Degradation of Nile Blue by Photocatalytic, Ultrasonic, Fenton, and Fenton-like Oxidation Processes

Nuket Kartal Temel iD

Faculty of Science, Sivas Cumhuriyet University, Sivas, Türkiye

Abstract: The aim of this study is to investigate new catalytic systems for the degradation of a dye that has been classified as first-degree toxic pollutant. Advanced oxidation process such as photocatalytic oxidation, ultrasonic oxidation, Fenton, and Fenton-like constitute a promising technology for the treatment of wastewater containing organic compounds. Waste effluents from textile industries are a major source of water pollution. These wastewaters contain dyes, which have high toxicity and low biodegradability. In this study, degradation of Nile Blue (NB), an azo dye, was studied using the photocatalytic oxidation (TiO_2 and silver-loaded TiO_2 ($Ag-TiO_2$) as catalyst), ultrasonic oxidation, Fenton ($Fe(II)/H_2O_2$), and Fenton-like ($Cu(II)/H_2O_2$, $V(IV)/H_2O_2$) processes. It was found that the photocatalytic degradation of NB increased with decreasing pH, and the degradation rate also increased in the presence of TiO_2/UV compared to UV irradiation alone. In addition, Ag loading on TiO_2 dramatically reduced the degradation time. The ultrasonic degradation of NB was also studied using different initial dye concentrations at different pH values and amplitudes. Concentrations of Fe(II), Cu(II), V(IV) and H_2O_2 on degradation ratio were investigated. It is found that Fe(II) ion is more effective than Cu(II) and V(IV) ions in the degradation of NB.

1. INTRODUCTION

Today, water pollution is one of the main factors that adversely affect human health. At the beginning of the 21st century, mankind has to face the problem of water as a major threat. Especially, industrial activity generates high amounts of wastewater, which resistant the biodegradability. Indeed, azo dyes represent a significant class of synthetic organic compounds widely used in various industries, including textiles, cosmetics, food, and pharmaceuticals. They are characterized by the presence of one or more azo (-N=N-) groups, which give them their distinctive color properties (Hsueh et al., 2005; Neamtu et al., 2003; Chacón et al., 2006).
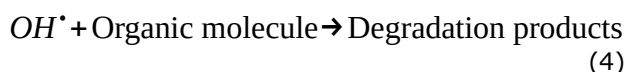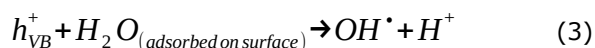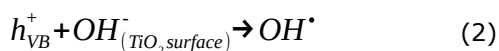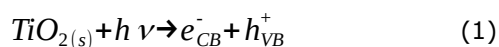
These industries effluents vary widely in composition, containing organic, inorganic compounds and high color and COD levels. Colored textile wastewater contains persistent dyes. Many of these dyes have been reported to be toxic and carcinogenic to humans (Anliker, 1979). Direct discharge of these effluents can result in the creation of toxic aromatic amines in the receiving environment under anaerobic conditions. This can lead to soil and groundwater contamination, necessitating appropriate treatment before discharge into the environment. Various methods are used to remove color from dye wastewater. However, these methods are not effective when treating wastewater that contains both soluble and insoluble dyes. For instance, the process of ozonation oxidation can efficiently remove color from wastewater that contains soluble dyes, such as reactive dyes (Perkins et al., 1980). However, it is important to note that ozonation oxidation is not effective in the degradation insoluble dyes, such as disperse dyes. Coagulation is an effective method for the degradation insoluble dyes, but it is not effective for soluble dyes (Netpradit et al., 2003). Finally, Fenton's reagent (Fenton, 1894) has been demonstrated to be effective in the degradation both soluble and insoluble dyes (Kuo 1992).

The Advanced Oxidation Techniques (AOPs) are primarily based on the generation of the hydroxyl radical (OH°), which has significant oxidation power.

The destruction of pollutants is traditionally attributed to the highly reactive hydroxyl radical (OH°). The application of these methods for various chemicals involving different processes was well reviewed by Titus et al. (Titus et al., 2004).

Photocatalytic oxidation processes are commonly known as AOPs. When a photon with energy matching or exceeding the semiconductor's band gap energy strikes the semiconductor surface, a conductive band electron will move to its valence band, leaving a positively charged hole (Saien et al., 2003). The first step in this photo-oxidation process is thought to be the creation of free hydroxyl radicals (Ollis et al., 1991; Wu et al., 1999). Hydroxyl radicals are produced through the oxidation of water (OH⁻ ions) by valence band positively charged holes. The mechanism of TiO_2 based photocatalytic degradation of dyes was described in previous work (Sökmen et al., 2001).
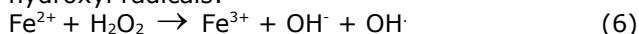
$$TiO_{2(s)} + h\nu \rightarrow e_{CB}^- + h_{VB}^+ \tag{1}$$

$$h_{VB}^+ + OH_{(TiO_2 surface)}^- \rightarrow OH^\cdot \tag{2}$$

$$h_{VB}^+ + H_2O_{(adsorbed on surface)} \rightarrow OH^\cdot + H^+ \tag{3}$$

$$OH^\cdot + \text{Organic molecule} \rightarrow \text{Degradation products} \tag{4}$$

However, the dissolved O_2 molecules are transformed into anionic superoxide ($O_2^{-\bullet}$) radicals via electrons from conductive band.

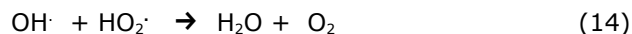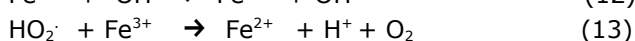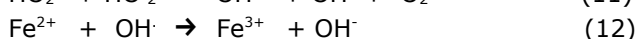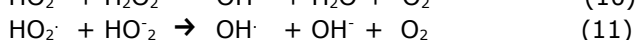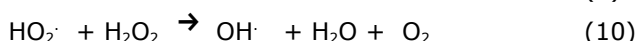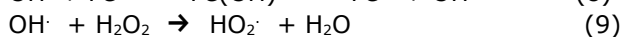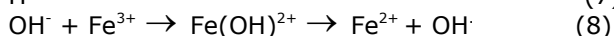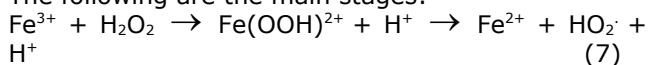$$e_{CB}^- + O_{2 \text{ (adsorbed on surface)}} \rightarrow O_2^{-\bullet} \tag{5}$$

Fenton's reagent is a mixture of ferrous (Fe (II)) ions and hydrogen peroxide that produces OH° radicals (as shown in equations 6-14). It has been widely used for the oxidation of organic matter in water (Goldstein et al., 1993; Nidheesh et al., 2013). The main advantage of this method is the complete destruction of contaminants, which are converted into harmless compounds such as CO_2, water, and inorganic salts (Xu et al., 2004). The mechanism of Fenton and Fenton-like oxidation of dyes was described in a previous work (Sökmen et al., 2011).

Ferrous ions react with hydrogen peroxide to form hydroxyl radicals:
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\cdot \tag{6}$$

The following are the main stages:
$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{2+} + H^+ \rightarrow Fe^{2+} + HO_2^\cdot + H^+ \tag{7}$$
$$OH^- + Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe^{2+} + OH^\cdot \tag{8}$$
$$OH^\cdot + H_2O_2 \rightarrow HO_2^\cdot + H_2O \tag{9}$$
$$HO_2^\cdot + H_2O_2 \rightarrow OH^\cdot + H_2O + O_2 \tag{10}$$
$$HO_2^\cdot + HO_2^- \rightarrow OH^\cdot + OH^- + O_2 \tag{11}$$
$$Fe^{2+} + OH^\cdot \rightarrow Fe^{3+} + OH^- \tag{12}$$
$$HO_2^\cdot + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2 \tag{13}$$

$$OH^\cdot + HO_2^\cdot \rightarrow H_2O + O_2 \tag{14}$$

Fenton oxidation has been used to degradation effluents from textile dyeing and dye manufacturing processes (Kim et al., 2004). Compared to other oxidation processes, such as UV/H_2O_2, Fenton oxidation is relatively inexpensive (Dutta et al., 2001). Recently, Fenton oxidation has been increasingly used in various treatment processes due to its ease of operation, simple system, and ability to work in a wide range of temperatures (Solozhenko et al., 1995).

For the oxidation of organic matter in water, Fenton's reagent has been widely used (Safarzadeh-Amiri et al., 1996). Its main advantage is that it thoroughly removes contaminants, producing innocuous materials such as CO_2, water, and inorganic salts (Neyens and Baeyens 2003). As discussed by Goldstein et al. (1993), new homogenous catalyst systems producing hydroxyl radicals can be developed for the oxidative degradation of organic compounds. Employing this type of catalyst systems would be an alternative to classical Fenton catalyst since it would help reducing hydroxide mud. On the other hand, it was previously reported that (Allen et al., 2002) multiple hydroxylated oxidation products were produced in Fenton-like systems employing Cu^{2+}, V^{4+}, Ti^{3+} catalyst which were more effective oxidant in some cases (Sökmen et al., 2002). Therefore, application of these type systems should be studied for oxidative degradation of different organic compounds.

Heterogeneous metal-supported catalysts are replacing homogeneous catalysts (Wang et al., 2016; Liu et al., 2021). The catalytic activity can be attributed to the generation of hydroxyl radicals from hydrogen peroxide, which are activated by iron ions and are simultaneously leached from the support material as a homogeneous catalyst (Jiang et al., 2010; Liu et al., 2007; Kumar et al., 2020; Sun et al., 2021; Abo-Farha 2010).

In this study, the degradation of NB dye from wastewater by AOP methods such as photocatalytic oxidation, ultrasonic oxidation, Fenton and Fenton-like were investigated. Catalytic action of copper(II) and vanadium(IV) ions in the presence of hydrogen peroxide were studied and compared with Fenton's reagent.

2. EXPERIMENTAL SECTION

Nile Blue (NB, FW= 353.85 g mol⁻¹) was kindly supplied from a textile dye branch of Ciba (Germany) in Turkey. Deionized water (100 mL) was used to make the NB solutions of desired concentration (100 μM).

2.1. Degradation of NB by Photocatalytic Process

Initially, 100 mL of an aqueous dye (NB) sample and 0.1 g of TiO_2 (either neat TiO_2 or Ag-loaded

TiO₂) were placed in a 250 mL Pyrex flask, which was covered with aluminum foil and fitted with a condenser. After adjusting the pH of the dye solution, the stirred suspension was illuminated with one OSRAM-Ultra Vitalux 300W lamp at about 5.8W at 254nm. To separate the TiO₂ for residual dye analysis, 3-mL aliquots of the irradiated sample were taken at regular intervals and centrifuged twice at 3500 rpm for 10 minutes. The concentration of the residual dye in the supernatant was monitored by spectrophotometry at a wavelength of 600 nm for 60 minutes.

2.2. Degradation of NB by Fenton and Fenton-like Processes

Hydrogen peroxide (%33 w/w) was obtained from Merck and used at a various range of concentration. Required amount of catalyst was dissolved in 5 mL of 0.1 M H_2SO_4 solution. H_2O_2 concentration was adjusted to desired ratio of catalyst to H_2O_2. Catalyst and H_2O_2 concentration ratios were used as 1:1, 1:5, 1:10 and 1:20.

Experimental studies were designed in a sealed flask. In the first stage 100 mL stock solution of dye and desired amount of catalyst were placed and pH was adjusted to 2.0. H_2O_2 was then slowly added to the reaction mixture. The reaction time in both Fenton and Fenton-like process was recorded after addition of H_2O_2 solution and 3-mL portions were withdrawn at certain intervals and absorbance of NB were measured at 600 nm.

2.3. Degradation of NB by Ultrasonic Process

Sonolyses were performed with an ultrasonic processor (Cole Parmer Instruments, Vernon Hills, Illinois, USA) operating at 20 kHz and 25 °C. In each experiment, 250 mL of aqueous dye sample with desired concentration was placed in to a 500 mL pyrex flask and its pH was adjusted. The solution was poured into ultrasonic processor and mechanical stirrer was used. At certain reaction intervals, 3 mL of sample was withdrawn. Concentrations of the residual dye in the supernatant were spectrophotometrically monitored for 60 min at 600 nm.

The following equation was used to calculate the degradation percentage from the relative abundance of the corresponding NB.

$$Degradation = \frac{[NB]_0 - [NB]_t}{[NB]_0} \times 100 \qquad (15)$$

t: time of sample collection

3. RESULTS AND DISCUSSION

The structure of the NB is given in Fig.1. Absorption spectra of the dye solutions were recorded and given in Figure 2 in the absence and presence of catalyst. NB has a maximum at 600 nm in aqueous solution at pH 2.0. From the observation it is visible that no new absorption peaks occurred near the original maximum wavelength.
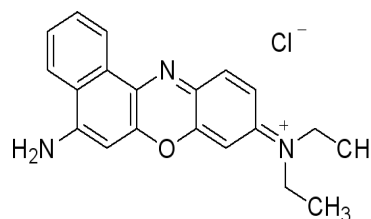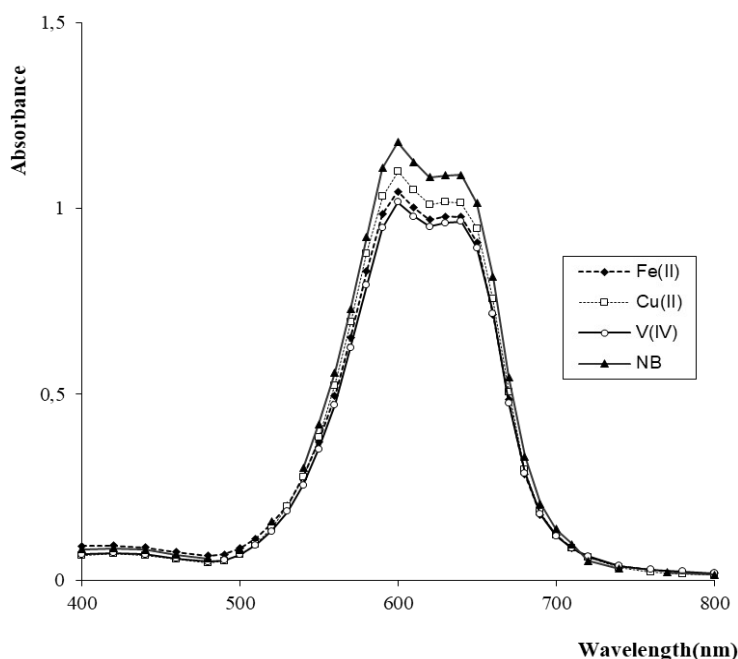

Figure 1: Chemical structure of NB.

Figure 2: Spectrum of NB and spectra when Fe(II), Cu(II), V(IV) salts are added to the NB solution.

3.1. Photocatalytic Degradation of NB

In the presence of TiO$_2$ particles, with and without UV illumination, a series of experiments were performed using NB dye. The same procedure was repeated for Ag-loaded TiO$_2$. The results are shown in Figure 3. Each data point shown in all the figures represents the average of three replicates.

It can be seen that the degradation time for the NB dye is dramatically reduced by the Ag-loading. While the undoped TiO$_2$ degradation approximately 50% of the initial amount within 15 min, the Ag-loaded TiO$_2$ degradation 90% of the initial amount in the same time period. As shown in Figure 3, the degradation of the dye in the absence of TiO$_2$ was very slow with UV irradiation, and the degradation with only TiO$_2$ without UV irradiation (in the dark) is also very slow. Complete degradation time is approximately 30-60 min with TiO$_2$ and UV irradiation. Complete degradation of the dye took as little as 20 minutes with the Ag-loaded catalyst.

As noted previously, the Ag-loading dramatically shortened the degradation time for the NB dye. Increasing the amount of Ag-TiO$_2$ steadily affected the degradation as shown in Figure 4.
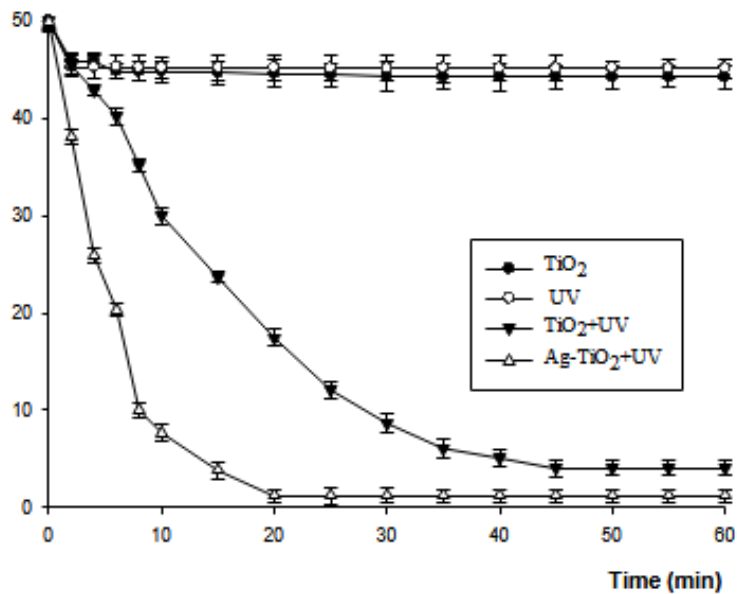

Figure 3: Photocatalytic degradation of NB versus irradiation time for several systems at pH 2.0.

The increase in removal rate is due to: (i) increasing the amount of catalyst, which increases the number of adsorbed dye molecules, and (ii) increasing the density of particles in the area of illumination (Woislawski 1953). The degradation rate is proportional to the TiO$_2$ concentration at TiO$_2$ concentrations below about 1.0 g L^{-1}. It is likely that the degradation rate was limited above 2.0 g L^{-1} of TiO$_2$ because the UV light can be blocked by the catalyst itself.
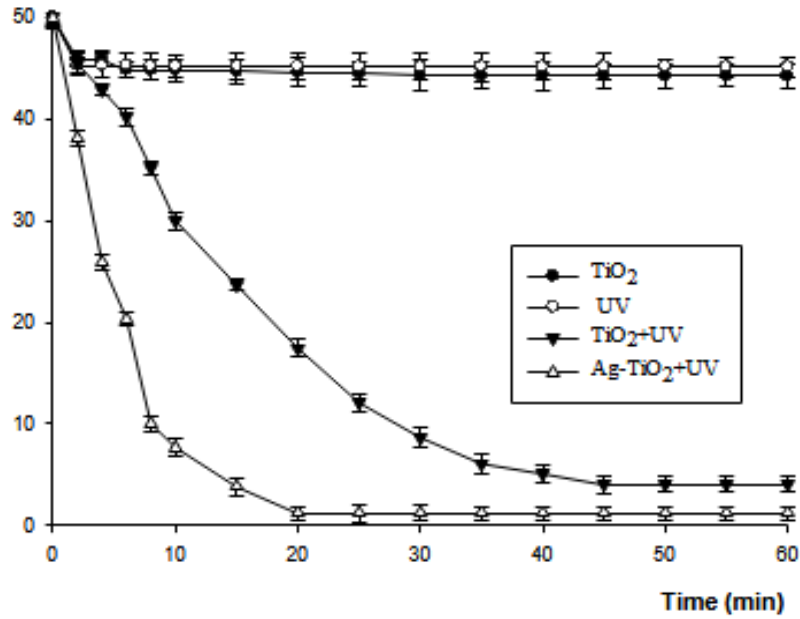
Figure 4: Photocatalytic degradation of NB versus irradiation time in TiO_2/UV and different amount of Ag-TiO_2/ UV systems at pH 2.0.

3.2. Ultrasonic Degradation of NB

The amplitude is another important factor that influences the efficiency of ultrasonic degradation. The study examined the impact of amplitude within the 20-50% range. The results are presented in Figure 5. As shown in the figure, the final concentration of NB decreases as the amplitude increases. According to reference (Kidak and Ince 2006), the reason for this is that as the volume decreases at the same energy input, there is a higher amount of energy dissipated to the system.
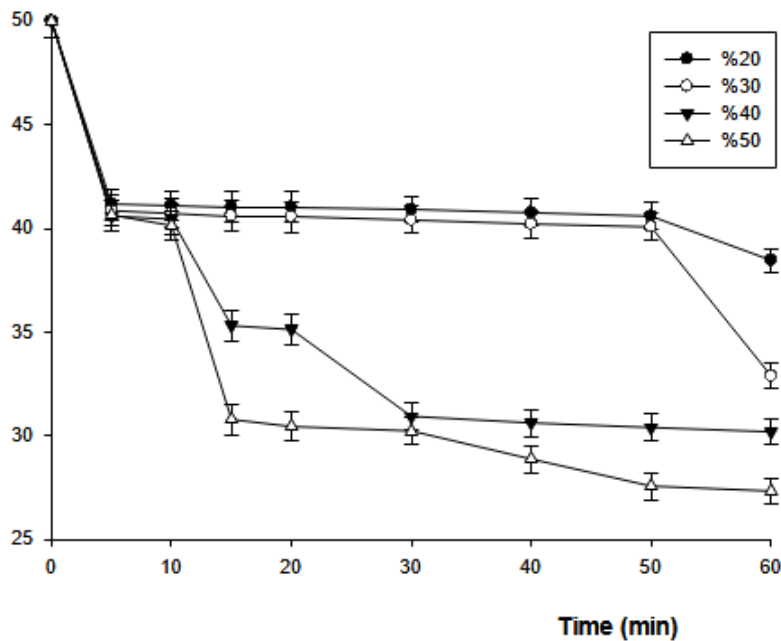

Figure 5: Effect of amplitude on the ultrasonic decolorization of NB at pH 2.0.

3.3. Degradation of NB with Fenton and Fenton-like processes

Time-dependent degradation of NB with Fenton's reagent is shown in Figure 6 employing different catalysts to hydrogen peroxide ratio at pH 2.0.
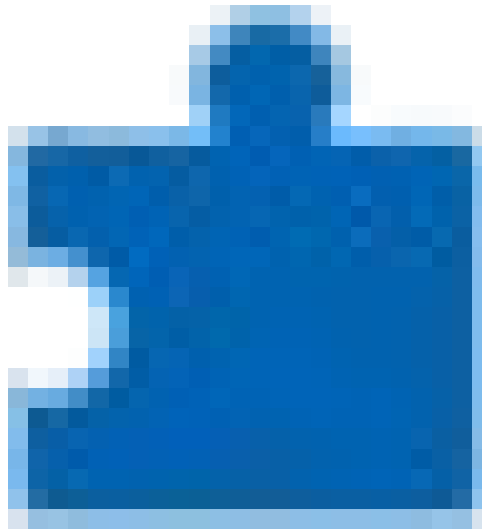
Figure 6: Time-dependent degradation of NB with Fenton's reagent at pH 2.0.

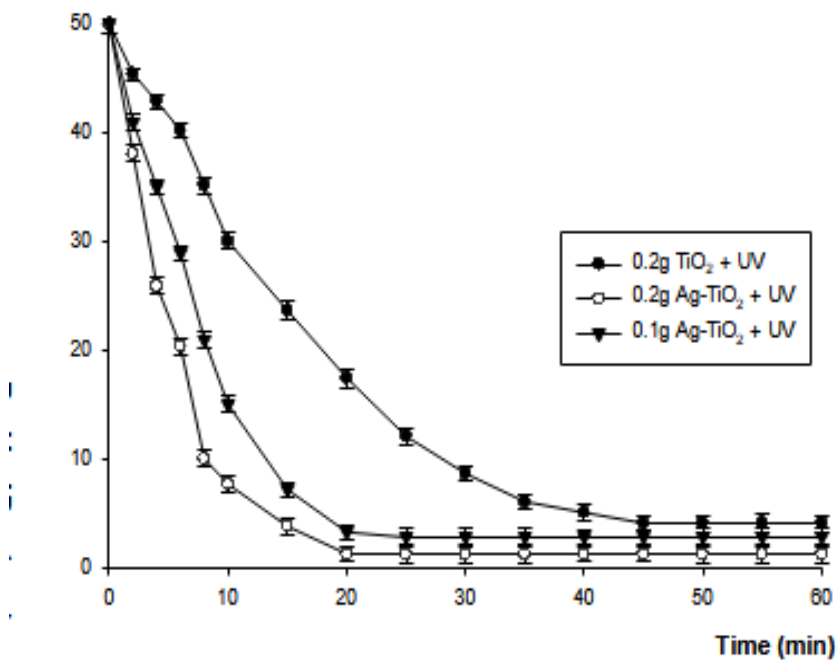Time-dependent degradation of NB with Fenton-like's reagents are shown in Figure 7 and in Figure 8.

Figure 7: Time-dependent degradation of NB with Fenton-like's reagent (Cu(II)/H_2O_2) at pH 2.0.
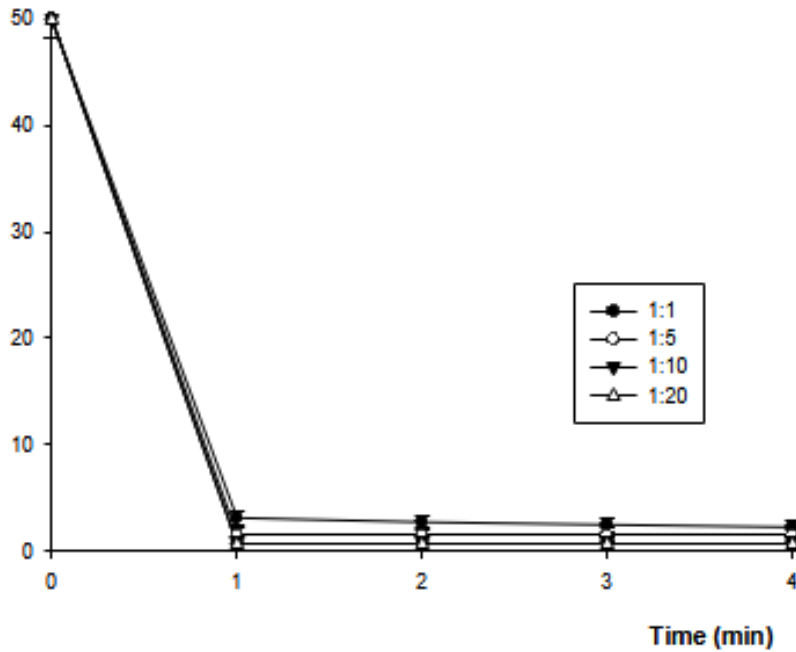
Figure 8: Time-dependent degradation of NB with Fenton-like reagent (V(IV)/H_2O_2) at pH 2.0.

The concentration of the residual dye in solution was calculated. Time versus concentration of the residual dye in solution results are shown Figure 9.
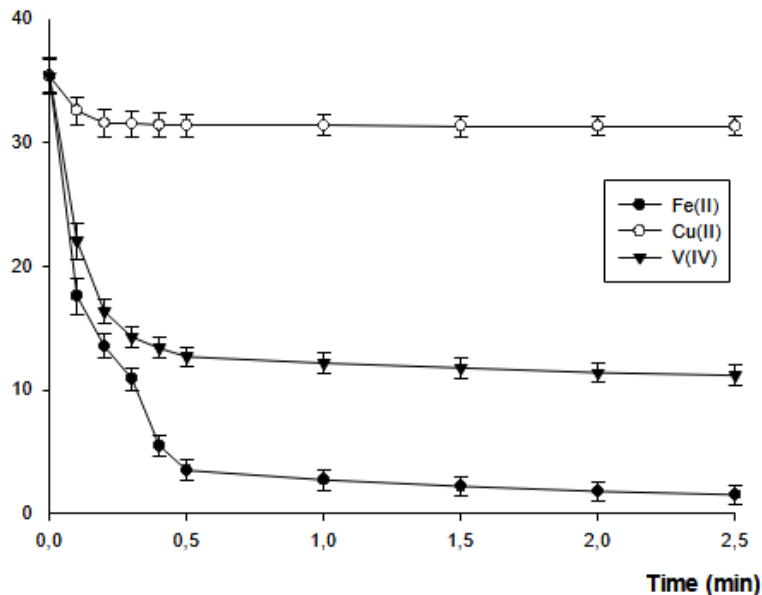
Figure 9: The concentration of the residual dye in solution after every process as a function of reaction time at pH 2.0.

4. CONCLUSION

NB dye is a common chemical used in the dyeing and printing industries, particularly in the production of cellulose acetate rayon, calico cotton, and wool. Consequently, the compound was selected as a model contaminant with which to evaluate the photocatalytic, ultrasonic, Fenton processes and Fenton-like activity. Singha, j. et al. were concluded that the photocatalytic oxidation shows high photocatalytic activities for the degradation of NB exhibited excellent degradation (93% removal in 120 min). Saleem and co-workers degradation NB by using TiO_2 nanoparticles as

photocatalyst in the presence of H_2O_2 (95% removal in 100 min).

In a similar study, Yasmeen, S., et al. observed a 97% reduction in NB in a 220-minute photocatalytic oxidation process. Yasmeen, S., et al. also found 90% removal of NB in 5 hours by photocatalytic oxidation. Kushwaha[a] et al.(2019) and Kushwaha[b] et al. (2018), obtained 66% removal of NB in 12 min and 92.46% removal in 20 min by Fenton and Fenton-like oxidation, respectively. The results obtained in our study are 95.64% for Fenton, 11.51% for Fenton-like(Cu(II)), 71.73% for Fenton-like (V(IV)) after 2 minutes. A comparison of the results obtained in this study with those reported in the literature reveals that the Fenton process is more efficient than other methods, with higher yields achieved in a shorter time.

In this work, the degradation of NB by photocatalytic processes, ultrasonic processes, Fenton processes and Fenton-like processes is studied. Among these methods, Fenton and Fenton-like processes was found to be the most effective method. In this process, complete degradation was observed after 2 minutes of treatment. Ag-loaded TiO_2/UV photocatalysis was found to be the most efficient method after Fenton oxidation to degrade NB. The Fenton and Fenton-like processes described here are more advantageous than other oxidation processes because they are faster, they require less energy, and the catalyst can be reused many times without the need for further treatment. It has been found that the H_2O_2 and iron concentration in the solution were the main factors that influence the degradation. $FeSO_4$ and H_2O_2 concentration ratios were studied as Fe(II):H_2O_2 ratio (1:1), (1:5), (1:10) and (1:20). The optimum Fe(II):H_2O_2 ratio for Fenton-like processes were found as 1:5. The results are %95.64 for Fenton, %11.51 for Fenton-like(Cu(II)), %71.73 for Fenton-like (V(IV)) after 2 minutes.

5. CONFLICT OF INTEREST

There is no conflict of interest between the authors.

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