

## Ferroin in dyes degradation by Fenton-like process: a chemical waste recycling perspective

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### ABSTRACT

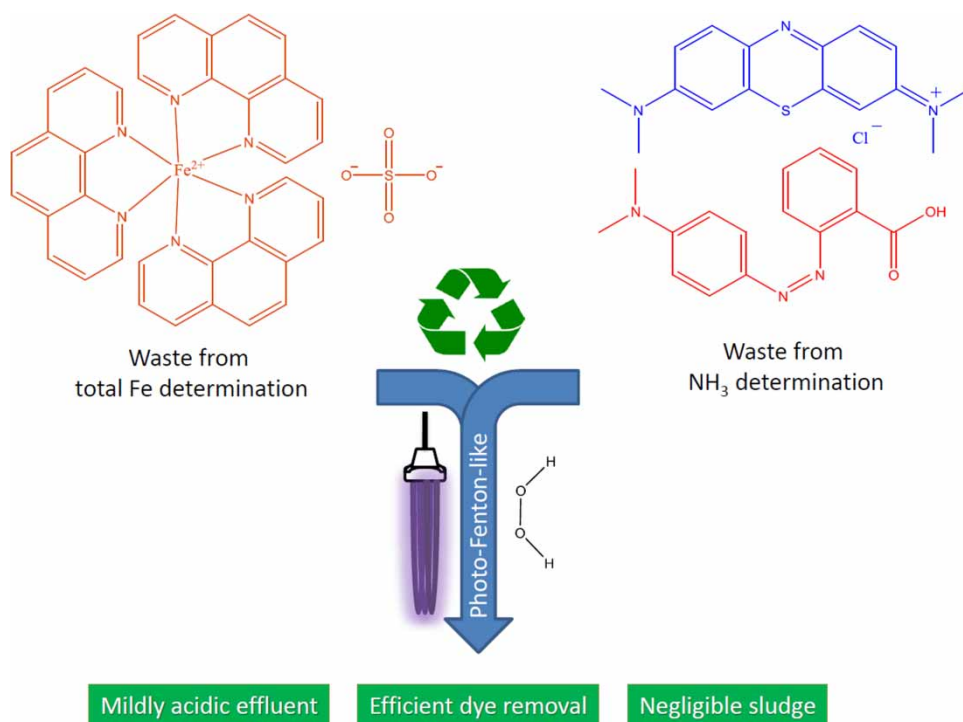
Published literature describes the formation of the Fe (II)–phenanthroline complex (ferroin) as a stop way for Fenton processes, reducing radical yield. By contrast, this study presents evidence that ferroin can be activated by UVA in mildly acidic media in a photo-Fenton-like process. Because ferroin is the main waste from total iron determination in environmental samples, a recycling approach is suggested. Based on the best practices of waste management planning, an application of the proposed method for treating another chemical waste is presented. Titrimetric ammonia determination waste containing  $2.67 \text{ mg L}^{-1}$  methyl red azo dye and  $1.33 \text{ mg L}^{-1}$  methylene blue was degraded using the optimized experimental conditions:  $\text{pH} = 5.2\text{--}5.4$ ;  $[\text{H}_2\text{O}_2] = 310 \text{ mg L}^{-1}$ ;  $[\text{ferroin}] = 1.4 \text{ mg L}^{-1}$ ;  $\text{temperature} = 36 \pm 1 \text{ }^\circ\text{C}$ ;  $\text{reaction time} = 165 \text{ min}$  under UVA irradiation. Attenuation of most intense spectroscopic bands for the dyes achieved 94% (510 nm) and 96% (665 nm) reduction for methyl red and methylene blue, respectively, with degradation of ferroin itself. The present work brings empirical evidence that is possible to recycle ferroin as photo-Fenton-like process catalyst, as well as determine the best conditions for providing less acidic treated effluents with negligible suspended solid concentration, better than that obtained from classical photo-Fenton processes.

**Key words:** advanced oxidation processes, experimental design, homogeneous photocatalysis, photodegradation, waste management

### HIGHLIGHTS

- Ferroin can act as a catalyst in photo-Fenton-like processes.
- Degradation of azodye by modified Fenton treatment.
- Drawbacks from classical Fenton processes are mitigated.
- Waste acting as a catalyst for treating another waste.
- Improvement for institutional waste management plan.

## GRAPHICAL ABSTRACT



## INTRODUCTION

The term Advanced Oxidation Processes (AOPs) is related to the generation of powerful oxidant radicals, highlighting the hydroxyl radical ( $\text{HO}\cdot$ ), and the several ways to yield them (Vilar *et al.* 2017). The main uses are to transform recalcitrant organic pollutants, to disinfect wastewater, and/or to remove potentially toxic metals from the abiotic compartments, providing a cleaner and safer environment in which the traditional biological and physicochemical processes are not sufficiently effective. Among a wide list of possibilities for wastewater treatment by AOP, those based on the Fenton reaction are very popular due to simplicity, low cost and efficiency (Babuponnusami & Muthukumar 2014; Miklos *et al.* 2018). Such processes classically use Fe(II) as catalyst to promote the formation of hydroxyl radicals from hydrogen peroxide in acidic media ( $\text{pH} \approx 3.0$ ). The main drawbacks of these techniques are the formation of Fe(III)-rich sludge, the corrosive operational pH, and the need for neutralizing the final effluent before adequate disposal. Photo-Fenton processes use UVA-visible radiation ( $<500 \text{ nm}$ ), which is able to regenerate Fe(II) from Fe(III) produced during the formation of hydroxyl radicals; unfortunately, the sludge production decreases but is not eliminated in the photomediated treatments, in addition the pH issue remains (Venny *et al.* 2012; Mirzaei *et al.* 2017; Santos-Juanes *et al.* 2017; Villegas-Guzman *et al.* 2017).

The search for eco-friendly and cheaper treatments led to the development of modified photo-Fenton processes or the so-called photo-Fenton-like processes, which normally present the metal catalyst (Fe species or another metal) linked to a chelating agent (homogeneous catalyst) or to a solid support (heterogeneous catalyst) acting under circumneutral pH conditions. Although the main Fenton reaction drawbacks are significantly reduced, the efficiency in the degradation of pollutants is normally lower than that reached with classical Fenton treatments. For this reason, the search for better chelating agents and optimal conditions is matter of concern and a need for wastewater treatment researchers (Neyens & Baeyens 2003; Bokare & Choi 2014; De Luca *et al.* 2014, 2015; Pliego *et al.* 2015; Wang *et al.* 2016; Ahsan *et al.* 2020; Chen *et al.* 2020; Ahile *et al.* 2021).

The reaction between Fe(II) and the complexing agent 1,10-phenanthroline (Phen), which yields an orange-reddish complex named ferroin, is well known and widely used. Many papers describe the use of Phen as an iron complexing agent for decreasing Fenton reaction efficiency, cancelling the Fe(II) catalytic action (Mello-Filho & Meneghini 1991; Babich *et al.* 1993; Dunford 2002; Avellar *et al.* 2004; da Silva *et al.* 2007; Whebi *et al.* Hafez 2010; Wada *et al.* 2014); citations of ferroin

complexes as catalysts in Fenton-like processes are very scarce in the literature (Zhang *et al.* 2011). Interestingly, the Cu(I)-Phen<sup>+</sup> complex is admittedly cytotoxic by inducing DNA cleavage (nuclease activity) via a Fenton-type reaction (Banasiak *et al.* 2018), which results in Cu(II)-Phen<sup>2+</sup> and hydroxyl radicals. For this reason, the potentiality of Fe(II)-Phen<sup>2+</sup> as a Fenton reaction catalyst deserves to be investigated and explored.

Due to the high affinity of Phen for Fe(II), but not for Fe(III), the quantification of soluble iron in many kinds of matrices is made after the addition of Phen under optimal conditions, followed by spectrophotometric analysis of the ferroin obtained, which has a maximum absorption wavelength at 510 nm. Ferroin is stable for long time within a wide range of pH (from 3.0 to 9.0) despite the best pH range for synthesis and/or for analytical purposes being 2.9–3.5. Acidic pH avoids iron precipitation and favors kinetics (APHA *et al.* 2017; Yang & Yao 2020). In spite of the simplicity and low cost of the referred technique, iron analysis results in acidic media and Fe-rich waste, which should be correctly managed.

Undergraduate programs related to water quality in Higher Education Institutions (HEI), such as Civil and Environmental Engineering schools, normally promote several laboratory experiments that generate organic dye waste from chemical analysis such as alkalinity, total hardness, nitrogen speciation, residual chlorine, residual ozone, and microbiological indicators, in addition to total iron (APHA *et al.* 2017). Regarding guidelines for HEI waste management plans (Fagnani & Guimarães 2017) and the principles of greener chemistry (Manahan 2006), a co-processed treatment able to combine different chemical waste and further safe disposal via eco-friendly techniques (photo-Fenton-like) is very positive and desirable. In this case, the waste from Fe determination would be used as the catalyst for the degradation of dye-rich waste. Both types of waste have recalcitrant compounds; therefore, a mutual degradation would be very useful. Chemical reduction of dyes, highlighting toxic azo compounds, is efficiently related in the published literature (Ahsan *et al.* 2019a, 2019b; Selvaraj *et al.* 2021); however, the resulting products are aromatic amines, which also present considerable toxicity (Albahnasawi *et al.* 2020). Therefore, oxidative processes remain as the best option for dye degradation, highlighting photocatalytic ones (Mudhoo *et al.* 2020; Sharma *et al.* 2020).

In this paper, the viability and the best conditions to use ferroin as an homogeneous catalyst for a photo-Fenton-like treatment was explored. Methylene blue (MB), a phenothiazine compound, and methyl red (MR), an azo compound (detailed information in the Supplementary Material) were chosen due to their frequent use in environmental chemical analyses and their potentially environmental impact and carcinogenicity (Devi *et al.* 2009; Auerbach *et al.* 2010; Umbuzeiro *et al.* 2017; Vacchi *et al.* 2017; Berradi *et al.* 2019). The main goal of the present work was to show that ferroin is not an inert substance in photo-Fenton-like process, but a photocatalyst instead. Additionally, recycling ferroin waste from water quality analysis adds value to a laboratory residue that was only an environmental problem before; treating a dye-rich analytical waste with ferroin, as can be seen here is, at the same time, a demonstration of efficiency of the catalyst and an example of best practices in waste management planning for HEI, by the combination and reciprocal decomposition of two different residues.

## METHODS

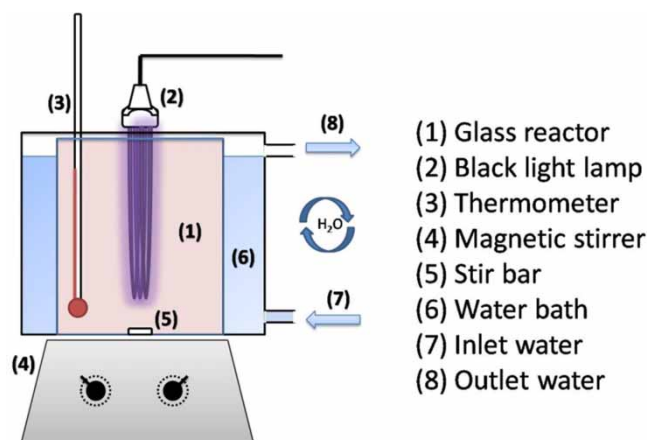
### Chemicals

All aqueous solutions were prepared using ultrapure water (Milli-Q<sup>(R)</sup> Academic, Millipore Co). Alcohol solutions were prepared using absolute ethanol 99.8% (Dinâmica). Reagents were all of analytical grade. Stock solutions of MB (Nuclear) and MR (Vetec) were prepared in alcohol at 2,000 mg L<sup>-1</sup> from their respective solids. Hydrogen peroxide 35.5% (Neon) was used in the concentrated form. Ferroin (56 mg Fe L<sup>-1</sup>) was synthesized and characterized according to the published literature (Zhang *et al.* 2011) from 0.300 g of 1,10-phenanthroline monohydrate (≥99.0%, Neon) and 0.200 g of ferrous ammonium sulfate hexahydrate (98.5%–101.5%, Neon) (Supplementary Material).

### Instrumentation

The experiments were carried out in a 2-L glass batch reactor equipped with a black light lamp (Tachibra, TKT 26-1 model, lamp socket E-27, 26 W), in which the bulb was sealed with high temperature-resistant silicone acetic glue (Interfix, 850 red model) for humidity protection. The reactor was partially immersed in a water bath on a magnetic stirrer (Fisatom, model 752 A). A peristaltic pump (Provitec, AW 5000 model) was used to recirculate the thermostated water of the bath. A schematic design of the reaction system is depicted in Figure 1.

Two spectrophotometers were used to monitor color changes during the experiments, according to demand: Cintra6 (GBC) UV-visible range double beam with a 1.0 cm optical path (wider range, less sensitive), and DR 3900 (Hach) visible range



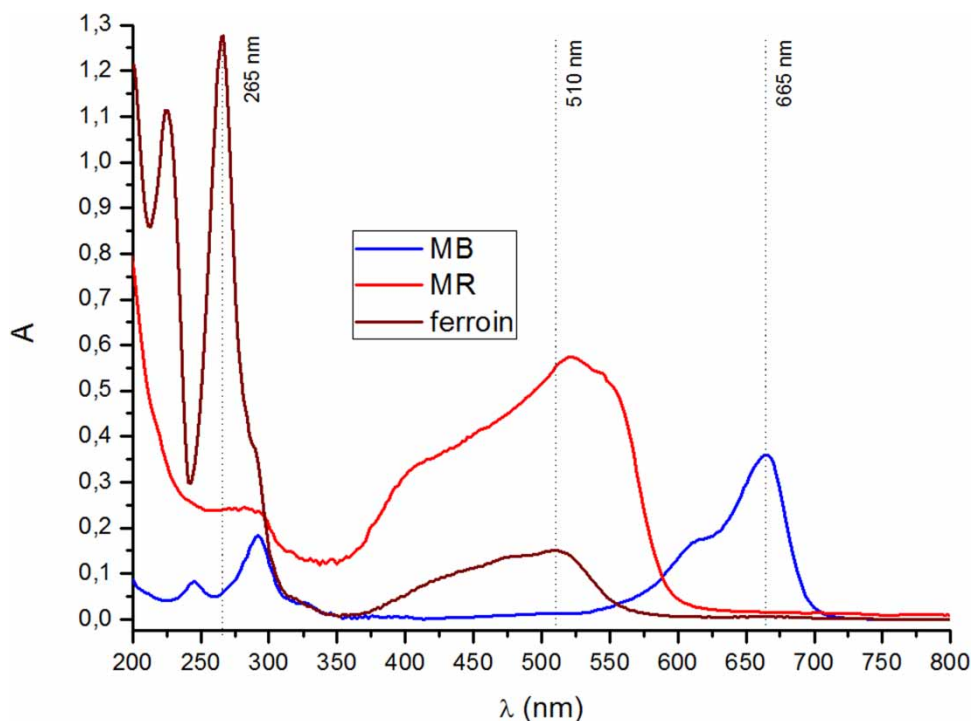
**Figure 1** | Experimental set-up. The black light lamp (2) and the thermometer (3) are kept suspended by universal holders through the top of the opened reactor.

single beam with 2.5 cm optical path (narrower range, more sensitive); degradation of MR and ferrioxin was monitored at  $\lambda = 510$  nm, while MB was monitored at  $\lambda = 665$  nm. Additionally,  $\lambda = 265$  nm was monitored for the degradation of Phen. Figure 2 shows the UV-vis spectral profiles for the involved substances.

Measurements of pH were carried out with a pH meter Starter 2100 bench model (Ohaus). A microwave digestion system Ethos Easy (Milestone) was used in the determination of iron from ferrioxin solutions, before quantification through flame atomic absorption spectrometry (iCE 3300, Thermo Fisher Scientific).

### Degradation experiments

For each degradation experiment, a 2-L solution containing  $2.67 \text{ mg L}^{-1}$  MR and  $1.33 \text{ mg L}^{-1}$  MB (by dilution of stock solutions) was used. In addition to these dyes,  $\text{H}_2\text{O}_2$  and ferrioxin at variable concentrations and ultrapure water were added.



**Figure 2** | UV-vis scanning for MB ( $6.7 \text{ mg L}^{-1}$ ), MR ( $13.3 \text{ mg L}^{-1}$ ), and ferrioxin ( $2.0 \text{ mg L}^{-1}$ ) at pH range 5.2–5.4. Spectra were obtained separately for each compound and gathered in the same figure for comparative purposes.

Initial pH was adjusted to 5.2–5.4 by adding diluted mineral acids to the solution under magnetic mixing; the measurement was carried out with a combined glass electrode. The reaction was monitored over 120 min. In order to evaluate the best concentration of H<sub>2</sub>O<sub>2</sub> and ferriox for dyes decomposition, a central composite design (CCD) followed by response surface methodology (RSM) was used (Pereira-Filho 2015) (Supplementary Material). Absorbance attenuation (E%) in  $\lambda = 510$  and 665 nm was spectrophotometrically monitored throughout the experiments.

Efficiency of two kinds of treatments was assessed: Fenton-like, with no UVA irradiation (dark degradation); and photo-Fenton-like, with UVA irradiation (photomediated degradation). Additionally, for both treatments, the influence of temperature was also tested, promoting the reaction at room temperature ( $22 \pm 1$  °C) and at  $35 \pm 1$  °C in thermostated water bath. Thermal stability of the reaction mixture was previously tested under 70 °C over 60 min, in the absence of H<sub>2</sub>O<sub>2</sub> and UVA irradiation.

## RESULTS AND DISCUSSION

Synthesized ferriox was analyzed by scanning spectrophotometry from  $\lambda = 200$  to 700 nm, and the spectrum was positively compared with previously published literature (Zhang *et al.* 2011). Ferriox did not present spectral variation within pH range from 4.9 to 11.0, with the maintenance of characteristic absorption bands in 226 nm, 265 nm, and 510 nm (Supplementary Material).

Initial pH and dyes concentrations for each batch experiment were based on the titrimetric method for ammonia determination (APHA *et al.* 2017), which yields a final waste with these characteristics. An efficient degradation process at this pH (5.2–5.4) means safe chemicals and financial resources in order to adjust the pH of the final effluent before disposal. The classical Fenton reaction is processed at a much more acidic pH (3.0).

In order to define the practical limits of concentration for the variables H<sub>2</sub>O<sub>2</sub> and ferriox in the CCD-RSM experiments, theoretical stoichiometry for dye degradation and Brazilian Environmental Legislation for iron disposal (ALESP 1976; CONAMA Conselho Nacional do Meio Ambiente 2011) were used. Finally, the optimal concentration obtained for ferriox reflected an iron concentration that was closer to that preconized by some European countries such as Portugal (Assembleia da República 1998) and Spain (BOE 1993).

Results from CCD-RSM experiments can be seen in Table 1.

The best conditions for the concomitant absorbance attenuation for all substances is that signaled as n. 3 (Table 1), which means [H<sub>2</sub>O<sub>2</sub>] = 270 mg L<sup>-1</sup>; [Ferriox] = 2.2 mg Fe L<sup>-1</sup>; use of UVA irradiation (photo-Fenton-like process) (Supplementary Material).

As the initial pH of the experiments was within 5.2–5.4, and the final pH reached 4.5 in most efficient cases, all the studied substances produced a constant and visible color. In other words, the absorbance attenuation at the end of the experiments was not a mere pH effect, but the result of an AOP. MB has a stable color under acidic or neutral pH. Only strongly basic pH can produce azure forms and methylene violet dye (Katafias *et al.* 2010). Ferriox was stable for long time within a wide range

**Table 1** | Absorbance attenuation (E%) obtained in the CCD-RSM experiments for Fenton-like and photo-Fenton-like treatments, at 510 and 665 nm

Condition	E <sub>510 nm</sub> (%)		E <sub>665 nm</sub> (%)	
	Fenton-type	Photo-Fenton-type	Fenton-type	Photo-Fenton-type
1	23	48	15	30
2	8	24	18	79
3	17	57	36	94
4	25	43	93	94
5	24	48	60	71
6	8	24	84	94
7	13	15	31	84
8	23	49	91	94
9–12 <sup>a</sup>	38 ± 1.7	37 ± 1.3	48 ± 5.3	95 ± 1.7

<sup>a</sup>Replicates for the central point of the CCD model.

of pH (from 3.0 to 9.0) (APHA *et al.* 2017; Yang & Yao 2020). MR is very stable, and its pH range for color changes is 4.2 (red) to 6.3 (yellow) (Vogel 1989); therefore, the color of MR during the experiments was reddish-orange.

In order to confirm the literature information regarding the inefficiency of isolated process on dye degradation (Salem & El-Maazawi 2000; Ashraf *et al.* 2006; Ikai *et al.* 2010; Katafias *et al.* 2010; Whebi *et al.* 2010; Fagnani *et al.* 2013; Sel *et al.* 2014), the reaction mixture was treated by peroxidation, UVA photolysis, and UVA photoperoxidation, and the comparative results can be seen in Supplementary Material. Therefore, the effective absorbance attenuation was due to hydroxyl radicals yielded by a photo-Fenton-like process.

### Influence of temperature

The CCD-RSM experiments were carried out with no temperature control. Since the black light lamp warms during the experiment, the temperature varied by 13 degrees in some experiments, and this issue had to be evaluated. Thermal stability tests (absence of oxidant and catalyst) showed no spectral variation, inferring that the temperature alone is not able to degrade the dyes in aqueous solutions up to 70 °C (temperature used for the ferriox synthesis). Therefore, temperature does not degrade the dyes by itself, but can interfere in the AOP.

To determine the influence of temperature on the system, tests were evaluated under the best CCD-RSM conditions (experiment 3, Table 1) for Fenton-like (dark) and photo-Fenton-like treatments (photomediated). The results are shown in Table 2.

It is possible to see that temperature exerts an important role in the Fenton-like processes, mainly in the photomediated one. After 120 min, attenuations of 85% can be reached for  $\lambda = 510$  nm, which infers that even ferriox suffered considerable degradation at  $36 \pm 1$  °C. That information is relevant and presents a new perspective for using solar photo-Fenton-like processes in dye degradation.

### Kinetics of MB degradation

Because no spectral interference or overlapping was verified at  $\lambda = 665$  nm, it was possible to determine the kinetics of MB degradation. For ferriox or MR this was not possible because both presented  $\lambda_{\max}$  very close and as large bands, leading to overlapping. Derivative spectrophotometry (Vidotti & Rollemberg 2006) was tried but with no success due to the very low signal obtained after the calculation:

Degradation of MB reaches an equilibrium condition after 60 min, with  $E\% = 96\%$  ( $\lambda = 665$  nm). The equation for the first order mechanism (Equation (1)) was integrated and rearranged (Equation (2)), and successfully applied to the results from MB degradation.

$$-\frac{d[MB]}{dt} = k[MB] \quad (1)$$

$$\ln [MB] = -kt + \ln [MB]_0 \quad (2)$$

The reaction obeys an apparent first order behavior, with  $k = 4.78 \times 10^{-2} \text{ min}^{-1}$  (Figure 3).

### Complementary evidences of the dyes degradation

In order to improve  $E\%$  at  $\lambda = 510$  nm under the optimal conditions, reaction time was extended up to 165 min. After this time, it was verified as  $E\% = 94\%$  ( $\lambda = 510$  nm) and maintenance of  $E\% = 96\%$  ( $\lambda = 665$  nm). It is possible to infer that all studied substances, including ferriox, were considerably degraded under experimental conditions. Degradation of the iron-

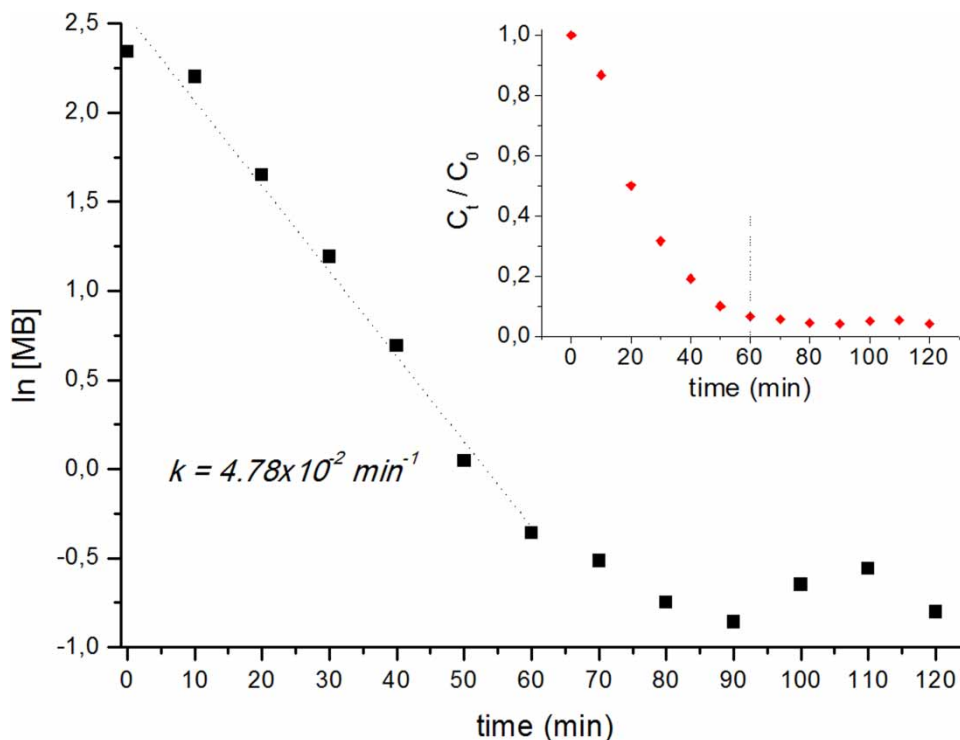
**Table 2** | Effect of temperature on Fenton-like and photo-Fenton-like treatments, under the optimal CCD-RSM conditions

Process	UVA	Temperature (°C) <sup>a</sup>		E% <sup>b</sup>	
		Initial	Final	510 nm	665 nm
Fenton-type	OFF	22	22	17	36
	OFF	35	37	50	98
Photo-Fenton-type	ON	23	25	12	45
	ON	36	35	85	96

<sup>a</sup>Thermostated conditions.

<sup>b</sup>Mean values from duplicates (4% < standard deviation < 6%).





**Figure 3** | Linearized first order equation applied to MB degradation data through a graphical method.

chelates concomitantly to the target contaminants in photo-Fenton-like processes is related in the literature (Ahile *et al.* 2021). Additionally, there is an inversely proportional increase of absorbance at  $\lambda = 322 \text{ nm}$ , evidencing the formation of Fe(III). Moreover, it is possible to infer that the stoichiometry of Fe(II) to Fe(III) conversion does not change during the reaction and no secondary processes occur due to the presence of an isosbestic point at  $\lambda = 377 \text{ nm}$  (IUPAC 2019) (Figure 4).

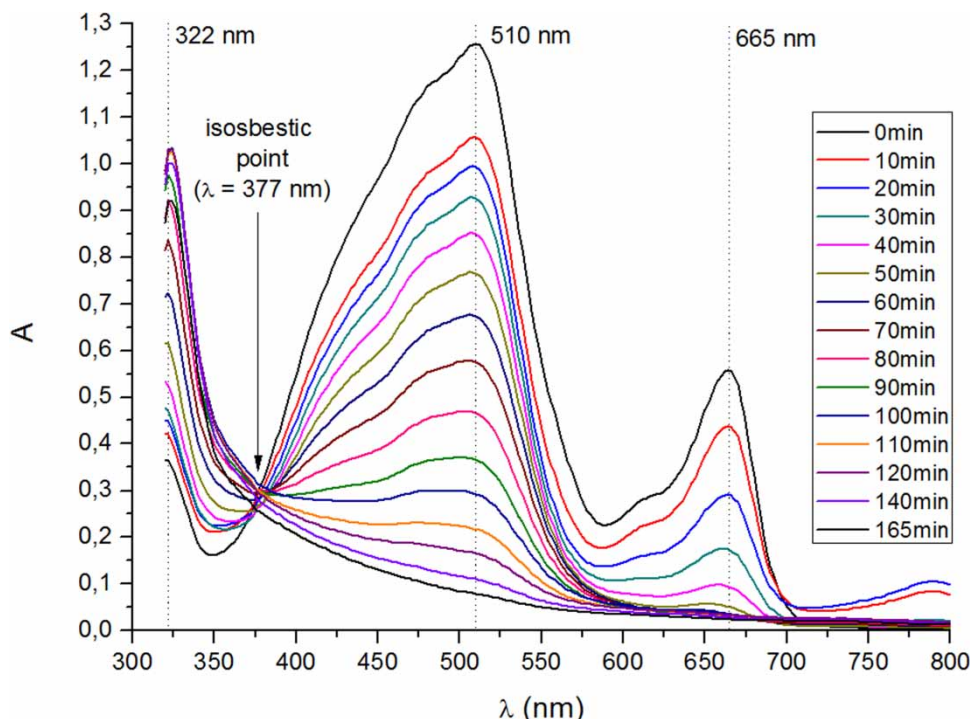
Moreover, aliquots of the final treated effluent were subjected to pH adjustments (3.0; 6.0; 9.0) in order to verify any spectral alterations that would indicate the residual presence of MR, as well as the formation of sludge. A visible spectral profile for MR as a function of pH can be seen in Supplementary Material, which evidences the absorbance of MR at  $\lambda = 430 \text{ nm}$  in pH = 6.0; but no spectral evidence for MR in the final effluent was obtained in any pH range.

Regarding sludge formation, it was not possible to visually verify any suspended or settled solid in the final effluent, even after pH adjustment to 9.0. However, absorbance at  $\lambda = 322 \text{ nm}$  decreased, evidencing the possible formation of  $\text{Fe}(\text{OH})_3$  at higher pH. Additions of large amounts of potassium thiocyanate were made to an aliquot of the final effluent for the qualitative identification of Fe(III) ions by the formation of the Fe(III)-SCN intense red complex ( $\lambda_{\text{max}} = 450 \text{ nm}$ ). An increase of absorbance at the characteristic wavelength could be verified.

Based on current literature (Gomes Júnior *et al.* 2018; Ahile *et al.* 2020, 2021; O'Dowd & Pillai 2020), the authors propose two main factors to consider regarding the apparent absence of Fe(III)-sludge: firstly, the proportion of Fe in comparison with the other components ( $\text{H}_2\text{O}_2$ , dyes) and the treatment conditions (pH, temperature) were very adequate in order to promote the degradation of target contaminants. The reaction time was not as short as initially desired, but the absence of sludge mitigates this effect. Secondly, Fe(III) yielded during the process would be complexed by organic acids as result of aromatic compounds degradation. The presence of nitrogen compounds would lead to more alkaline by-products, which produced a buffered system in combination with the referred organic acids, avoiding a significant change in pH value as shown.

### Final considerations

Many factors such as temperature, reaction time, pH, oxidant concentration, and contaminant concentration affected the performance of photo-Fenton processes (Bhat & Gogate 2021). The influence of temperature is not often highlighted and most of the authors normally control the temperature in order to demonstrate that the chemical degradation, and not the thermic degradation, is responsible for the results. Normally, photoassisted reactions are much influenced by temperature. Thermic



**Figure 4** | Spectral scanning for reaction mixture throughout 165 min of photo-Fenton-like treatment.

degradation of  $\text{H}_2\text{O}_2$  is not importantly verified below  $90^\circ\text{C}$  and, instead of this, efficiency in the hydroxyl radical formation is likely to improve (Carbajo *et al.* 2021). In the present study, it was possible to see that temperature exerts a synergistic effect on the contaminant degradation, increasing substantially the efficiency even in dark processes, showing kinetic effects.

Fenton and photo-Fenton are typical acidic processes (pH 3.0 or less) due to speciation of iron. Fenton-like processes allow reactions under mildly acidic conditions, increasing the lifespan of reactors and saving financial resources in order to adjust pH for the treatment itself and for the final disposal of treated effluent according to environmental policies worldwide. In this paper, the operational pH was about 5.0, which already was the original pH of the ammonia analysis waste; thus, it was possible to treat this effluent with no additional concerns regarding pH. Additionally, precipitation of Fe(III) was not verified in the described conditions.

Concentration of  $\text{H}_2\text{O}_2$  exerts a key role in Fenton processes. Low concentrations of the oxidant lead to inefficient production of radicals, at the same time very high concentrations, and unnecessary costs, lead to scavenging of hydroxyl radicals by the own hydrogen peroxide, decreasing the efficiency of treatments (Henry & Donahue 2011). Additionally, contaminant concentration can affect positively or negatively photoassisted treatments. Kinetics is initially increased as the concentration of contaminant also increases; however, a critical value is achieved and no improvements are verified. If the contaminant concentration is comparatively very high, the concentration of oxidant becomes insufficient and the kinetics is undoubtedly affected. The optimal concentration of oxidant used in the present work was estimated by stoichiometric calculations for degradation of the dyes and empirically confirmed.

The use of dyes is a constant reality in many areas such as the textile industry, food industry, telecommunications, clinical and environmental analysis. Azo dyes like MR are predominant in industrial scenarios and present chemical stability due to the  $\pi$  electronic cloud of aromatic rings, yielding recalcitrant behavior and potential ecotoxicity once present in the environment (Haque *et al.* 2021). The solution shared in this paper is useful for education, research and pharmaceutical institution, as well as many industries that employ dyes in their processes or quality control. Institutional waste must be managed, reused or recycled whenever possible, or properly treated and disposed according to the current waste management plan (Fagnani & Guimarães 2017). The combination of ferrioxalate with other kinds of chemical waste, through a very effective physicochemical treatment, is an attractive and elegant solution for waste management planning. The possibility to use solar energy in the process is especially useful for developing countries that normally belong to privileged regions of the planet regarding insolation.



## CONCLUSIONS

The present work was able to prove the photoactivity of ferrioxalate as a catalyst in photo-Fenton-like processes. Toxic dyes were satisfactorily degraded under mildly acidic conditions (pH = 5.2–5.4) after 165 min at  $36 \pm 1$  °C, with no visual sludge formation. Experimental conditions were less aggressive than normally used in classical photo-Fenton treatments, resulting in safe chemicals for pH adjustment of the final effluent before disposal. Ferrioxalate itself was considerably degraded throughout the experiment, with no spectral evidence of its presence or free 1,10-phenanthroline. The proposed method has a tangible potential for treating liquid waste containing toxic dyes from research and educational activities, integrating an eco-friendly waste management plan. Additionally, the study suggests the possibility of using solar energy as heat and UVA source.

## ACKNOWLEDGEMENTS

The authors thank the São Paulo Research Foundation (Fundação de Amparo à Pesquisa do Estado de São Paulo – FAPESP) [grant number 2014/17774-1; 2016/50460-6; and 2018/02507-9], the Brazilian National Council for Scientific and Technological Development (Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq), and the Teaching, Research and Extension Support Foundation (Fundação de Auxílio ao Ensino, Pesquisa e Extensão – FAEPEX) of the University of Campinas (UNICAMP) for the financial support. Additional thanks to Anjaína Fernandes de Albuquerque for technical support.

## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 26 February 2021; accepted in revised form 21 July 2021. Available online 4 August 2021