Fenton process combined with precipitation for the removal of Direct Blue 1 dye: A new approach

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Abstract: Azo dyes are recalcitrant pollutants present in effluents of several industries. Due to their chemical stability, their degradation efficiency is not satisfactory by conventional technologies. Advanced oxidation processes, such as Fenton, can be applied for the removal of recalcitrant compounds. However, these methods are still costly. In this work, Fenton and precipitation treatments were combined for the removal (*i.e.*, decolorization) of direct blue 1 (DB1), as an option to decrease operational costs. The individual treatments were studied separately using DB1 solutions 0.04 mmol L^{-1} to determine the effects of the parameters involved in each process. For the Fenton treatment, the $c(\mathrm{Fe}^{2+}){:}c(\mathrm{H_2O_2})$ ratio that allowed the highest DB1 decolorization was 1:40. Regarding precipitation, the highest dye decolorization was achieved at a pH value of 6.0. Moreover, it was determined that a minimum $c(\mathrm{DB1}){:}c(\mathrm{Fe}^{2+})$ ratio of 1:7.7 is needed to allow the decolorization of the dye by precipitation. Fenton assisted with precipitation tests were performed with DB1 solutions 0.09 mmol L^{-1} and using a $c(\mathrm{DB1}){:}c(\mathrm{Fe}^{2+})$ ratio of 1:7.3 (which allows only partial precipitation of DB1). The results suggested that the dye can be treated by a Fenton process for 5 min and then precipitated to achieve the almost total decolorization of the dye (97.79 %).

Keywords: advanced oxidation processes; azo dyes; degradation of dyes; hydrogen peroxide, ferrous sulfate.

INTRODUCTION

Dyes are substances that impart color to a specific substrate. For this reason, they are widely employed in several applications including the coloring of paper, textile, food, clinical products, cosmetics, and others. Until the middle of the 19th century, almost all dyes were obtained from natural sources. However, the limit-

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ations of natural dyes (*i.e.*, limited availability of colors or low stability) promoted the production of a variety of synthetic dyes.[1,2]

Azo dyes represent one of the largest groups of synthetic dyes produced worldwide. It has been estimated that the production of azo dyes is around 60 to 70 % of the entire worldwide production of dyes.[3] This kind of dyes is characterized by the presence of one or more azo groups (–N=N–) in their chemical structure. Furthermore, they have chemical, photolytic, and microbial resistance. These characteristics coupled with a complex structure determine that these substances are recalcitrant and xenobiotic.[1,4]

The discharge of wastewaters containing azo dyes could have a serious impact on the environment and human health. There are some reports about the toxicity of azo dyes to various aquatic organisms. They could inhibit the photosynthesis of algae by blocking the penetration of light. In addition, the natural degradation of some azo dyes under certain conditions can generate mutagenic and carcinogenic by-products such as aromatic amines.[5]

Conventional treatments such as biological oxidation, chemical coagulation, and adsorption are not always effective for the removal of azo dyes.[6,7] For this reason, some studies have been focused on the application of advanced oxidation processes (AOPs) as feasible technologies for the treatment of water that contains this kind of pollutants.[8–10] AOPs are characterized for the *in situ* formation of hydroxyl radicals ($\bullet$OH) which allow the degradation of recalcitrant compounds to form biodegradable molecules or even its mineralization to CO_2, H_2O and inorganic ions.[11] These radicals are considered strong non-selective oxidants with a standard oxidation–reduction potential of 2.80 V.[12]

Among AOPs, the Fenton treatment has some advantages over other processes such as easy operation and maintenance, simple equipment, no toxic reagents, atmospheric conditions, and no mass transfer limitations due to its homogeneous catalytic nature.[13,14] The Fenton reactions are based on the formation of $\bullet$OH using a combination of hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}) at acidic conditions.[15] Some studies demonstrated that Fenton treatment can successfully remove dyes and other recalcitrant pollutants.[15,16] However, its industrial application in some cases could be tough task due to the relatively high costs of the treatment.[1,17] For instance, Santiago *et al.* reported a price of 2.06 € m^{-3}. From this, more than 60 % of the operational costs were attributed to Fenton treatment.[18] The combination of AOPs with traditional methods could represent a solution to decrease operational costs, reaction time, and the amount of reagents required.[19,20] There are some reports on the application of the Fenton process with conventional treatments such as biological treatment and precipitation.[21–23] Among these processes, precipitation, using inorganics salts or certain polymers, has been widely used for wastewater treatment. In such cases, the addition of

these reagents can destabilize the particles of the pollutants in the solution and force them to precipitate.[24]

Although some studies have tested the combination of Fenton oxidation (using ferrous sulfate and hydrogen peroxide) and precipitation using polymers (*i.e.*, cationic polyacrylamide – CPAM, polymeric aluminum – PAC),[25,26] there are also some reports about the capacity of iron to precipitate azo dyes by adjusting the pH value.[17,27] Taking this fact into consideration, it seemed interesting to evaluate if both Fenton and precipitation processes could be combined using only iron, thus reducing the quantity of reagents required.

In this work, the combination of Fenton and precipitation processes using soluble Fe^{2+} and H_2O_2 are proposed for the treatment of direct blue 1 (DB1) in solution. Such combination implies a decrease in iron requirements and thus a reduction in treatment costs. The individual treatments were studied separately to determine the effects of the parameters involved in each process. Then, the treatments were combined in a process called, for the purpose of this work, "Fenton assisted with precipitation."

EXPERIMENTAL

Reagents

0.04 mmol L^{-1} (40 mg L^{-1}) and 0.09 mmol L^{-1} (90 mg L^{-1}) solutions of Direct Blue 1 ($C_{34}H_{24}N_6Na_4O_{16}S_4$, DB1) were prepared using commercial Direct Blue 1 dye obtained from Dyetex (Ecuador) and bi-distilled water. Hydrogen peroxide, H_2O_2 (30.0 %) and ferrous sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$ (≥ 99.0 %) were purchased from Fisher Chemical. For all the experiments, a batch scale system that consisted of a vessel with a magnetic stirrer (400 rpm) was employed for the treatment of DB1 solutions (250 mL). The dye concentration after each treatment was measured using a spectrophotometer UV–Vis (Hitachi U-1900) at a wavelength of 565 nm (determined experimentally based on the UV–Vis spectra of the dye). The chemical structure of DB1 is provided in Fig. 1.
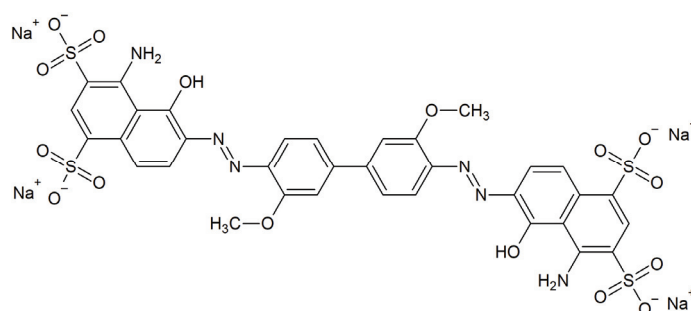

Fig. 1. Chemical structure of Direct Blue 1 (DB1) ($\lambda_{max} = 565$ nm).

Treatment of the DB1 solution by Fenton process

The Fenton process was carried out using samples of 250 mL of DB1 solutions (0.04 mmol L^{-1}). For these experiments, the initial concentration of $FeSO_4 \cdot 7H_2O$ was set at 0.66

mmol L^{-1}, and three different $c(Fe^{2+})$:$c(H_2O_2)$ ratios were tested (1:10, 1:20 and 1:40). These values were selected based on previous studies.[28,29] The initial pH value of the solutions was regulated to 2.8 (considered optimum for the Fenton process by various authors[16,30]) using sulfuric acid (0.1 N). The total time of the Fenton reaction was 10 min. Aliquots (5 mL) were taken each minute in order to follow the degradation reaction kinetics. A completely randomized experimental design was applied for this part of the work. The $c(Fe^{2+})$:$c(H_2O_2)$ ratio that allowed the higher degradation of DB1 (considering the statistical analyzes) was selected for the subsequent tests. All runs were carried out in triplicate at room temperature (~18 °C).

Treatment of the DB1 solution by precipitation

For the treatment of DB1 by precipitation, the experiments were conducted in two parts. In the first part, a solution of FeSO$_4$·7H$_2$O (0.66 mmol L^{-1}) and DB1 (0.04 mmol L^{-1}) was prepared ($c(DB1)$:$c(Fe^{2+})$ = 1:16.3). The initial pH of this solution was regulated to 2.8 (to allow the dissolution of FeSO$_4$·7H$_2$O) using sulfuric acid (0.1 N). The solution was homogenized for 10 min. Then, the precipitation was promoted by adding sodium hydroxide (0.1 N) to increase the pH value. Three final pH values (6.0, 8.0 and 9.3) were tested. The remaining concentration of DB1 in the solution was spectrophotometrically measured. The final pH value of the precipitation process was selected following the decolorization of the DB1 solution.

In the second part of the precipitation analyzes, the effect of using different $c(DB1)$:$c(Fe^{2+})$ ratios on the decolorization of the DB1 solution, was studied. In this case, the precipitation process was performed using the following $c(DB1)$:$c(Fe^{2+})$ ratios: 1:3.3; 1:4.4; 1:6.5; 1:7.3; 1:8.2; 1:9.3; 1:10.9; 1:13.1 and 1:16.3. The concentration of Fe^{2+} was set at 0.66 mmol L^{-1}, and the concentration of DB1 was varied from 0.04 to 0.20 mmol L^{-1}.

Decolorization of the DB1 solution by Fenton assisted with precipitation

Fenton and precipitation processes were combined for the treatment of aqueous solutions of DB1 (0.09 mmol L^{-1}). The aim of these experiments was to initiate the treatment with a $c(DB1)$:$c(Fe^{2+})$ ratio below the minimum, one that has to be applied to allow at least 95 % decolorization of the DB1 solution by precipitation. In other words, the idea was to treat the solutions with a Fenton process until the $c(DB1)$:$c(Fe^{2+})$ ratio reaches the value in which the decolorization could be completed by precipitation.

In this study, the Fenton assisted by precipitation tests were carried out with one $c(DB1)$:$c(Fe^{2+})$ ratio (chosen according to the conditions explained) as an example of how these processes can be combined. The time needed for the Fenton process was established for the $c(DB1)$:$c(Fe^{2+})$ ratio chosen. Two aliquots were taken each 5 min for a total time of 20 min. The first aliquot was used to measure the decolorization of the DB1 solution by Fenton, and the second one was used to precipitate the dye by increasing the pH of the sample. The remaining concentration of DB1 in the samples was spectrophotometrically measured.

Potential electrostatic map

A potential electrostatic map of DB1 anion was modeled by quantum chemical calculations using the software Gaussian 16W and Gaussview 6. The surface was generated from the optimized structure of the DB1 anion (4-) at B3LYP/6-311G(d,p) level of calculation.[31]

RESULTS AND DISCUSSION

Treatment of the DB1 solution by Fenton process

Fig. 2a shows the degradation of DB1 applying a Fenton process using different $c(Fe^{2+})$:$c(H_2O_2)$ ratios. The degradation reaction was adjusted to

pseudo-first-order kinetics. Other studies have also applied pseudo-first-order kinetics to describe the degradation reaction of other dyes by a Fenton process.[32]
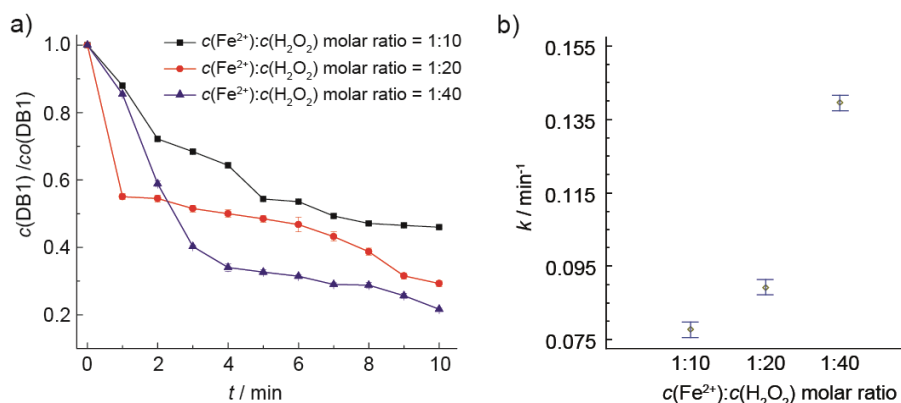

Fig. 2. a) Decolorization of the DB1 solution by a Fenton treatment for the different $c(Fe^{2+})$:$c(H_2O_2)$ ratios tested; b) Effect of $c(Fe^{2+})$:$c(H_2O_2)$ ratio on the rate constants of the degradation of DB1 by the Fenton process ($c(DB1)$:$c(Fe^{2+})$ = 1:16.3; initial pH 2.8).

The rate constants of DB1 degradation by Fenton are reported in Table I. A completely randomized experimental design was applied to determine the best $c(Fe^{2+})$:$c(H_2O_2)$ ratio. The results of the statistical analysis (Fig. 2b) shows that the rate constant increased with the increment of $c(Fe^{2+})$:$c(H_2O_2)$ ratio. The highest rate constant (0.1395±0.0025 min^{-1}) corresponded to a $c(Fe^{2+})$:$c(H_2O_2)$ ratio of 1:40. The decolorization of the DB1 solution at this condition was around 78.47 %.

TABLE I. Rate constants (k) of the degradation of DB1 by a Fenton process using different $c(Fe^{2+})$:$c(H_2O_2)$ ratios ($c(DB1)$:$c(Fe^{2+})$ = 1:16.3; initial pH 2.8)

$c(Fe^{2+})$:$c(H_2O_2)$	k / min^{-1}	R^2
1:10	0.0778 ± 0.0008	0.9317 ± 0.0109
1:20	0.0892 ± 0.0025	0.8273 ± 0.0049
1:40	0.1395 ± 0.0025	0.8658 ± 0.0070

As mentioned before, the Fenton reaction is produced by the reaction of Fe^{2+} ions and H_2O_2. During this process, hydroxyl radicals ($^\bullet$OH) are produced. These radicals react with the dye due to its strong oxidant capacity (they have a standard oxidation–reduction potential of 2.80 V). An increase in H_2O_2 improves the generation of $^\bullet$OH.[12] This fact can explain the better decolorization of the DB1 solution with the increment of $c(Fe^{2+})$:$c(H_2O_2)$ ratio. Other authors have found a similar effect in the decolorization of other dyes when the quantity of H_2O_2 increases.[12,14]
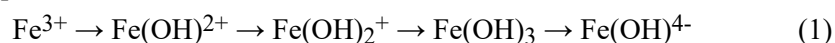
Treatment of the DB1 solution by precipitation

The effect of the pH value on the precipitation of DB1 was studied. In this case, the assays were performed at a c(DB1):c(Fe^{2+}) ratio of 1:16.3. Table II shows the results on the decolorization of the DB1 solution by precipitation. The results showed that the pH range that allowed at least 90 % decolorization of the DB1 solution was 6.0 to 8.0. The highest decolorization (98.67 %) was achieved at pH 6.0. In addition, the precipitation of DB1 at lower pH values than 6.0 and higher than 8.0 was almost negligible. Other studies have addressed the speciation of Fe^{2+} and Fe^{3+} as a function of the pH value. According to the data presented by Bokare and Choi, both Fe^{2+} and Fe^{3+} species remain in their dissolved form at the pH of the Fenton treatment (2.8). When the pH value is in the range of 6.0 to 8.0, soluble Fe^{2+} species and insoluble Fe^{3+} hydroxides are present in the solution.[33] Due to the presence of this variety of chemical species, the precipitation phenomena can be understood as a combination of various mechanisms. Some of these mechanisms are explained in the following paragraphs.

TABLE II. Influence of pH value on the decolorization of the DB1 solution by precipitation; c(DB1):c(Fe^{2+}) = 1:16.3; initial pH 2.8

pH	DB1 decolorization, %
5.0	No precipitation observed
6.0	98.67 ± 0.14
8.0	90.28 ± 0.08
9.3	2.86 ± 0.21

The precipitation of azo dyes using metal salts of iron has been reported in the past. For instance, it was found that certain anionic azo dyes, such as Acid Orange 7, Reactive Red 45, and Acid Yellow 23, form insoluble complexes, upon the addition of FeCl$_3$, creating colored suspensions and achieving around 40 to 70 % removal of the dyes by precipitation. [27] Furthermore, the removal of other dyes such as Disperse Blue 106, Disperse Yellow 54, Reactive Blue 49, and Reactive Yellow 84 by Fenton oxidation and chemical coagulation using Fe^{3+} and different pH values (4.0–9.0) has been tested. [17]

One of the phenomena that could be involved in precipitation is charge neutralization. Many pollutants on water are negatively charged (such is the case of DB1 due to sulfonate groups, –SO$_3^-$). On the other hand, metals like iron or aluminum in the forms of Fe^{2+}, Fe^{3+} or Al^{3+}, could give cationic hydrolysis products. For example, Eq. (1) presents a simplified scheme on the formation of hydrolysis products of Fe^{3+}:[24]

$$Fe^{3+} \rightarrow Fe(OH)^{2+} \rightarrow Fe(OH)_2^+ \rightarrow Fe(OH)_3 \rightarrow Fe(OH)^{4-} \qquad (1)$$

The positively charged hydrolysis products (*i.e.*, Fe(OH)$^{2+}$ and Fe(OH)$_2^+$) can neutralize the negative charges of DB1 and induce the precipitation of DB1.

Clearly, the pH value plays an important role in this kind of precipitation of dyes since the formation of species with a less positive charge is promoted as the pH increases. Other authors have also found a decrease in the decolorization of dyes by precipitation when the pH value was higher than 7.0. They also attributed the results to a generation of negatively charged ferric species (Fe(OH)$^{4-}$) which hinders the precipitation of the dyes (which are negatively charged too).[17]

Another mechanism that could be involved in the precipitation of dyes is the formation of complexes between the pollutants and iron. The ability of certain organic ligands to complex iron was reported in earlier works.[34,35] Consequently, it is expected that DB1 could also form complexes of iron due to the presence of amino, sulfonic, and hydroxyl substituents in the chemical structure of the dye. The formation of complexes and their solubility could be affected by the pH value. In fact, the calculated potential map surface of DB1 anion, shown in Fig. 3, indicated that the studied dye has several active sites to establish metal–ligand (M–L) bindings. The presence of the –OH group near to the –N=N– gives the possibility to form FeL$_2$ complex like those reported for similar structures.[36–39] Something similar could happen with the –OCH$_3$ group, even more, the formation of a higher coordinator number complex would be possible if the –NH$_2$ and –SO$_3^-$ groups took part in the complex.[1,40,41] On the other hand, it is well known that sulfonate groups contribute to the solubility of compounds[42] and, considering the fast precipitation process observed, also complex between Fe cations and –SO$_3^-$ should not be ruled out.
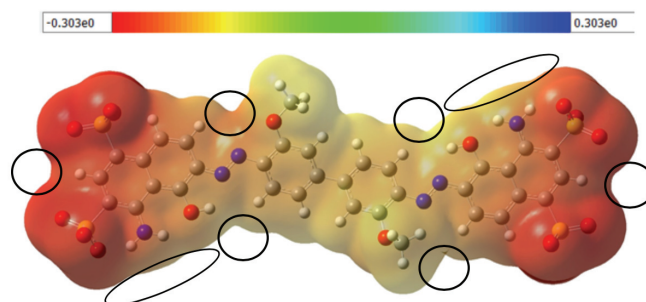

Fig. 3. Potential electrostatic map of DB1 anion (4–) modeled at B3LYP/6-311G(d,p) method.

Even though charge neutralization and formation of complexes can contribute to the precipitation phenomenon, the description of the processes that allow the azo dye precipitation by metal ions may be difficult to explain. In fact, as mentioned before, precipitation can include the combination of various mechanisms, such as adsorption, bridge formation, and surface precipitation onto solid hydroxide precipitates,[43] in addition to charge neutralization and formation of

complexes. Future studies should be focused on a deep understanding of the mechanisms involved in azo dye precipitation phenomena.

There is a possible existence of a stoichiometric relationship between the dye and ferrous ions. In order to verify the effect of c(DB1):c(Fe^{2+}) ratio on the decolorization of the DB1 solution by precipitation, several tests were carried out using different c(DB1):c(Fe^{2+}) ratios (1:3.3; 1:4.4; 1:6.5; 1:7.3; 1:8.2; 1:9.3; 1:10.9; 1:13.1; 1:16.3). The results of these tests are provided in Fig. 4a. An increment of DB1 decolorization was observed when the c(DB1):c(Fe^{2+}) ratio increased. A sudden increase of DB1 decolorization was observed using the c(DB1):c(Fe^{2+}) ratios 1:7.3 (27.49 %) and 1:8.2 (96.41 %). Furthermore, no decolorization reduction was observed for higher c(DB1):c(Fe^{2+}) ratios. A similar trend was reported in earlier studies for the precipitation of Direct Black 19, Direct Red 28, and Direct Blue 86 using aluminum salts.[44]
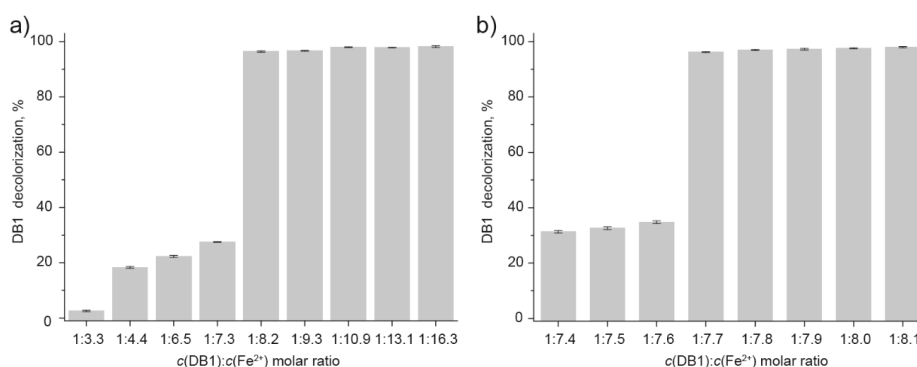

Fig. 4. Influence of c(DB1):c(Fe^{2+}) ratio on the decolorization of the DB1 solution by precipitation: a) results between c(DB1):c(Fe^{2+}) ratios of 1:3.3 to 1:16.3; b) detailed study between c(DB1):c(Fe^{2+}) ratios of 1:7.4 to 1:8.1 (c(Fe^{2+}) = 0.66 mmol L^{-1}, pH 6.0).

More detailed precipitation assays were performed at c(DB1):c(Fe^{2+}) ratios between 1:7.3 and 1:8.2 (1:7.4; 1:7.5; 1:7.6; 1:7.7; 1:7.8; 1:7.9; 1:8.0; 1:8.1). The results of these tests are detailed in Fig. 4b. From the results observed, it was concluded that the minimum c(DB1):c(Fe^{2+}) ratio that has to be applied to allow at least a 95% decolorization of the dye solution by precipitation was 1:7.7. Ratios below this value only allowed partial precipitation of the dye.

Decolorization of the DB1 solution by Fenton assisted with precipitation

As explained, the aim of the decolorization of the DB1 solution by Fenton assisted with precipitation was to start the treatment with a Fenton process using a c(DB1):c(Fe^{2+}) ratio below 1:7.7 (which only allows partial precipitation of the dye). During the treatment, the concentration of the dye decreases and the c(DB1):c(Fe^{2+}) ratio increases (because of the decolorization of the DB1 solution by Fenton) allowing the total precipitation of the dye. The assays in this study

were performed with an initial c(DB1):c(Fe^{2+}) ratio of 1:7.3 as an example of how Fenton and precipitation processes can be combined.

Fig. 5 shows the measurements of DB1 decolorization by applying Fenton and Fenton assisted with precipitation treatments. For the specific c(DB1):c(Fe^{2+}) ratio of 1:7.3, the time required to achieve a ratio which allows the precipitation of the dye was 5 min (DB1 decolorization by sole Fenton of 67.97 %). After this treatment, the dye was precipitated by increasing the pH of the solution from 2.8 to 6.0. The total decolorization of the dye was 97.79 %.
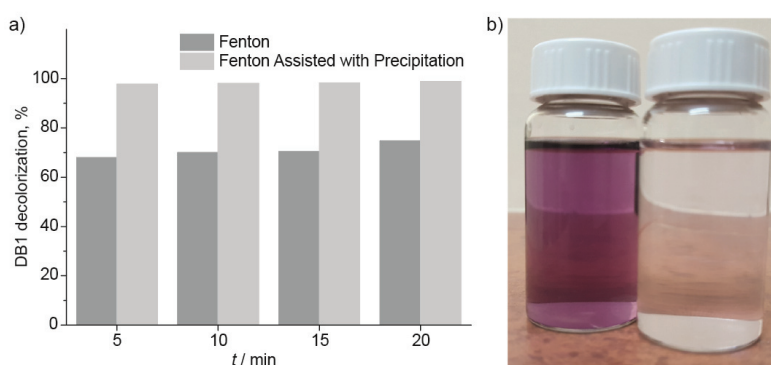

Fig. 5. a) DB1 decolorization by applying Fenton and Fenton assisted with precipitation treatments (initial c(DB1):c(Fe^{2+}) = 1:7.3, c(Fe^{2+}):c(H$_2$O$_2$) = 1:40, initial pH 2.8). b) DB1 solution after Fenton (left) and Fenton assisted with precipitation (right) treatments (reaction time = 5 min).

CONCLUSION

Fenton and precipitation treatments were combined for the decolorization of Direct Blue 1 dye (DB1). The individual treatments were studied separately to determine the effects of the parameters involved in each process. For the Fenton treatment, the reaction kinetics was adjusted to a pseudo-first-order model for all the c(Fe^{2+}):c(H$_2$O$_2$) ratios tested. Moreover, an increase of the rate constant was observed with the increment of c(Fe^{2+}):c(H$_2$O$_2$) ratio. The highest rate constant (0.1395±0.0025 min^{-1}) was obtained using a c(Fe^{2+}):c(H$_2$O$_2$) ratio of 1:40. The increase in the decolorization of the DB1 solution was attributed to the improvement in the generation of $^\bullet$OH caused by the addition of more H$_2$O$_2$. Regarding precipitation, the pH range that allowed at least 90 % decolorization of DB1 was 6.0 to 8.0. Almost no precipitation occurred at lower pH values than 6.0 and higher than 8.0. The highest DB1 decolorization (98.67 %) was achieved at a pH value of 6.0. In addition, it was found that the c(DB1):c(Fe^{2+}) ratio influences the precipitation of the dye. Indeed, it was determined that the minimum c(DB1):c(Fe^{2+}) that has to be applied to allow at least a 95 % decolorization of the dye by precipitation was 1:7.7. Ratios below this value only allowed partial

precipitation of the dye. Fenton assisted with precipitation tests were carried out using an initial $c(DB1):c(Fe^{2+})$ ratio of 1:7.3 (which allows only partial precipitation of DB1). The results suggested that the dye has to be treated by a Fenton process for 5 min (to achieve the ratio needed for precipitation) and then be precipitated by increasing the pH of the solution from 2.8 to 6.0. The decolorization of the dye after the combined process was 97.79 %.

ИЗВОД

ФЕНТОНОВ ПРОЦЕС, У КОМБИНАЦИЈИ СА ТАЛОЖЕЊЕМ, ЗА УКЛАЊАЊЕ БОЈЕ DIRECT BLUE 1: НОВИ ПРИСТУП

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Азо-боје су тешко разградиви загађивачи присутни у отпаду неких индустрија. Због велике хемијске стабилности, њихова разградња није ефикасна употребом уобичајених технолошких поступака. За бољу разградњу могу се применити напредни поступци оксидације као што је Фентонов. Међутим, ове методе су још увек скупе. У овом раду су комбиновани третмани Фентоновим процесом и таложењем, како би се извршило уклањање боје Direct Blue 1, DB1 (обезбојавање), у циљу смањивања трошкова поступка. Проучени су, одвојено, појединачни третмани коришћењем раствора DB1 од 0,04 mmol L^{-1} како би се утврдили ефекти параметара сваког процеса. За третман Фентоновом реакцијом, однос $c(Fe^{2+}):c(H_2O_2)$ који је омогућио највеће обезбојавање био је 1:40. Што се тиче таложења, највеће обезбојавање је постигнуто при pH 6,0. Штавише, установљено је да је за обезбојавање таложењем потребан минимални однос $c(DB1):c(Fe^{2+})$ од 1:7,7. Фентонове реакције потпомогнуте таложењем испитане су са DB1 растворима од 0,09 mmol L^{-1} и коришћењем односа $c(DB1):c(Fe^{2+})$ од 1:7,3 (што омогућава само делимично таложење DB1). Резултати указују да ова боја може бити третирана Фентоновим процесом током 5 min, а затим таложењем, како би се постигло скоро потпуно обезбојавање (97,79 %).

(Примљено 4. августа, ревидирано 4. новембра, прихваћено 7. новембра 2019)

REFERENCES

1. A. Bafana, S. S. Devi, T. Chakrabarti, *Environ. Rev.* **19** (2011) 350 (https://doi.org/10.1139/a11-018)
2. R. Saraf, C. Shivakumara, S. Behera, H. Nagabhushana, N. Dhananjaya, *Spectrochim. Acta, A* **136** (2015) 348 (https://doi.org/10.1016/j.saa.2014.09.038)
3. A. Tripathi, S. K. Srivastava, *Int. J. Biosci. Biochem. Bioinform.* **1** (2011) 37 (https://doi.org/10.7763/IJBBB.2011.V1.7)
4. K. Meerbergen, S. Crauwels, K. A. Willems, R. Dewil, J. Van Impe, L. Appels, B. Lievens, *J. Biosci. Bioeng.* **124** (2017) 668 (https://doi.org/10.1016/j.jbiosc.2017.07.005)
5. M. Arslan, S. Sayin, M. Yilmaz, *Water Air Soil Pollut.* **224** (2013) 1527 (https://doi.org/10.1007/s11270-013-1527-z)

6. Z. Liu, L. Zhang, F. Dong, J. Dang, K. Wang, D. Wu, J. Zhang, J. Fang, *ACS Appl. Nano Mater.* **1** (2018) 4170 (https://doi.org/10.1021/acsanm.8b00930)
7. H. T. Van, L. H. Nguyen, T. K. Hoang, T. P. Tran, A. T. Vo, T. T. Pham, X. C. Nguyen, *Sep. Purif. Technol.* **224** (2019) 431 (https://doi.org/10.1016/j.seppur.2019.05.048)
8. L. Bilińska, M. Gmurek, S. Ledakowicz, *Chem. Eng. J.* **306** (2016) 550 (https://doi.org/10.1016/j.cej.2016.07.100)
9. C. Sandoval, G. Molina, P. Vargas Jentzsch, J. Pérez, F. Muñoz, *J. Adv. Oxid. Technol.* **20** (2017) (https://doi.org/10.1515/jaots-2017-0006)
10. E. Yabalak, B. Külekçi, A. M. Gizir, *J. Environ. Sci. Heal., A* (2019) (https://doi.org/10.1080/10934529.2019.1647749)
11. M. A. Oturan, J.-J. Aaron, *Crit. Rev. Environ. Sci. Technol.* **44** (2014) 2577 (https://doi.org/10.1080/10643389.2013.829765)
12. J.-H. Sun, S.-P. Sun, G.-L. Wang, L.-P. Qiao, *Dyes Pigments* **74** (2007) 647 (https://doi.org/10.1016/j.dyepig.2006.04.006)
13. A. Cihanoğlu, G. Gündüz, M. Dükkancı, *Water Sci. Technol.* **76** (2017) 2793 (https://doi.org/10.2166/wst.2017.416)
14. S. Wang, *Dyes Pigment* **76** (2008) 714 (https://doi.org/10.1016/j.dyepig.2007.01.012)
15. S.-P. Sun, C.-J. Li, J.-H. Sun, S.-H. Shi, M.-H. Fan, Q. Zhou, *J. Hazard. Mater.* **161** (2009) 1052 (https://doi.org/10.1016/j.jhazmat.2008.04.080)
16. A. Maslahati Roudi, S. Chelliapan, W. H. M. Wan Mohtar, H. Kamyab, *Water* **10** (2018) 595 (https://doi.org/10.3390/w10050595)
17. T.-H. Kim, C. Park, J. Yang, S. Kim, *J. Hazard. Mater.* **112** (2004) 95 (https://doi.org/10.1016/j.jhazmat.2004.04.008)
18. D. E. Santiago, O. González-Díaz, J. Araña, E. Pulido Melián, J. Pérez-Peña, J. M. Doña--Rodríguez, *J. Photochem. Photobiol., A* **353** (2018) 240 (https://doi.org/10.1016/j.jphotochem.2017.11.038)
19. S. O. Ganiyu, E. D. van Hullebusch, M. Cretin, G. Esposito, M. A. Oturan, *Sep. Purif. Technol.* **156** (2015) 891 (https://doi.org/10.1016/j.seppur.2015.09.059)
20. B. K. Shanmugam, S. N. Easwaran, A. S. Mohanakrishnan, C. Kalyanaraman, S. Mahadevan, *J. Environ. Manage.* **242** (2019) 106 (https://doi.org/10.1016/j.jenvman.2019.04.075)
21. A. Azizi, M. R. Alavi Moghaddam, R. Maknoon, E. Kowsari, *J. Hazard. Mater.* **299** (2015) 343 (https://doi.org/10.1016/j.jhazmat.2015.06.044)
22. N. Kulik, Y. Panova, M. Trapido, *Sep. Sci. Technol.* **42** (2007) 1521 (https://doi.org/10.1080/01496390701290185)
23. S.-T. Ong, P.-S. Keng, W.-N. Lee, S.-T. Ha, Y.-T. Hung, *Water* **3** (2011) 157 (https://doi.org/10.3390/w3010157)
24. J. Duan, J. Gregory, *Adv. Colloid Interface Sci.* **100**–**102** (2003) 475 (https://doi.org/10.1016/S0001-8686(02)00067-2)
25. W. Sun, M. Tang, Y. Sun, Y. Xu, H. Zheng, *Can. J. Chem. Eng.* **96** (2018) 1256 (https://doi.org/10.1002/cjce.23069)
26. X. Xiao, Y. Sun, W. Sun, H. Shen, H. Zheng, Y. Xu, J. Zhao, H. Wu, C. Liu, *Can. J. Chem. Eng.* **95** (2017) 1245 (https://doi.org/10.1002/cjce.22752)
27. W. Baran, A. Makowski, W. Wardas, *Chemosphere* **53** (2003) 87 (https://doi.org/10.1016/S0045-6535(03)00435-1)
28. M. Pérez, F. Torrades, X. Domènech, J. Peral, *Water Res.* **36** (2002) 2703 (https://doi.org/10.1016/S0043-1354(01)00506-1)

29. C. L. Hsueh, Y. H. Huang, C. C. Wang, C. Y. Chen, *Chemosphere* **58** (2005) 1409 (https://doi.org/10.1016/j.chemosphere.2004.09.091)
30. X.-R. Xu, Z.-Y. Zhao, X.-Y. Li, J.-D. Gu, *Chemosphere* **55** (2004) 73 (https://doi.org/10.1016/j.chemosphere.2003.11.017)
31. Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT, 2016
32. S. Papić, D. Vujević, N. Koprivanac, D. Šinko, *J. Hazard. Mater.* **164** (2009) 1137 (https://doi.org/10.1016/j.jhazmat.2008.09.008)
33. A. D. Bokare, W. Choi, *J. Hazard. Mater.* **275** (2014) 121 (https://doi.org/10.1016/j.jhazmat.2014.04.054)
34. K. Davididou, E. Chatzisymeon, L. Perez-Estrada, I. Oller, S. Malato, *J. Hazard. Mater.* (2018) (https://doi.org/10.1016/j.jhazmat.2018.03.016)
35. A. S. Giri, A. K. Golder, *J. Environ. Sci.* (2018) (https://doi.org/10.1016/j.jes.2018.09.016)
36. R. Kılınçarslan, E. Erdem, H. Kocaokutgen, *Transit. Met. Chem.* **32** (2007) 102 (https://doi.org/10.1007/s11243-006-0134-x)
37. S. Parra, V. Nadtotechenko, P. Albers, J. Kiwi, *J. Phys. Chem., B* **108** (2004) 4439 (https://doi.org/10.1021/jp031127o)
38. S. Sinha, S. Das, R. Sikari, S. Parua, P. Brandaõ, S. Demeshko, F. Meyer, N. D. Paul, *Inorg. Chem.* **56** (2017) 14084 (https://doi.org/10.1021/acs.inorgchem.7b02238)
39. M. Szymczyk, A. El-Shafei, H. S. Freeman, *Dyes Pigments* **72** (2007) 8 (https://doi.org/10.1016/j.dyepig.2005.07.009)
40. A. R. Kennedy, P. C. Andrikopoulos, J.-B. Arlin, D. R. Armstrong, N. Duxbury, D. Graham, J. B. A. Kirkhouse, *Chem. - A Eur. J.* **15** (2009) 9494 (https://doi.org/10.1002/chem.200802555)
41. W. H. Ojala, E. A. Sudbeck, L. K. Lu, T. I. Richardson, R. E. Lovrien, W. B. Gleason, *J. Am. Chem. Soc.* **118** (1996) 2131 (https://doi.org/10.1021/ja951121f)
42. K. Lemr, M. Holčapek, P. Jandera, A. Lyčka, *Rapid Commun. Mass Spectrom.* **14** (2000) 1881 (https://doi.org/10.1002/1097-0231(20001030)14:20<1881::AID-RCM107>3.0.CO;2-I)
43. J.-W. Lee, S.-P. Choi, R. Thiruvenkatachari, W.-G. Shim, H. Moon, *Dyes Pigments* **69** (2006) 196 (https://doi.org/10.1016/j.dyepig.2005.03.008)
44. B. Shi, G. Li, D. Wang, C. Feng, H. Tang, *J. Hazard. Mater.* **143** (2007) 567 (https://doi.org/10.1016/j.jhazmat.2006.09.076)
45. B. Kordestani, R. Jalilzadeh Yengejeh, A. Takdastan, A. K. Neisi, *Microchem. J.* **146** (2019) 286 (https://doi.org/10.1016/j.microc.2019.01.013)
46. J. B. Parsa, M. Golmirzaei, M. Abbasi, *J. Ind. Eng. Chem.* **20** (2014) 689 (https://doi.org/10.1016/j.jiec.2013.05.034).