single hydrodynamic cavitation process at pH 4. The highest decolorization level was 79.39%, achieved by the combination at pH 11 and 156.48 mg/h of ozone. The mineralization level in the form of a percentage of Total Organic Carbon (TOC) removal by ozonation, hydrodynamic cavitation, and their combination was 14.81, 1.85, and 19.9%, respectively. Due to its better performance, degradation of Blue KN-R was conducted by the hybrid method for 120 min, resulting in 92.63% of decolorization and 24.54% of TOC removal. The degree of synergetic decolorization and mineralization was due to the mechanical and chemical effect of hydrodynamic cavitation in increasing ozone solubility and production of hydroxyl radicals. Degradation of batik effluent has been investigated in optimum conditions for 120 min. The color, COD, BOD, and TSS removal were 67.96, 68.72, 66.54, and 79.84%, respectively.

**Keywords:** Blue KN-R; decolorization; dye; hydrodynamic cavitation; ozonation

### ■ INTRODUCTION

The textile industry is one of the industries that makes a significant contribution to Indonesia, and synthetic dyes are one of the raw materials in the industry, such as the batik industry. Textile dyes contain azo, anthraquinone, oxazine, phthalocyanine, and formazan functional groups such as the chromophore group [1]. Reactive dyes are widely used since the capacity of the reactive functional group makes it easy to bond with the hydroxyl functional group of the textile fibers to form covalent bonding. Thus, increasing interaction between the dye and the fibers occurs, as does decrease energy consumption [2]. Reactive Blue 19 is commonly used and is easily available [3]. Also known as Blue KN-R, it is a

type of anthraquinone dye and is more difficult to decolorize than azo dyes because of its conjugated structure [4].

Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of non-easily removable organic compounds. These processes are based on generating hydroxyl radicals ( $\bullet\text{OH}$ ), a powerful non-selective oxidizing agent that can react with various types of organic and inorganic compounds [5]. One of the AOP methods is ozonation. It is well known that ozone is a strong oxidant which can form a more powerful, non-selective hydroxyl radical at high pH values. However, ozone has some deficiencies, namely its solubility and stability in water is relatively low, and also the selectivity of ozone itself [6]. Ozone can be

combined with hydrodynamic cavitation to increase its solubility and stability.

Cavitation is defined as the phenomenon of the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small intervals of time (milliseconds), which release large amounts of energy [7]. In hydrodynamic cavitation, cavities are formed by passing the liquid through the constriction provided in flowline [8]. The extreme cavity condition can be used to attack the molecule bonds of organic pollutants [9]. Under such extreme conditions, water molecules are dissociated into  $\bullet\text{OH}$  and  $\text{H}\bullet$ . These  $\bullet\text{OH}$  then diffuse into the bulk liquid, where they react with organic pollutants and oxidize or mineralize them [10]. The combination of hydrodynamic cavitation and ozone can be used to intensify degradation efficiency due to the enhanced mass transfer of ozone molecules from the gas phase to the bulk solution, which reacts with organic pollutants in cavitating conditions [8]. Consequently, by combining ozonation and hydrodynamic cavitation, hydroxyl radical production will increase.

The purpose of this study is to investigate the degradation of Blue KN-R using a combination of ozonation and hydrodynamic cavitation and compare it with corresponding singular methods in order to assess the significance of the combination. The effect of certain important variables, namely circulation flow rate, initial pH and dosage of ozone, were evaluated. The optimum operational condition was also used to treat batik effluent from Handayani Geulis Batik plant in Bogor.

## EXPERIMENTAL SECTION

### Materials

The Blue KN-R dye molecule structure is shown in Fig. 1. (molecular weight: 626.55 g/mol; molecular formula:  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{Na}_2\text{O}_{11}\text{S}_3$ ). Ozone gas was generated using a commercial ozonator from HANACO. Sodium hydroxide (NaOH p.a.) and sulphuric acid ( $\text{H}_2\text{SO}_4$  p.a.) from Merck were used to adjust the initial pH values, and potassium permanganate ( $\text{KMnO}_4$  p.a.) from Merck was employed in the hydroxyl radical quantification. An indigo reagent (HACH Cat. 2518025) was used to determine

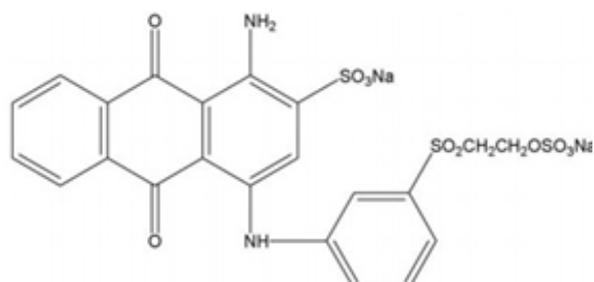


Fig 1. The molecular structure of Blue KN-R

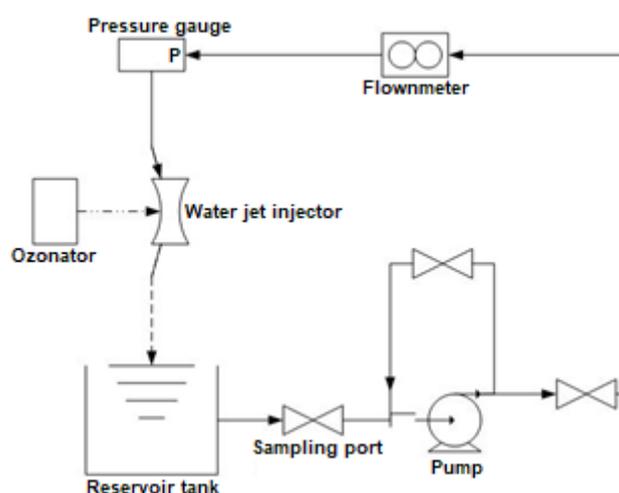


Fig 2. Schematic diagram of the experiment

the residual ozone concentration, and a COD reagent (HACH Cat. 2125925) to determine COD concentration.

### Instrumentation

The experimental setup is shown in Fig. 2. It included a 6 L reservoir tank, a pump (power rating 370 W), two control valves, flowmeter, pressure gauge, and injector (Venturi Mazzei type 384).

### Procedure

#### Quantification of hydroxyl radical

Six Liters of aquademin was used for quantifying hydroxyl radical produced using three method configurations, single ozonation, single hydrodynamic cavitation, and a combination of the two, for 60 min. The experiment using single hydrodynamic cavitation was conducted at various flow rates (2, 4, 6 LPM), while those using single ozonation and the combination were conducted at various initial pH values (4, 7, 11) and ozone dosages (72, 120.96, 156.48 mg/h).

### Degradation of Blue KN-R

Degradation of Blue KN-R was achieved using single ozonation, single hydrodynamic cavitation, and a combination of the two in various conditions, with a fixed aqueous Blue KN-R concentration of 100 mg/L. All the experiments were conducted at various levels of initial pH (4, 7, 11). Ozonation and the combined method were also conducted at various ozone dosages (72, 120.96, 156.48 mg/h). All the experiments were performed for 60 min.

### Degradation of batik effluent

The degradation of batik effluent (Handayani Geulis Batik in Bogor) was carried out in optimum conditions, and the experiment was performed for 120 min. The degradation parameters of batik effluent were color scale using Platinum-Cobalt scale (Pt/Co) based on SNI 06-6989.80:2011 method; COD using a COD reagent and spectrophotometer for concentration analysis; BOD<sub>5</sub> using SNI 6989.72:2009; and TSS using a colorimeter.

## RESULTS AND DISCUSSION

### Quantification of the Hydroxyl Radicals

Hydroxyl radicals play an important role in the degradation of Blue KN-R dye because they are the main oxidizing agents that react with the original and intermediate compounds to achieve mineralization. The quantification of hydroxyl radicals for each of the configuration methods has therefore been investigated. For the hydrodynamic cavitation method, Fig. 3 shows that the number of hydroxyl radicals increased with an increase in flow rate; 6 LPM of flow rate yielded 7.23 mg/L of hydroxyl radicals. Increasing the inlet velocity increases the pressure drop at the tubule, which causes the cavitation effect to be higher and leads to an increase in the level of hydroxyl radicals.

The results can be related to the cavitation number ( $C_V$ ), a dimensionless parameter that is used to characterize the cavitation intensity inside the cavitating device. It is defined as the ratio of pressure drop between the throat and extreme downstream section of the cavitating device (Fig. 4) to the kinetic head at the throat [11], and is given by Eq. 1:

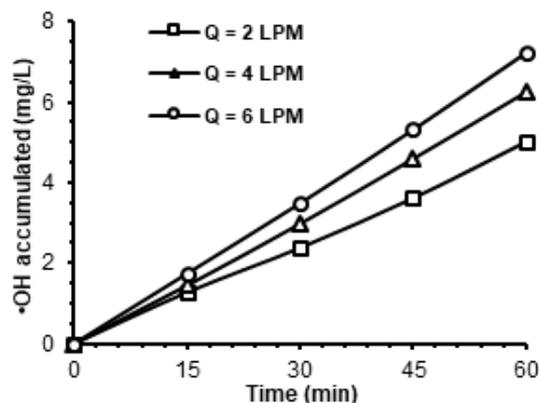


Fig 3. Effect of flow rate on hydroxyl radical production by hydrodynamic cavitation

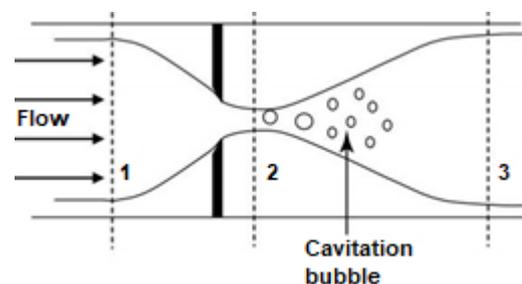
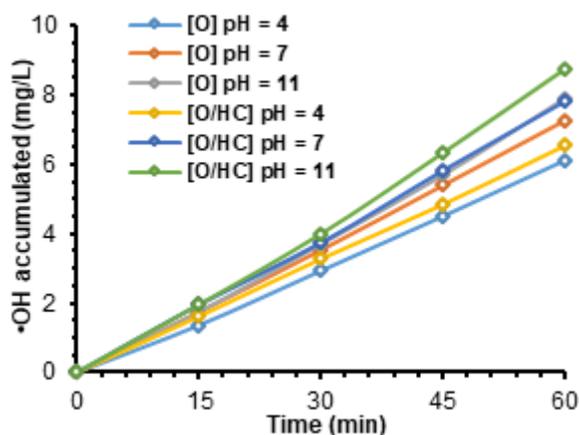


Fig 4. Pressure profile in the hydrodynamic cavitation where  $P_2$  is the fully recovered downstream pressure,  $P_V$  is the vapor pressure of the liquid,  $v_0$  is the velocity at the throat of the cavitating device, and  $\rho$  is the density of the liquid. As the inlet pressure increases, the velocity at the throat increases, which in turn reduces the cavitation number. In this experiment, the cavitation numbers at 2, 4, and 6 LPM were 8.67, 2.18, and 0.97, respectively. As the flow rate increases, the cavitation number decreases, which in turn generates more hydroxyl radicals

$$C_V = \left( \frac{P_2 - P_V}{\frac{1}{2}\rho v_0^2} \right) \quad (1)$$

For the ozonation method, Fig. 5 shows that the level of hydroxyl radicals increased with the increase in initial pH value. This initial pH value (4, 7, 11) yielded 6.12, 7.27, and 7.91 mg/L of hydroxyl radicals, respectively. In acidic conditions, ozone molecules will react directly and are not easily decomposed to hydroxyl radicals. However, in alkaline conditions ozone



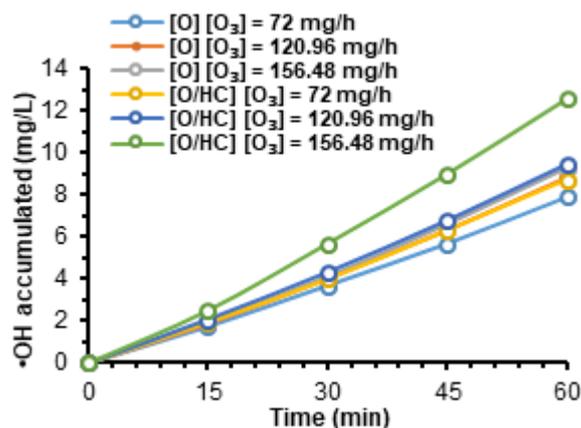
**Fig 5.** Effect of pH on hydroxyl radical production by ozonation [O] and the combination of ozonation and hydrodynamic cavitation [O/HC]

molecules will be decomposed to form hydroxyl radicals due to the presence of hydroxide ions. Fig. 6 shows that increasing the dosage of ozone will increase the level of hydroxyl radicals.

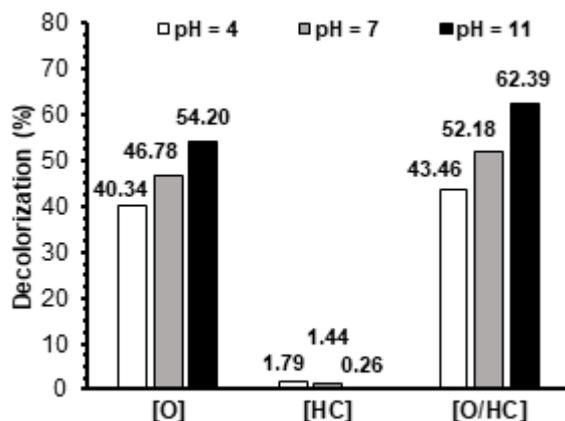
For the combination method, Fig. 6 shows the same trend as the ozonation method. The level of hydroxyl radicals at various initial pH (4, 7, 11) were 6.55, 7.82, 8.76 mg/L, respectively, which was greater than in the ozonation method. Fig. 6 also shows a similar pattern to the ozonation method but is higher than single ozonation. The results indicate an increase in ozone mass transfer and the addition of hydroxyl radicals due to the mechanical and chemical effects of hydrodynamic cavitation.

### Degradation of Blue KN-R

The degradation of Blue KN-R was conducted with various configuration methods and fixed dye concentration (100 mg/L) for 60 min. Fig. 7 shows that in the ozonation method, the highest decolorization occurred under the alkaline condition (pH 11). In this condition, there are hydroxyl radicals which have higher oxidation potential than ozone molecules [12]. Fig. 8 shows that the decolorization is more effective if conducted at 156.48 mg/h of ozone. Increasing the dosage of ozone will increase the level of hydroxyl radicals from ozone decomposition, resulting in increasing decolorization of Blue KN-R.



**Fig 6.** Effect of dosage of ozone on hydroxyl radical production by ozonation [O] and the combination of ozonation and hydrodynamic cavitation [O/HC]

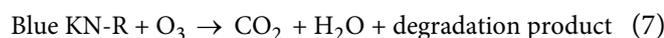
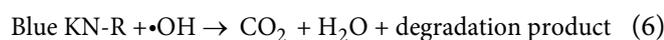


**Fig 7.** Effect of pH on Blue KN-R decolorization by ozonation [O], hydrodynamic cavitation [HC], and their combination [O/HC]

For the hydrodynamic cavitation method, Fig. 7 shows that decolorization increases with the decreases in initial pH. The increase in decolorization at a lower pH can be attributed to the fact that dye molecules are present in a molecular state at lower pH rather than in ionic state. In this molecular state, dye molecules become more hydrophobic, and hence can easily locate or prefer to be at the gas-water interface of the collapsing cavities [8].

The combination of ozonation and hydrodynamic cavitation can increase the efficiency of degradation due to the increase in the ozone mass transfer from the gas phase to the bulk solution and its reaction with

organic pollutants in cavitating conditions. Moreover, under the cavitation effect, ozone is easily decomposed, yielding molecular O<sub>2</sub> and atomic oxygen which reacts with a water molecule to form hydroxyl radicals. The following reactions (Eq. 2-7) can occur during the process of combined ozone and hydrodynamic cavitation [10-11].



For the combination method, the results shown in Fig. 7 have a similar pattern to the effect of pH in the ozonation method. The highest decolorization was observed at pH 11, which is higher than the decolorization by single ozonation. Moreover, Fig. 8 shows that the highest decolorization by the combination method was observed at the highest dosage of ozone, which is greater than decolorization by single ozonation. Moreover, the difference in decolorization level between the three configuration methods shows a synergetic effect and indicates that the combination of ozonation and hydrodynamic cavitation can improve the degradation of Blue KN-R.

The optimum operational conditions were observed using a combination of ozonation and hydrodynamic cavitation at pH 11 and 156.48 mg/h dosage of ozone. Consequently, the degradation of Blue KN-R was investigated using optimum conditions for 120 min, and decolorization reached 92.63% remaining 7.37 mg/L of dyes.

The ultimate goal of the oxidation process is mineralization, namely the conversion of organic

compounds into simple inorganic compounds such as CO<sub>2</sub> and H<sub>2</sub>O. The number of organic compounds converted into minerals is expressed in Total Organic Carbon (TOC). Thus the TOC removal rate is also called the level of mineralization of an oxidation process. In order to study the mineralization rate, TOC was evaluated for the three configuration methods at 60 min. The TOC removal for ozonation, hydrodynamic cavitation, and the combined method was 14.81, 1.85, and 19.9%, respectively. Moreover, TOC removal in optimum conditions after 120 min was 24.54%.

Shen et al. [13] investigated the degradation of reactive red X-3B dye by ultrasonic (US) cavitation and ozone oxidation. They reported that the O<sub>3</sub>/US cavitation system has synergetic degradation effect on reactive red X-3B dye compared with O<sub>3</sub> alone or US cavitation alone. Under the condition that the initial concentration of 100 mg/L, pH of 6.52, ozone flux of 40 L/h, and 99.2% decolorization efficiency was obtained in O<sub>3</sub>/US cavitation system.

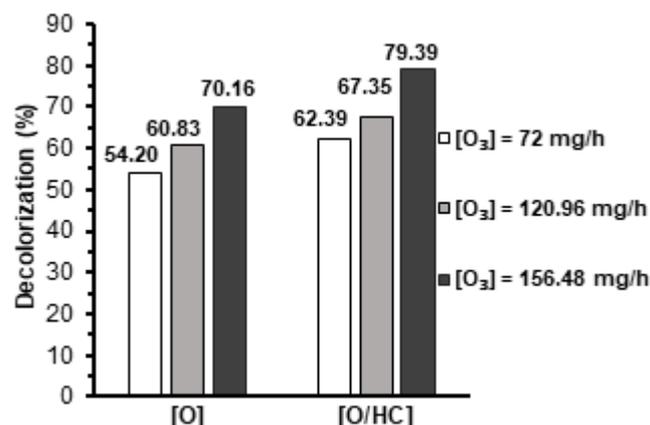


Fig 8. Effect of dosage of ozone on Blue KN-R decolorization by ozonation [O] and the combination of ozonation and hydrodynamic cavitation [O/HC]

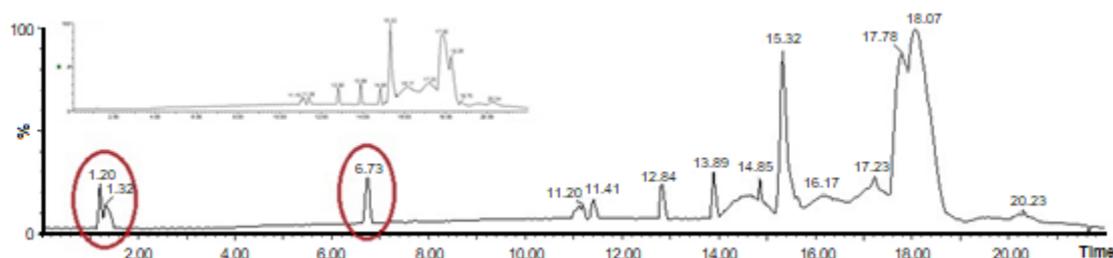


Fig 9. LC-MS chromatogram of mobile phase and sample of 120 min degradation process

**Table 1.** Identification of degradation product by LC-MS

No.	Retention time (min)	m/z	Chemical formula	Area (%)
1	1.20	125.9	C <sub>2</sub> N <sub>5</sub> S	25.05
2	1.32	164.9	C <sub>2</sub> N <sub>2</sub> OS <sub>3</sub>	28.25
3	6.73	183.0	C <sub>8</sub> H <sub>9</sub> NO <sub>2</sub> S	41.37

### Degradation Products

In order to identify the degradation products of Blue KN-R, liquid chromatography-mass spectrometry (LC-MS) analysis was performed on the sample from the optimum conditions at 120 min. Based on the chromatogram, three peaks were detected in three retention times (Fig. 9). These peaks indicate three different compounds in the sample, as shown in Table 1.

### Degradation of Batik Effluent

The degradation of batik effluent from Handayani Geulis Batik Bogor was evaluated using optimum operating conditions for 120 min. The batik effluent was diluted to aquademin with a volume ratio of 1:5 (batik effluent:aquademin). The evaluation of the dye degradation consisted of two parameters, Blue KN-R concentration, and color (Pt-Co units). The decolorization of Blue KN-R was 66.66%, with an initial concentration of 70.31 mg/L. Color concentration in the initial conditions was 2422 Pt-Co units and after the degradation process fell to 744 Pt-Co units (69.28%). The low level of degradation color in the batik effluent might be explained by the content of effluent being not only Blue KN-R but also other ingredients used in the dyeing process.

The initial COD concentration from batik effluent was 169.98 mg/L, and after degradation for 120 min, the COD removal yield was 68.72% (53.17 mg/L). The low COD removal may be related to the presence of organic compounds that easily oxidize and partially oxidize [14]. BOD reduction reached 66.54% with an initial BOD concentration of 28 mg/L. However, the BOD/COD ratio before and after the degradation process only increased from 0.16 to 0.18 (lower than 0.2). This result indicates the presence of non-biodegradable oxidation products.

The other parameter that was evaluated from the degradation of batik effluent was TSS (Total Suspended Solids). This proposed method was able to reduce TSS

from 610 to 123 mg/L (79.84%). This TSS reduction was caused by the reaction of ozone in the effluent, which formed flocks that absorbed the colloids [15]. Other than that, the oxidation process by ozone molecules or hydroxyl radicals caused the decomposition of large organic compounds to become smaller, so TSS concentration decreased [16]. Rajoriya et al. [17] investigated the treatment of textile dyeing industry effluent using hydrodynamic cavitation (HC) in combination with several advanced oxidation reagents such as air, oxygen, ozone and Fenton's reagent. They found that all combined processes exhibited higher TOC, COD and color removal as compared to that obtained by HC alone.

### CONCLUSION

Ozonation, hydrodynamic cavitation, and a combination of the two were evaluated for the degradation of Blue KN-R. It was found that the combined method gave the synergetic effect compared to the single methods. The higher the pH and the more ozone used, the better the decolorization achieved. The highest degradation was achieved in alkaline conditions and with the highest dosage of ozone. For a 120 min degradation process in optimum conditions, the decolorization level and TOC removal were 92.63 and 24.54%, respectively. The result of the degradation of batik effluent was over 60% of degradation for each parameter. In addition, the hybrid method shows a higher mechanical and chemical effect from hydrodynamic cavitation, indicated by the increases in the ozone solubility, level of hydroxyl radicals and degree of degradation.

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