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# Removal of Acid Violet 90 Dyestuffs in Aqueous Solutions by Ozonation Method

Füsun BOYSAN<sup>\*1</sup>

#### Abstract

Due to the colored wastewater from many industries, especially textile dyehouses, the dyestuffs that increase in variety with the developing technology, the risk of toxicity, as well as the aesthetic concerns, create a danger for human and environmental health and their treatment is becoming increasingly important. Color in wastewater can only be partially removed by conventional treatment methods. However, by treating with ozone, which is a strong oxidant, not only the color of the waste water is removed, but also the amount of organic pollution is reduced. In this study, color removal was investigated by ozonation method in synthetic water containing Acid Violet dye with an initial concentration of 50 mg/L. As a result of the study, the maximum efficiency was reached with pH 7, ozone dose 0.375 g/L.h, time 7.5 minutes, and 48.578 mg/L substance removal was achieved.

Keywords: Ozonation, Acid Violet 90, Dyestuff, Oxidation

#### **1. INTRODUCTION**

Water is considered the most effective and the leading solvent in textile production. Textile factories are the branch that consumes the most water in the industrial field, 0.2-0.5 m<sup>3</sup> of water is normally required to create 1 kg of finished products. The waste of textile dyeing factories generally consists of various refractory materials such as intense color, chemical oxygen demand (COD), suspended solids, heavy metals and non-ionic surfactants [1]. Also, the textile industry

uses a lot of water due to the versatile washing of dyed fabrics to remove paint residues from their surfaces [2]. The presence of dyes at even very low concentrations in the effluent is undesirable as it can be highly visible [3]. Colored wastewater disrupts the clear appearance of the water and reduces the transparency of the water surface of and also distrupts the photosynthetic activity of aquatic organisms [4]. Since textile wastewaters containing toxic and potentially carcinogenic substances, they should be treated properly before discharging into water bodies [5, 6].

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It is used to process most impurities in the form of and mechanical action chemical during processing, dirt, salt, oil, grease and colors of natural fibers, used and dead dyes, chemicals, polymers and fibers. Many other industries, such as textile manufacturing and pharmaceutical, food, paper and ink manufacturing, use more than 30,000 industrial dyes with 8,000 different chemical structures and are often released into waste water [7]. Approximately 10-20% of the dyes used in textile dyehouses are directly discharged without interacting with the fabric. [8]. These potentially toxic organic and mineral compounds create wastewater that returns to the environment [9, 10].

Reactive dyes have been used more in the last decade. In addition, the wastewater treatment units of the dyehouses have started to be inadequate due to the more difficult biological degradation of these dyes, especially those containing azo groups [11]. Also, since these dyes have carcinogenic and toxic properties, more careful treatment is required before discharging [12].

Acid Violet 90 is an aromatic azo compound. Aromatic azo compounds are formed by converting the aryl diazonium cation to another aryl ring containing an electron releasing group [13]. Azo coupling reactions are carried out at cold temperatures where diazonium salts are more stable. Oxidation of hydrazines (R-NH-NH-R ') also yields azo compounds. Azo dyes derived from benzidine are carcinogens; classically their exposure to bladder cancer. Therefore, azo dye pollution is a problem to be avoided in the textile industry [14].

Since ozone is a widely used and effective oxidant, it is a treatment method used for the removal of organic and inorganic substances in water, as well as taste and color removal [15, 16]. The reaction rate of ozone is affected by both reaction kinetics and mass transfer, just like other gas absorption reactions [17]. The rate limiting step of ozone is due to a gas-liquid mass transfer rate due to its low solubility [18]. The mass transfer rate of ozone depends on the properties of the ozone mixing system, the degradation kinetics of ozone, and the size and amount of bubbles formed [13, 19]. The efficiency of ozone can be increased with a higher ozone surface area by forming smaller bubbles [20].

In this study, the removal of Acid Violet 90 dyestuff by ozonation method was investigated and optimum removal efficiency was studied. pH, reaction time and ozone dose parameters were studied in ozone removal of Acid Violet 90 dyestuff prepared as stock. Optimum results and removal efficiency have been achieved.

# 2. MATERIAL AND METHOD

# 2.1. Acid Violet 90 measurement

The dye used in the study is CI Acid Violet 90 (I18762). An aqueous dye solution with a concentration of 50 mg/L was prepared and the absorption spectrum of the dyestuff was measured in Shimadzu UV / VIS 1700 spectrophotometer, and the wavelength at which the dyestuffs showed maximum absorbance was determined to be 525 nm. Calibration was performed between 0.1 mg/L and 50 mg/L. Line equation 1 determined as:

ABS = 0.	0198. <i>C</i> - 0.0019	(1)
C		

C : concentration (mg/L)

ABS : absorbance value

NaOH and HCl solutions were used for pH adjustments. A magnetic stirrer is used to make the ozonation process homogeneous. In order to find the optimum removal results, studies of pH, ozone dose and reaction time were conducted. The chemicals used in the studies are of analytical grade.

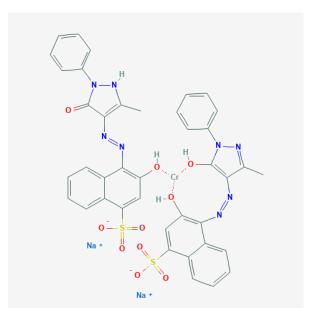


Figure 1.Acid Violet 90 molecular structure [21]

#### 2.2. Ozonation System

Ozonation process has been done using SABO SL-10 ozone generator and its maximum capacity is 15 g/L h. In the study, 50 mL solutions were placed in 100 mL beakers as the reactor and as can be seen in Figure 2, a magnetic stirrer was used to distribute homogeneously.

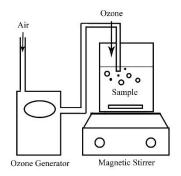


Figure 2. The diagram of the ozone purification reactor system

# **3. RESULT AND DISCUSSION**

# 3.1. Effect of pH

In the study, pH adjustments were made to be 3, 5, 7, 9 and 11 and the treatment process was carried out for 5 minutes using 0.15 g/L.h ozone

dose, dye concentration was 50 mg/L and the sample volume was 100 mL. As can be seen in Figure 3, while the treatment efficiency increased at neutral pH, it decreased in low and high pH. pH removal at pH 3, 5, 7, 9 and 11 respectively; 28.623, 30.804, 34.959, 30.246, 30.155 mg/L. The optimum pH result was found to be 69.91% at 7. The high removal efficiency of pH around 7 indicates that the purification process is predominantly with hydroxyl radicals [22]. In the study conducted by Chen et al., The highest color removal rate for the ozone treatment of Orange-13 dyestuff occurred at pH 10, while the highest color removal rate for Blue-19 dyestuff occurred at pH 3 [23].

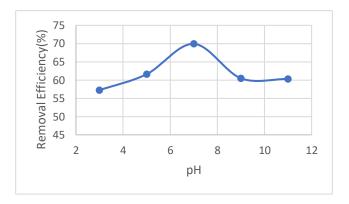


Figure 3. The effect of pH on removal efficiency (Ozone dose: 0.15 g /L.h, ,reaction time: 5 min., dye concentration: 50 mg/L, sample volume: 100 mL)

According to Chu and Ma, while ozone provides more effective oxidation at low pH, the hydroxyl radical is more effective at high pH [24]. Because of the slower decomposition rate at low pH,  $O_3$ has a higher concentration in the aqueous phase. Ozone and OH provide a more effective reaction at high pH values, and more hydroxyl radicals are released at high pH. The effect of this on color removal is as follows:

- Hydroxyl radical provides better oxidation at high pH conditions.
- O<sub>3</sub> oxidation is more dominant in low pH conditions.

The oxidation capacity of the hydroxyl radical showed greater results than the oxidation capacity of the ozone molecule on dyestuffs in other studies in the literature, as in this study [25]. On the other hand, Liu et al. also showed that the decolorization capacity of ozone is higher for some dyes at low pH [26].

#### 3.2. Effect of Ozone Dose

In the study, at pH 7, 0.075, 0.15, 0.225, 0.3, 0.375 and 0.4 g/L.h ozone doses were treated for 5 minutes, dye concentration was 50 mg/L and the sample volume was 100 mL. As can be seen in Figure 4, as the ozone dose increases, the removal efficiency increases. While the lowest removal efficiency was found to be 59.9% at the ozone dose of 0.75 g/L.h, the highest removal efficiency should be 4.0 g/L.h, 93.5% from the ozone dose, then 93% was obtained from the 0.375 g/L.h dose. However, 0.375 g/L.h ozone dose was chosen as the optimum ozone dose with 93% efficiency in order to achieve the optimum result and the lowest cost.

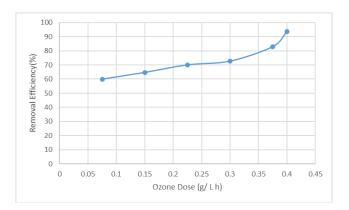


Figure 4. Effect of ozone dose on removal efficiency (pH: 7, reaction time: 5 min, dye concentration: 50 mg/L, sample volume: 100 mL)

The high ozone dose caused little increase in the color removal rate. This is because ozone passes from the gas phase to the liquid phase to form OH<sup>-</sup> radicals [24, 27, 28]. Increasing the ozone dose causes the formation of more OH<sup>-</sup> radicals and increases the removal efficiency of the dye. When the ozone concentration in the liquid phase becomes saturated, the reason why the excess ozone dose increases the color removal of dyes more is that the solubility of ozone is higher than a certain temperature and optimum dose, and it means that the hydroxyl free radicals and ozone concentrations in solution are close to unchanged [24].

### **3.3. Effect of Reaction Time**

In the study, removal efficiencies of 1.5, 2.5, 5, 7.5, dye concentration was 50 mg/L and the sample volume was 100 mL and 10 minutes reaction time were obtained as pH 7 and ozone dose at 0.375 g/L.h. As can be seen in Figure 5, the lowest removal efficiency was 70.7% in 1.5 minutes reaction time, while the highest efficiency was reached 93% in 7.5 minutes reaction time. It was determined that 7.5 minutes was optimum because 93% yield was obtained in 10 minutes reaction time.

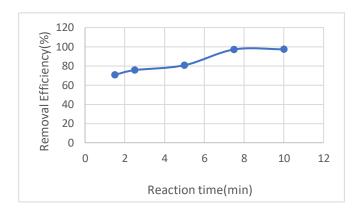


Figure 5. Effect of reaction time on removal efficiency (pH: 7, ozone dose: 0.375 g/L.h, dye concentration: 50 mg/L, sample volume: 100 mL)

As seen in the study of Öktem et al., when the reaction time increases, the curve flattens after a while and the removal almost reaches its maximum[29]. This result is consistent with mass transfer theories [30]. According to these theories, as the concentration of ozone in air bubbles increases, the driving force for transferring ozone to the paint solution increases with the increase in the ozone concentration in the solution and the dye oxidation rate.

#### 4. CONCLUSSION

Ozonation process is an effective method for treatment and disinfection and high removal efficiencies can be achieved. From an economic point of view, advanced oxidation methods appear to be not cheap [31]. Acid Violet dye used in this study was purified using ozonation, one of the advanced oxidation methods. High removal efficiencies were obtained in this laboratory scale dye removal study. Optimum results were measured as pH 7, ozone dose 0.375 g/L.h, reaction time 93% in 7.5 minutes. The pH value being optimum at 7 indicates that the oxidation takes place with hydroxyl ions.

Dyestuffs are very harmful to human and environmental health and therefore their purification is of great importance. In this study, very high treatment efficiency was obtained with ozonation, but more studies are needed on this subject. Efforts should be made to treat more than one dyestuff at the same time, to use more than one oxidation method together in treatment, and to ensure dye treatment from wastewater in subsequent studies. In addition, the economic aspects of these treatment methods should be considered and their costs should be compared.

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#### The Declaration of Conflict of Interest/ Common Interest

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# Authors' Contribution

All authors of the paper contributed actively to the parts of study such as experiments, analysis, writing and submission of article.

# The Declaration of Ethics Committee Approval

The authors declare that this document does not require an ethics committee approval or any special permission.

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The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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