Influence of anions and cations on the oxidation of basic blue 26 and basic violet 3 dyes by the Fenton process

Influência de ânions e cátions na oxidação dos corantes basic blue 26 e basic violet 3 pelo processo Fenton

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Kumar Djamil Belaid
PhD in Process and Environmental Engineering
Institution: LPEME, Laboratory, Djillali Liabes University of Sidi Bel-Abbes
Address: Sidi Bel-Abbes, 22.000, Algeria
E-mail: kumar.d.belaid@gmail.com

Hichem Seddiki
Master’s in Applied Chemistry
Institution: Faculty of Exact Sciences, Djillali Liabes University of Sidi Bel-Abbes
Address: Sidi Bel-Abbes, 22.000, Algeria
E-mail: hichemzati@gmail.com

ABSTRACT
Among the advanced oxidation processes (AOP) used to treat textile effluents, the Fenton process is particularly appreciated for its ability to effectively treat pollutants that are difficult to degrade by other conventional methods, such as synthetic dyes, especially basic or cationic dyes, which present the highest poisoning rates, underscoring the harmful nature of these substances. We conducted an examination in this context, concentrating on the impact of ions on dye degradation at a temperature of 294 K. This is because ions in solution left over from chemicals used during manufacturing processes can have a significant impact on the efficiency of the Fenton reaction, as they can act as catalysts or inhibitors of the reaction. The degradation of cationic, Basic Blue 26 (BB26) and Basic Violet 3 (BV3) dyes at an initial concentration of 10 mg/L by the Fenton process (Fe^{2+}/H_2O_2) was studied in this paper. The results showed a discoloration and degradation of 75.5% for BB26 and 45.4% for BV3 after 30 minutes. The effects of monovalent anions (Cl^- and NO_3^-), divalent anions (SO_4^{2-} and CO_3^{2-}), and cations (Na^+, K^+, and Ca^{2+}) on degradation rates were evaluated. The decrease in degradation yield by the presence of Na^+, K^+ and Ca^{2+} cations and Cl^-, NO_3^- and SO_4^{2-} anions for BB26 dye and by the presence of Na^+ and Ca^{2+} cations and Cl^- and SO_4^{2-} anions for BV3 dye was discussed. On the other hand, K^+ and NO_3^- ions have somewhat favoured the yield of BV3 dye degradation, while the presence of carbonate anion (CO_3^{2-}) increased the degradation rate of our two dyes.

Keywords: Fenton process, advanced oxidation, basic blue 26, basic violet 3, anions, cations.
RESUMO
Entre os processos de oxidação avançada (POA) utilizados para tratar efluentes têxteis, o processo Fenton é particularmente apreciado pela sua capacidade de tratar eficazmente poluentes que são difíceis de degradar por outros métodos convencionais, como os corantes sintéticos, especialmente os corantes básicos ou catiónicos, que apresentam as taxas de envenenamento mais elevadas, sublinhando a natureza nociva destas substâncias. Realizámos uma análise neste contexto, concentrando-nos no impacto dos íons na degradação dos corantes a uma temperatura de 294 K. Isto porque os íons em solução, provenientes de produtos químicos utilizados durante os processos de fabrico, podem ter um impacto significativo na eficiência da reação de Fenton, uma vez que podem atuar como catalisadores ou inibidores da reação. A degradação dos corantes catiónicos Basic Blue 26 (BB26) e Basic Violet 3 (BV3) a uma concentração inicial de 10 mg/L pelo processo Fenton (Fe2+/ H2O2) foi estudada neste trabalho. Os resultados mostraram uma descoloração e degradação de 75,5% para o BB26 e 45,4% para o BV3 após 30 minutos. Foram avaliados os efeitos de aniões monovalentes (Cl- e NO3-), aniões divalentes (SO42- e CO32-) e catiões (Na+, K+ e Ca2+) nas taxas de degradação. Foi discutida a diminuição do rendimento da degradação pela presença dos catiões Na+, K+ e Ca2+ e dos aniões Cl-, NO3- e SO42- para o corante BB26 e pela presença dos catiões Na+ e Ca2+ e dos aniões Cl- e SO42- para o corante BV3. Por outro lado, os íons K+ e NO3- favoreceram ligeiramente o rendimento do rendimento da degradação do corante BV3, enquanto a presença do anião carbonato (CO32-) aumentou a taxa de degradação dos nossos dois corantes.


1 INTRODUCTION
The textile industry, a major consumer of fuel and chemical products (Lellis et al., 2019), is a significant source of environmental contamination (Chiu et al., 2019). It's a top water consumer, generating large volumes of wastewater (Lyu et al., 2021). The most concerning pollution in these effluents is from colourants, which are soluble organic compounds, particularly direct, reactive, acidic, and basic dyes (Shindhal et al., 2020). Among these, basic and direct dyes have the highest poisoning rates (Rafiq et al., 2021), highlighting the harmful nature of these substances (Dutta et al., 2021).

Conventional methods for colorant removal are generally ineffective (Neto et al., 2023). Therefore, alternative techniques such as coagulation (Wei et al., 2023), ion exchange (Joseph et al., 2019), membrane filtration (Nozada et al., 2022), adsorption (Adel et al., 2021), aerobic/biological treatment (Azimi et al.,
2020), ozonation (Muniyasamy et al., 2020), and photocatalytic degradation (Rojviroon et al., 2022) have been adopted.

Advanced oxidation processes, particularly Fenton reactions, are extensively employed for the effective treatment of wastewater-containing colorants due to their simplicity and efficiency (Bello et al., 2020). Fenton processes involve the production of hydroxyl radicals (HO•) through the catalytic decomposition of hydrogen peroxide (H₂O₂) by ferrous ions (Fe²⁺) under acidic conditions (Rivera et al., 2020).

Studies on the degradation of textile effluent colorants using the Fenton oxidation process focus on optimizing key parameters such as Fenton reagent dosages (Suhan et al., 2021), reaction pH (Wang et al., 2020), temperature effects on degradation performance (Nuñez et al., 2024), potential oxidant or catalyst modifications (Belaid et al., 2022; Bhowmick et al., 2021), and combining the process with electrical current (electro-Fenton) (Thor et al., 2022), visible light radiation (photo-Fenton) (Guan et al., 2020), or ultrasound (Moradi et al., 2020).

To our knowledge, there is limited research on the influence of ion presence on the degradation of textile effluent colorants using the Fenton oxidation process. This study aims to determine the effects of certain ions, including monovalent anions (Cl⁻ and NO₃⁻) or divalent anions (SO₄²⁻ and CO₃²⁻) as well as cations (Na⁺, K⁺ and Ca²⁺), on the degradation of two cationic colorants from the triarylmethane class: Basic Blue 26 (BB26) and Basic Violet 3 (BV3). Consequently, the results of this study will contribute to a better understanding of similar studies, facilitating the optimization of operational conditions for large-scale cationic colorant treatment, given that these ions, often added upstream as salts in the textile industry process, persist in effluents and affect treatment efficiency.

2 MATERIALS AND METHODS
2.1 CHEMICALS AND REAGENTS

The colorants selected for this study are Basic Blue 26 (BB26) (M = 506.08 g/mol) and Basic Violet 3 (BV3) (M = 407.98 g/mol). They belong to the category of triarylmethane cationic dyes, as illustrated in Figure 1. Soluble in water, they are widely used as dyes in various applications, in the textile industry. Their use is
widespread, due to their ability to effectively dye a variety of materials. The main characteristics of these two studied dyes are presented in Table 1.

The various experimental conditions conducted as part of this study necessitated the use of several analytical-grade reagents: Chemical oxidant: Hydrogen peroxide 10V (H₂O₂). Catalyst: Iron sulfate (FeSO₄·7H₂O). Salts: Sodium chloride (NaCl), potassium chloride (KCl), sodium nitrate (NaNO₃), sodium sulfate (Na₂SO₄·10H₂O), sodium carbonate (Na₂CO₃), and calcium chloride (CaCl₂). Additionally, sulfuric acid (H₂SO₄) and caustic soda (NaOH) solutions were employed for pH adjustment.

2.2 EXPERIMENTAL METHOD

All degradation experiments by the Fenton process of the two dyes BB26 and BV3 were conducted in batch mode in 250 ml beakers with a volume of 100 ml, under magnetic stirring at 550 revolutions per minute and at a temperature of 294 K (Figure 2).

The colored solutions of BB26 and BV3, with initial concentrations equal to 10 mg/L, were prepared by diluting stock solutions with a concentration of 1 g/L. The pH of the study solutions was adjusted to a value equal to 3 with sulfuric acid H₂SO₄ and caustic soda NaOH.

During the Fenton oxidation experiments, a volume of 0.75 ml of the Fenton reagents was added simultaneously under stirring to the colored solution, with a concentration of 5.10⁻³ M for ferrous sulfate FeSO₄ solution and 44.64.10⁻³ M for hydrogen peroxide H₂O₂ solution. The reaction duration is 30 minutes.

Under the same conditions, the effect of ions on dye degradation was monitored by adding a corresponding mass of salt to achieve a concentration of 0.1 M. The salts used are, for monovalent anions, sodium chloride (NaCl) and
sodium nitrate (NaNO₃), for divalent anions, sodium sulfate (Na₂SO₄) and sodium carbonate (Na₂CO₃), and for cations, sodium chloride (NaCl), potassium chloride (KCl), and calcium chloride (CaCl₂).

### Table 1 – Main characteristics of the Basic Blue 26 and Basic Violet 3

<table>
<thead>
<tr>
<th>Generic Name</th>
<th>Basic Blue 26</th>
<th>Basic Violet 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trade Name</td>
<td>Victoria Blue B</td>
<td>Violet Gentiane</td>
</tr>
<tr>
<td>CAS Number</td>
<td>2580-56-5</td>
<td>548-62-9</td>
</tr>
<tr>
<td>Colour Index</td>
<td>44045</td>
<td>42555</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>506.08</td>
<td>407.98</td>
</tr>
<tr>
<td>λmax (nm)</td>
<td>616</td>
<td>579</td>
</tr>
<tr>
<td>Linear Formula</td>
<td>C₃₃H₃₂ClN₃</td>
<td>C₃₅H₃₀ClN₃</td>
</tr>
<tr>
<td>IUPAC Name</td>
<td>[4-[bis[4-(dimethylamino) phenyl]methylidene]naphthal en-1-yldiene]-phenyl azanium;chloride</td>
<td>[4-[bis[4-(dimethyl amino)phenyl]methylidene] cyclohexa-2,5-dien-1-yldiene]-dimethyl azanium;chloride;hydrate</td>
</tr>
</tbody>
</table>

Source: Authors.

![Figure 2 – Experimental setup for the treatment of dyes solution](image)

2.3 ANALYSIS

The reactions are monitored through spectrophotometric analyses of samples taken from the reaction mixture at predetermined time intervals, measuring the absorbance at the respective maximum wavelengths: 616 nm for BB26 and 579 nm for BV3. The UV-visible absorption spectra for various concentrations of the dye solutions and the corresponding calibration curves are depicted in Figure 3 for dye BB26 and Figure 4 for dye BV3. The analyses were conducted using a double-beam UV-Vis spectrophotometer of the Helios Alpha model.
The percentage of dye removed was determined using the following equation:

\[
\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  

(1)

Where \(C_0\) and \(C_e\) represent the initial and equilibrium concentrations of the dye in the aqueous solution, respectively.

Figure 3 – UV–vis absorption spectra of BB26 at increasing known concentrations (a) and calibration plot (b)

![Graph](image)

Source: Authors.

Figure 4 – UV–vis absorption spectra of BV3 at increasing known concentrations (a) and calibration plot (b)

![Graph](image)

Source: Authors.

3 RESULTS AND DISCUSSION

3.1 FENTON OXIDATION

The degradation of both BB26 and BV3 dyes by Fenton oxidation was conducted on a colored solution of 100 mL with an initial dye concentration of 10
mg/L and a pH fixed at a value of 3 by the addition of a few drops of 0.1 M H$_2$SO$_4$. A volume of 0.75 mL of Fenton reagents was added simultaneously to the colored solution, with a concentration of 5×10$^{-3}$ M for ferrous ion solution and 44.64×10$^{-3}$ M for hydrogen peroxide solution.

The degradation progress of both dyes by the Fenton process is depicted in Figure 5 by plotting the ratio of concentrations C$_t$/C$_0$ against time. The findings are summarized in Table 2.

From the curves shown in Figure 5, it is initially observed that BB26 dye is more effectively degraded than BV3 under the same operating conditions. The curves exhibit a similar trend, with a more or less distinct decrease during the first 5 minutes, followed by a slowing down of the degradation rate until the end of our experiment. The degradation rate recorded after 5 minutes is approximately 30% for BV3 and 60% for BB26. After 30 minutes of reaction, the rate reached 45% for BV3 and 75% for BB26, representing a 15% increase recorded during the last 25 minutes.

![Figure 5 – Degradation of dyes BB26 and BV3 by Fenton oxidation](image)

**Table 2 – Results of degradation of BB26 and BV3 dyes by Fenton oxidation**

<table>
<thead>
<tr>
<th>Dye</th>
<th>% Removed (5 min)</th>
<th>% Removed (30 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB26</td>
<td>60.8</td>
<td>75.5</td>
</tr>
<tr>
<td>BV3</td>
<td>30.4</td>
<td>45.3</td>
</tr>
</tbody>
</table>

Source: Authors.
3.2 EFFECT OF MONOVALENT ANIONS (Cl\(^{-}\) AND NO\(_3^{-}\))

The influence of the presence of monovalent anions (Cl\(^{-}\) and NO\(_3^{-}\)) in reactive media on the degradation of dyes by Fenton oxidation was monitored by adding a corresponding salt mass to achieve a concentration of 0.1 M. The experimental conditions in this section are consistent with those of Fenton oxidation.

The influence of monovalent anions (Cl\(^{-}\) and NO\(_3^{-}\)) on the degradation of the two dyes BB26 and BV3 are represented on Figure 6 for dye BB26 and Figure 7 for dye BV3, by plotting the ratio of \(C_t/C_0\) concentrations over time. The final yield of the reaction following the influence of the added monovalent anions is reported in Figure 8. Results found are reported on Table 3.

Table 3 – Results of degradation of BB26 and BV3 dyes by Fenton oxidation in the presence of monovalent anions

<table>
<thead>
<tr>
<th>Dye</th>
<th>Without Salt</th>
<th>Cl(^{-})</th>
<th>NO(_3^{-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB26</td>
<td>75.5</td>
<td>48.3</td>
<td>71.9</td>
</tr>
<tr>
<td>BV3</td>
<td>45.4</td>
<td>11.8</td>
<td>57.1</td>
</tr>
</tbody>
</table>

Source: Authors.

Figure 6 – Effect of monovalent anions on the degradation of BB26

Source: Authors.
The influence of the presence of Cl\(^{-}\) and NO\(_3\)^{-}, added as corresponding salt NaCl and NaNO\(_3\), on the yield of the degradation reaction of the two Fenton oxidation dyes was observed.

In the case of chloride ions (Cl\(^{-}\)), the degradation rate of the two dyes was decreased. For BB26, less than 49% of the initial quantity was degraded, for BV3 it is about 12%. The decrease in the rate of degradation of our dyes by Fenton oxidation may be explained by the reaction of chloride ions (Cl\(^{-}\)) with hydroxyl...
radicals (HO•) in competition with dyes, leading to less reactive entities than hydroxyl radicals (Dong et al., 2007).

In the case of nitrate ions (NO₃⁻), however, the degradation rate is significantly better than the results found in the presence of chloride (Cl⁻) ions, exceeding 71% for the colorant BB26. While in the case of the dye BV3 the difference is clear, the yield has been significantly improved reaching 57% compared to the test yield (without salts) which is 45.4%. It should be noted that in all cases for the BB26 dye, the presence of salts did not improve the test yield (without salts) which is 75.49%, however the drop is noticeable from the beginning for all three experiments, which expresses rapid degradation.

3.3 EFFECT OF DIVALENT ANIONS (SO₄²⁻ AND CO₃²⁻)

The influence of divalent anions (SO₄²⁻ and CO₃²⁻) in reactive media on the degradation of dyes by the Fenton process was followed by the addition of a corresponding salt mass, Na₂SO₄ and Na₂CO₃ to a concentration of 0.1 M. The operating conditions of the experiments in this section are identical to those of Fenton oxidation.

The influence of divalent anions (SO₄²⁻ and CO₃²⁻) on the degradation of dyes is represented by the plot of the ratio of $C_t/C_0$ concentrations over time, on Figure 9.

for BB26 dye and on Figure 10 for BV3 dye. The final yield of the reaction following the influence of the monovalent anions added is reported in Figure 11. Results found are reported on Table 4.

Table 4 – Results of degradation of BB26 and BV3 dyes by Fenton oxidation in the presence of divalent anions

<table>
<thead>
<tr>
<th>Dye</th>
<th>Without Salt</th>
<th>SO₄²⁻</th>
<th>CO₃²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB26</td>
<td>75.5</td>
<td>69.3</td>
<td>80.0</td>
</tr>
<tr>
<td>BV3</td>
<td>45.4</td>
<td>39.1</td>
<td>94.7</td>
</tr>
</tbody>
</table>

Source: Authors.
The influence of Na$_2$SO$_4$ and Na$_2$CO$_3$ salts on the yield of the degradation reaction of the two dyes was observed.

In the case of sulfate ions (SO$_4^{2-}$), the rate of degradation of the two dyes decreased by approximately 6% compared to the Fenton process tests without the presence of salt, although the curves appeared to be similar. For the BB26 dye a degradation rate of 69% was recorded and for the BV3 dye the recorded rate is around 39%. The decrease in the degradation rate of the two dyes may be due to the fact that ferrous and ferric ions in solution in the presence of sulphate ions lead to complex formation, thus reducing the amount of ferrous and ferric ions that are important reagents in the Fenton process (Khan et al., 2018).
On the other hand, in the case of carbonate ions (CO$_3^{2-}$), the degradation efficiency of the two dyes was improved. An increase of more than 4% in the case of BB26 dye thus recorded a degradation rate of 80%, whereas for BV3 dye the difference is clearly noticed by an increase of more than 49%, with a degradation rate of about 90% recorded after 10 minutes of reaction only and a final rate exceeding 94%.

The influence of sulfate ions and carbonate ions on the yield of the degradation reaction of the two dyes was observed, if the first to decrease the yield of the degradation of the two dyes from the second to the reverse improved and in a very pronounced way for the purple dye, contrary to what has been reported (Elmorsi et al., 2010), or the presence of carbonate ions (CO$_3^{2-}$) react with hydroxyl radicals produced in solution by Fenton reagents, thus forming less reactive carbonate radicals.

![Figure 11 – Effect of divalent anions on degradation yield](source: Authors.)

![Figure 12 – Effect of cations on the degradation of BB26](source: Authors.)
3.4 EFFECT OF CATIONS (Na\(^+\), K\(^+\) AND Ca\(^{2+}\))

In this part of the study, the effect of cations (Na\(^+\), K\(^+\) and Ca\(^{2+}\)) was determined on the degradation of the two dyes by the Fenton process. The experiments were carried out by adding a corresponding salt mass, NaCl, KCl and CaCl\(_2\), to a concentration of 0.1 M. The operating conditions of the experiments in this section are identical to those of Fenton oxidation. Figures 12 and 13 show the effect of Na\(^+\), K\(^+\) and Ca\(^{2+}\) cations on the degradation of BB26 and BV3 dyes by the Fenton process. The reaction performance is illustrated on Figure 14 and the results found on Table 5.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Without Salt</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>Ca(^{2+})</th>
<th>% Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB26</td>
<td>75.5</td>
<td>48.3</td>
<td>49.2</td>
<td>54.3</td>
<td></td>
</tr>
<tr>
<td>BV3</td>
<td>45.4</td>
<td>11.8</td>
<td>51.0</td>
<td>24.1</td>
<td></td>
</tr>
</tbody>
</table>

Source: Authors.

It is obvious that the rate of degradation of our dyes decreases compared to the Fenton experiments in the absence of ions, since all the salts added closing chloride ions, as seen above. However, as a comparison between cationic antagonists, the yield found was almost the same around 50% in the case of BB26 dye far from the salt-free yield of 75.5%, although a small increase in the rate of degradation was observed in the same direction as the cation diameter used. On the other hand, for BV3, the logic is not the same, although the presence of chloride ions
inhibited the reaction by limiting the rate of degradation, but by comparison between cations, the highest yield is that of K\(^+\) ion which is 51% higher than that of Fenton in the absence of salts which is 45.5%, whereas the rates recorded in the presence of other cations were slightly less than 12% for Na\(^+\), and about 24% for Ca\(^{2+}\).

![Figure 14 – Effect of cations on degradation yield](image)

4 CONCLUSION

Our work focused on the degradation of two cationic dyes, BB26 and BV3, by the Fenton process. The study showed that BB26 was better degraded than BV3, with a degradation rate of 75.5% for BB26 reached in 30 minutes at pH 3.0 and at 21 °C, while the degradation rate recorded for BV3 was only 45.5% under the same operating conditions.

The influence of the presence of anions and cations on the yield of the degradation reaction of the two Fenton oxidation dyes was observed. The presence of Na\(^+\), K\(^+\), and Ca\(^{2+}\) cations, as well as some anions such as Cl\(^-\), NO\(_3\)^- and SO\(_4\)^2-, in BB26 dye solution decreased the rate of degradation. For BV3 the degradation rate was decreased in the presence of Na\(^+\) and Ca\(^{2+}\) cations and Cl\(^-\) and SO\(_4\)^2- anions. This decrease in the degradation yield of our Fenton oxidation dyes may be due to complexation or capture of radicals. However, for BV3 only K\(^+\) and NO\(_3\)^- ions slightly favoured its degradation rate. Finally, the presence of carbonate anion (CO\(_3\)^2-) in our operating conditions increased the degradation rate of both dyes.
In textile effluents, these anions, cations and other ions can be present jointly and at different concentrations, which can lead to a multitude of complex interactions. The Fenton process can be used for the treatment of textile wastewater, which contains dyes, and more specifically cationic dyes such as BB26 and BV3, especially since it can be effective and easy to implement.

The future prospects for Fenton processes are promising, particularly for the treatment of textile wastewater and the degradation of dyes, and more specifically cationic dyes such as BB26 and BV3. Current innovations focus on improving efficiency, taking account of real effluent conditions, with the aim of increasing applicability in a variety of industrial contexts.
REFERENCES


