



Stability and efficiency of Fe³⁺ EDDS complex for the treatment of secondary effluent in the photo-Fenton process

Ungwanen J. Ahile^a, Raymond A. Wuana^b, Adams U. Itodo^b, Rufus Sha'Ato^b,
Jacqueline A. Malvestiti^c, Renato F. Dantas^{c,*}

^aDepartment of Chemistry, Benue State University, PMB 102119, Makurdi, Nigeria, Tel. +2348064049464;
email: ahileuj@gmail.com

^bDepartment of Chemistry, University of Agriculture, PMB 2373, Makurdi, Nigeria, Tel. +2348066645047;
email: raynewton73@gmail.com (R.A. Wuana), Tel. +2348039503463; email: itodoson2002@gmail.com (A.U. Itodo),
Tel. +2348036196970; email: rshaato@gmail.com (R. Sha'Ato)

^cSchool of Technology, University of Campinas – UNICAMP, Paschoal Marmo 1888, 13484332, Limeira, SP, Brazil,
Tel. +551921133305; email: renatofalcaod@ft.unicamp.br (R.F. Dantas), Tel. +5519997148293;
email: JAC_EDF@yahoo.com.br (J.A. Malvestiti)

Received 29 May 2020; Accepted 25 January 2021

ABSTRACT

This study focuses on the use of Fe³⁺ EDDS for degradation of methylene blue and wastewater disinfection using the photo-Fenton process. The stability of Fe³⁺ EDDS was tested at different pH values ranging from 4 to 11. The study finds that an increase in the iron precipitate and a decrease in degradation efficiency comes about as pH increases. An investigation into the Fe:L ratio shows that when a high amount of ligand is used, the amount of iron released from the complex is reduced; with an iron-ligand ratio of 1:1.5 being the most suitable one for the Fe³⁺ EDDS system. Furthermore, the result of careful examination of temperature changes shows that at the increase in temperature of the reaction system, there was a decrease in the efficiency of degradation of reaction. The process was more effective at a temperature of 25°C than at higher temperatures, occasioned by higher iron precipitate. The results of the disinfection and regrowth of microorganisms also show that the efficiency of the process is pH-dependent with pH 7 having the best disinfection and less regrowth rate as compared to a pH value of 9, for instance.

Keywords: Advanced oxidation processes; Disinfection; Fenton reaction; Iron precipitation;

1. Introduction

Water is important in daily human life. This is seen in its use for agricultural, industrial, and domestic purposes. However, the availability of clean and safe water is threatened by pollution through organic and inorganic compounds. Pollutants such as personal care products, pharmaceutically active compounds, natural and synthetic hormones, pesticides, and industrial chemicals (such as plasticizers, flame retardants, and food additives) are constantly

being released into the environment. The negative effects these pollutants have on ecosystems, in turn, affect the health of humans and aquatic organisms [1]. These chemicals, also known as contaminants of emerging concerns (CECs), are usually detected in aquatic ecosystems, sometimes at low concentrations (ng/L–µg/L). Large amounts of CECs are usually discharged and then transported to wastewater treatment plants (WWTPs). The presence of the most ubiquitous ones in WWTP secondary effluents has been a subject of scholarly investigation over time. For instance, a study of

* Corresponding author.

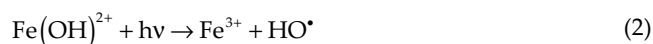
WWTP effluents in Asia (China and Korea), Europe, and the US revealed that the amount of the major CECs in effluents was within a threshold of between 0.001 and 10 µg/L. In addition, there were pharmaceutically active compounds (PhACs) in concentrations that were oftentimes higher than 1 µg/L [2].

A list of international priority PhACs was developed by the Global Water Research Coalition (GWRC) identifying compounds that pose health risks when released into water sources. The GWRC classified 44 of these compounds into three main groups: the Class I group with 10 compounds, Class II, 18 compounds, and Class III with 16 compounds. In arriving at this classification, the GWRC considered occurrence in the environment and resistance to treatment, ecotoxicity, degradability, and human toxicity. The treatment and monitoring of solutions for a group of 45 priority compounds were proposed by the newer European Union Directive 2013/39/EU. The European Union Decision 2015/495/EU put forward on 20/03/2015, which was later updated on 05/06/2018 in Decision 2018/840/EU, proposed the first watch list of compounds for Union-wide monitoring. The list includes CECs: natural hormones (estrone (E117 beta-estradiol (E2)); synthetic hormones (17 alpha ethinylestradiol (EE2)); pesticides (thiacloprid, thiamethoxam, acetamiprid, oxadiazon, clothianidin, methiocarb, imidacloprid, and triallate); antibiotics (clarithromycin, azithromycin, and erythromycin); the pharmaceutical diclofenac; a UV filter (2-ethylhexyl 4-methoxycinnamate); and an antioxidant (2,6-di-*tert*-butyl-4-methylphenol) which is used as food seasoning [1]. Furthermore, in trying to safeguard against water contamination, the new Swiss Water Protection Act [3] which has been implemented since January 2016, with implementable timelines extending to 2040, recommends that CECs in WWTP effluents should be reduced by 80% before discharge.

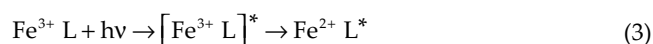
The use of conventional secondary methods like activated sludge or tertiary treatment procedures (including disinfection and filtration) in municipal WWTPs has proved to be ineffective in the treatment of some CECs present in WWTPs [3]. This leads to incomplete removal of the target species, which in turn, constitutes another source of pollution [4]. As such, effluents from WWTPs account for most of the CECs emanating from anthropogenic sources into the environment. Aside ozonation which has found full scale application [1], other advanced oxidation processes such as ultraviolet light/hydrogen peroxide [5], ozone/hydrogen peroxide [6], Fenton, photo-, and electro-Fenton [7,8], have proved to be effective in the treatment of wastewater. Nevertheless, due to restrictions that have hindered their development, the application of these methods has remained at a lab scale [3].

Advanced oxidation processes (AOPs) are techniques employed in order to degrade different groups of organic pollutants and in the process, attain high stages of mineralization [9,10]. They are also effective in the disinfection of micro-organisms in water or wastewater [11]. While there are several AOP techniques, the photo-Fenton (p-F) technique is one of the most studied due to its simplicity in design, the cheap reagents involved, and the effects of the reagents (H_2O_2 , Fe) used on the environment. The main oxidant in the p-F technique is the hydroxyl radical (HO^\bullet). The simplified reaction mechanism which leads to the generation of HO^\bullet

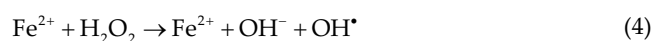
from H_2O_2 in the p-F reaction is illustrated using Eqs. (1) and (2) [12]:



The optimum results for the p-F process have been reported at a pH of 2.8 [12,13]. This is because, at this pH, minimum iron precipitation is recorded. However, it is more expedient to conduct p-F reactions at circumneutral pH values so that the acidification of effluents and neutralization-related costs are minimized. Accordingly, much attention is now paid to the use of p-F process at circumneutral pH. There are, however, reported cases of low efficiency associated with p-F processes at circumneutral pH, which is traceable to high precipitation of iron at these pH values. The precipitation of iron in the solution can be minimized by the use of iron chelates. For a chelate to be suitable for application in a p-F process, it should be capable of forming complexes that are stable with Fe(III), and absorb UV-vis light. The chelates should also allow the reduction of Fe^{3+} to Fe^{2+} under photochemical conditions as illustrated in Eq. (3) [14]:



The aminopolycarboxylates and polycarboxylates are chelates which have the ability to complex with Fe(III), absorb UV or solar light better than aqua-complexes [14]. They also possess the ability to undergo photoreduction via the ligand-to-metal charge transfer (LMCT), producing Fe^{2+} [15]. The complexation of chelates with metals in photo-Fenton process is important in improving the performance of the system [14]; as this extends the operational pH of the system and improves the efficiency. Ethylenediamine-*N,N'*-disuccinic acid (EDDS) is an example of amino polycarboxylic acids (APCAs), with its structure having two chiral centers. It occurs as enantiomeric isomer ((*S,S'*)-EDDS and (*R,R'*)-EDDS). It also has one meso isomer (*R,S*)-EDDS [16]. These isomers have the same stability constant and ability to form complexes. EDDS exists as a complex (i.e., EDDS complex) or as a chelate (EDDS acid) with different stabilities [16]. The (*S,S*)-EDDS isomer is completely biodegradable, while the (*R,R*)-EDDS and (*R,S*)-EDDS isomers are non-biodegradable. There are many publications on the use of EDDS in the degradation, decontamination, or disinfection of wastewaters in the photo-Fenton like process with encouraging results [17,18]. The mechanism for Fe^{3+} EDDS in the p-Fenton reaction is as follows [19]:





Though many works have been published on EDDS as a complexing ligand for iron in the p-F process [13,20], there has been no work dealing with the stability of Fe-EDDS at different pH values and temperatures. This present work, therefore, aims at: (1) assessing the appropriate metal-ligand dosage for chelation which will ensure a minimum iron precipitation; (2) investigating the effect of hydroxyl radical attack on the complex; and (3) demonstrating the ability of Fe³⁺ EDDS to degrade an organic pollutant and also disinfect wastewater at different pH values. In this study, Methylene blue was used as a pollutant for degradation, while a secondary effluent which was collected from a pilot waste treatment plant was used for disinfection studies.

2. Materials and methods

2.1. Reagents and sample preparation

The following chemicals were used in this study: anhydrous iron(III) chloride (FeCl₃), methylene blue (Ecibra Quimica, Brazil), 30% wt. hydrogen peroxide solution (H₂O₂), NaOH, H₂SO₄, 18% ethylenediamine-N, N¹-disuccinic acid ((S, S) EDDS) (Sigma Aldrich, Brazil). Analytical grade reagents were also employed in this study while distilled water was used in preparing all solutions. Preparation of Fe³⁺ EDDS solution was done by mixing volumes of freshly prepared EDDS and anhydrous ferric chloride at an appropriate ratio. The solution was stirred constantly using a magnetic stirrer to ensure homogeneity and allowed to stand for 1 h. The preparation of Methylene blue (MB) solution was done by dissolving an initial concentration of 20 mg MB in 1 dm³ of distilled water, while the pH was adjusted using NaOH or H₂SO₄ [21].

2.2. Photodegradation experiment

The photodegradation experiments were done in a 1.2 L Pyrex jacketed photo-Fenton reactor (Brazil) which allowed maintenance of constant temperature by passing water from a thermostated water bath through the outer casing. The reactor was furnished with three high-pressure UVA mercury lamps (Philips, BLBF8T5, 8 W, Brazil) which emitted radiation of 4.05×10^{-5} Einstein's s⁻¹ at a wavelength of 365 nm. The radiation dose was measured using the ferrioxalate actinometry [21,22]. In order to prevent direct contact of the UV lamps with the sample, the lamps were housed in borosilicate tubes. The pH of the sample was adjusted after adding an appropriate amount of iron chelate, the solution was then transferred to the reactor [23] and pH maintained during the reaction by adding a phosphate buffer (K₂HPO₄:NaOH). Loss of radiation was prevented by covering the reactor with aluminum foil [24]. After the effluent was transferred into the reactor, the UV lamps were turned on, and a calculated amount of H₂O₂ was added while the

reaction was timed using a stop watch. Homogeneity was maintained by stirring the solution using a magnetic stirrer [25]. A syringe was used to withdraw samples at different time intervals for analysis. The absorbance of MB decolorization was measured using a UV-visible spectrophotometer model DR/3900 (Hach, USA) at a $\lambda_{\text{max}} = 664$ nm. The vanadate method was used for quantification of H₂O₂ [26].

2.3. Disinfection reaction

Bacterial residual concentration was monitored during treatment using Fe³⁺ EDDS to ascertain the efficacy of the iron chelate to disinfect microorganisms in secondary effluent. To carry out the disinfection analysis, 1,000 mL of the sample was measured and transferred to the reactor. Fe³⁺ EDDS was then added to the sample and mixed thoroughly using a magnetic stirrer. The effluent was homogenized for 5 min [27] and then 10 mL of the sample was collected in the dark and analyzed as time 0 min. After that, the UV light was turned on and H₂O₂ was added. Treated samples were collected with a syringe at 10, 20, 30, 40, 50, and 60 min and microbial analysis conducted. 10 mL of the sample was collected and analyzed for *Escherichia coli* and total coliforms using the commercial Collilert[®] method [28,29]. Duplicate analyses were done on each experiment in order to ensure reproducibility. The pH of the effluent was adjusted using 2 M H₂SO₄ or 1 M NaOH solution. Bacterial regrowth analyses were conducted by re-incubating the test Collilert[®] and the bacteria count done after 24, 48, and 72 h. The number of bacteria seen during the regrowth test that exceeded the number seen after disinfection represented the reactivated/repared or, partially damaged bacteria which became reactivated after the treatment [30].

To perform the Collilert[®] method [28], 10 mL sample was added into 90 mL of dilution water which was previously prepared by adding 1.0 g peptone bacteriological reagent in 1,000 mL of distilled water. The Collilert[®] media snap was then added to 100 mL of the sample. It was mixed thoroughly until the Collilert[®] media was dissolved. The mixture was then transferred to a 97-well Quanti-Tray[®] consisting of 49 big and 48 small wells. The Quanti-Tray[®] was later fitted into a rubber fitting which had equal number of holes as the Quanti-Tray[®]. The Quanti-Tray[®] together with the rubber fitting was later slid into a preheated Quanti-Tray[®] sealer and then incubated at 35°C ± 0.5°C for 24–28 h. The color of the wells was observed and compared with the yellow color of the Quanti-Tray[®] comparator. The yellow colored wells were considered to be total coliform positive. The results were then compared with the most probable number (MPN) table to determine the number of total coliforms. The total coliform positive trays were later checked for fluorescence with a UV light. The blue coloured trays were deemed to be *E. coli* positive. The number of *E. coli* was also determined by comparing the results with the Quanti-Tray[®] MPN table [28,31–33]. Duplicate analyses were done for each experiment to ensure reproducibility.

The first-order kinetic model was used to evaluate the efficiency of microorganism after disinfection. Eq. (10) is the illustration of the first-order model:

$$-\frac{dN}{dt} = kN \quad (10)$$

At constant heat (isothermal conditions), the value of k can be evaluated. When Eq. (10) is integrated, we have:

$$\ln \left[\frac{N}{N_0} \right] = -kt \quad (11)$$

From the equation: $[N]$ is the microorganism concentration [MPN/100 mL], $[N_0]$ is the initial microorganism concentration [MPN/100 mL], k is the rate constant [min^{-1}], and t is the time [min].

2.4. Iron precipitation measurement

The ISO 6332 method [34] was used for iron precipitation determination. The samples were collected at various times and filtered through 0.45 μm pore size Polytetrafluoroethylene (PTFE) syringe-driven filters (Millipore Millex® GN). Then 4 mL of the filtered sample were mixed with 1 mL of 1, 10-phenanthroline solution (0.1% w/v in distilled water) and 1 mL buffer solution (250 g/L ammonium acetate and 700 mL/L acetic acid in distilled water). The test was then allowed to stand for 10 min and the assay's absorbance read at 510 nm using a spectrophotometer at 510 nm. The blank was prepared by replacing the 1, 10-phenanthroline solution in the test with 1 mL of deionized water.

3. Results and discussion

3.1. Effect of iron–ligand molar ratio on iron loss

To achieve good results in the p-F process, the appropriate Ligand-Fe (L-Fe) molar ratio had to be determined. Iron–Ligand molar ratio is a very important parameter because for good chelation to occur, the molar ratio of iron to ligand must be correct and be at least 1:1 [35]. However, in their work, Da Luca et al. [36] recommended a higher ratio. They explained that even though the molar ratio can easily be identified in theory, in practice, a much greater ratio is required for complexation of iron. When the amount of the ligand is not sufficient to appropriately chelate the metal, limited metal chelation will be obtained. Another factor of interest is the precipitation of the iron as a result of an attack on the complex from HO^\bullet during photo-Fenton process [36]. To determine the best chelating ratio for Fe:EDDS process, the amount of iron precipitation after an attack on the complex by HO^\bullet was measured and total iron determined as the reaction progressed for iron–ligand ratio (Fe:L) of 1:1, 1:1.5, and 1:2 (Fig. 1).

To decide the best chelating ratio for use in this study, several experiments were performed using a fixed amount of iron while the amount of the ligand was varied. The essence of this experiment was to determine which ratio would produce the least amount of iron precipitates after a hydroxyl radical attack on the complex. This is because for p-F process to be effective, the ligand must be able to keep the iron soluble without precipitation. Fig. 2 shows that at a molar ratio of 1:1, the iron was highly precipitated

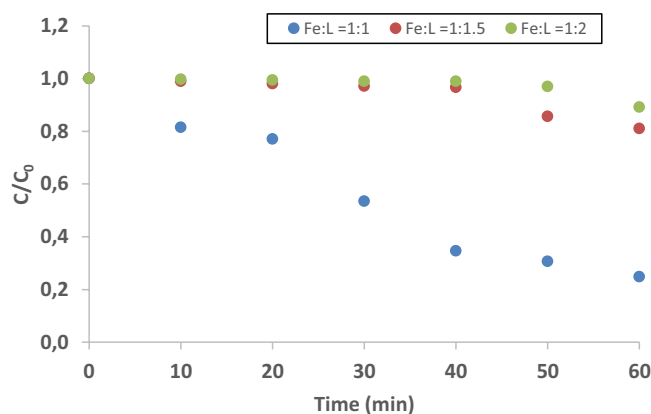


Fig. 1. Effect of Fe:EDDS molar ratio on the complex resistance to HO^\bullet , $\text{Fe}^{3+} = 20 \text{ mg/L}$; $\text{H}_2\text{O}_2 = 90 \text{ mg/L}$; $\text{pH} = 7$.

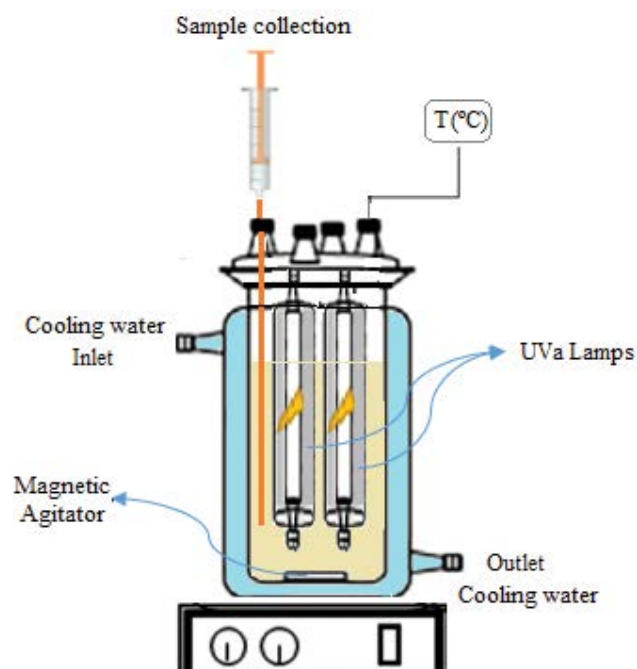


Fig. 2. Schematic representation of the photo-Fenton experiment.

leaving only 26% of soluble iron in solution at the end of the reaction time. This shows a high iron precipitation; hence the use of this ratio is not appropriate for photo-Fenton process. Iron–ligand molar ratio of 1:1.5 and 1:2 produced very little iron loss. Since the amount of iron precipitated in the 1:1.5 was not high, it is therefore recommended that this ratio be used for the Fe:EDDS system.

The choice of 1:1.5 molar ratio is predicated on the fact that, the use of molar ratio higher than 1:1 enhances better chelation process due to an increased presence of free chelators in solution. The free chelators in solution are reported to act by re-coordinating with the iron ions which are released from the breakage of the complex as a result of HO^\bullet radical attack [36]. Also, in the chelate assisted process, the HO^\bullet degrades both the contaminants as well as the chelate (ligand); leading to the commencement of iron

precipitation as soon as the excess ligand is consumed [18]. This is the reason behind the higher iron precipitation in the reaction with Fe-L molar ratio of 1:1. Although iron precipitation is an important factor to consider before the choice of Fe-L molar ratio is arrived at, the adverse effects associated with increase in the total organic carbon of the effluent on addition of the chelate cannot not be ignored. Secondly, there is the risk associated with heavy metal remobilization [36]. Therefore, applying a ratio above 1:1.5 will only lead to an increase in the cost of operation because of high usage of chemicals and high consumption of H_2O_2 .

3.2. pH influence on HO^\bullet attack on the chelate

The HO^\bullet is a highly reactive species which oxidizes any organic molecule that is in contact with it. The effect of pH on the release of iron from the chelate when there is HO^\bullet attack on the complex was investigated to monitor the amount of iron released from the complex at varying pH values. When iron is released from the complex, two possibilities exist. It either recaptures free chelators in solution forming the complex [36]; or if no free chelators are present, the released iron from the complex may form the insoluble hydroxide [37]. When the hydroxide is formed, the amount of iron available for decomposition of hydrogen peroxide to generate HO^\bullet reduces, resulting in reduced efficiency of the process. Fig. 3 demonstrates the precipitation of iron from Fe^{3+} EDDS. The result shows an increasing iron precipitation as the pH of the solution increase from acidity to alkalinity with the highest iron precipitation at pH 11. This is because as the pH of the solution increases, the ease with which it forms precipitates increases. The results of this study show that Fe^{3+} EDDS is suitable for application in effluents with a pH as high as 8, with higher efficiency at lower pH values. When the pH value is high, the amount of iron release is very high and may produce poor results when applied in the photo-Fenton process.

The effect of pH was further investigated using Methylene blue removal. The results obtained in Fig. 3 show that an increase in pH resulted in a decrease in the degradation of Methylene blue which is as a result of reduced decomposition of H_2O_2 at higher pH values [38]. Usually, at higher pH values, there is an attack on the Fe-ligand

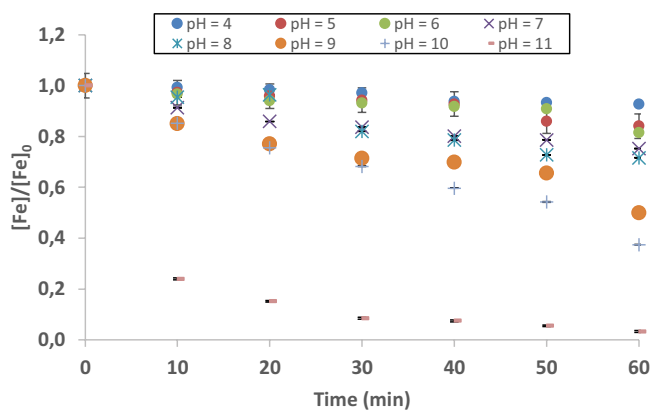
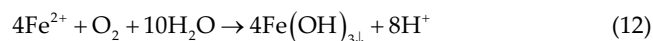


Fig. 3. Effect of pH on HO^\bullet attack on the chelate using $Fe^{3+} = 20$ mg/L; $H_2O_2 = 90$ mg/L; Fe:EDDS = 1:1.5.

chelate and then iron is gradually released from the chelate in form of precipitate. Aside the pH, inorganic ions such as NO_3^- , Cl^- , SO_4^{2-} , and CO_3^{2-} are reported to reduce the degradation of organic compounds in a reaction matrix [39] due to scavenging effect. Since a secondary effluent was used in this study, the presence of these inorganic ions might have affected the degradation of the MB.

3.3. Effect of temperature on the performance of Fe^{3+} EDDS

The classical p-F process has the ability to function with higher efficiency when temperature is raised [18] until a threshold temperature of about $45^\circ C$ is reached; above which there is precipitation of iron, and therefore, a loss of efficiency. This phenomenon is attributed to the increased rate of formation of ferric hydroxides.



Series of experiments were performed using methylene blue to demonstrate the Fe^{3+} EDDS efficiency with temperature changes (Fig. 4). The result shows an increase in efficiency with a corresponding increase in temperature from $25^\circ C$ to $30^\circ C$. A further increase in the temperature led to lower efficiency as well as a lower rate of decomposition of H_2O_2 . At elevated temperatures, an increase in the precipitation of iron was also noticed. This might be caused by either an increase in rate of $Fe(OH)_3$ formation (reaction 12) which overcomes the rate of residual ligand recapture, and/or an increase in the kinetics of Fe^{3+} -EDDS photolysis which leads to the depletion of the

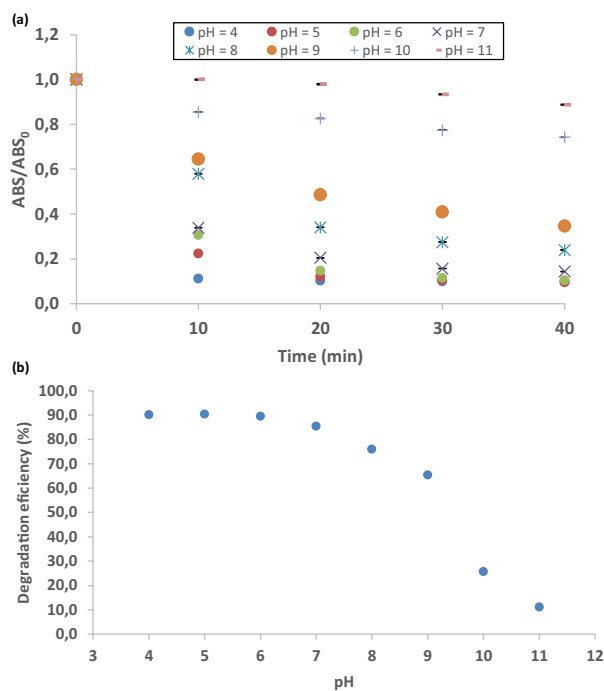


Fig. 4. Effect of pH on the degradation of methylene blue using $Fe^{3+} = 20$ mg/L; $H_2O_2 = 90$ mg/L; Fe:EDDS = 1:1.5. (a) Variation of MB removal with time and (b) percentage removal efficiency against pH.

chelate and then faster iron precipitation [18]. A test of mean difference (one way *t*-test; Table 1) was conducted on the temperature values at 95% confidence level. The *t*-statistic values observed were: 14.183, 9.299, 10.188, and 10.667 with significance values of 0.000 each at 25°C, 30°C, 35°C, and 40°C, respectively. The significance of the *t*-statistic values indicates the existence of significant mean difference in the degradation of the dye at each tested temperature.

3.4. Wastewater disinfection and microbial and regrowth

The efficiency of Fe³⁺ EDDS in wastewater disinfection was demonstrated at pH values of 7 and 9 using a secondary effluent (Fig. 6). Blank experiments were conducted using UVA/H₂O₂ and Fe³⁺ EDDS without UVA. The results presented in Fig. 5 show higher inactivation efficiency at pH 7. This is because Fe³⁺ EDDS undergoes photolysis under UV radiation, resulting in the reduction of Fe³⁺ to Fe²⁺ [Eq. (5)]. The conversion of Fe³⁺ to Fe²⁺ happens faster at alkaline pH when compared to acidic pH. Once this happens, Fe²⁺ can react with: (a) EDDS again [Eq. (13)]; or (b) H₂O₂ [Eq. (1)]. Furthermore, when the breakage of Fe³⁺ EDDS complex occurs, the p-F efficiency will become dependent on the species of Fe³⁺/Fe²⁺ formed in water. Since the reactive species of soluble iron exist at acidic pH, the disinfection efficiency depends on iron availability in solution, and partly due to iron precipitation at alkaline pH. This is because of the breakage of Fe³⁺ EDDS complex. The bacterial inactivation efficiencies are better at pH 7 than 9.

Similar results were obtained by García-Fernández et al. [40] who studied the disinfection of *Enterococcus faecalis* and *E. coli* using solar p-F. They observed that microorganism disinfection was more efficient at acidic pH than at neutral or alkaline pH owing to the availability of iron at acidic pH. It is worthy of note that the mechanism of microbial disinfection is a very complex process. Several reactions and processes work together in the wastewater decontamination process at neutral or near pH. Basically, the main decontamination mechanism involves an attack

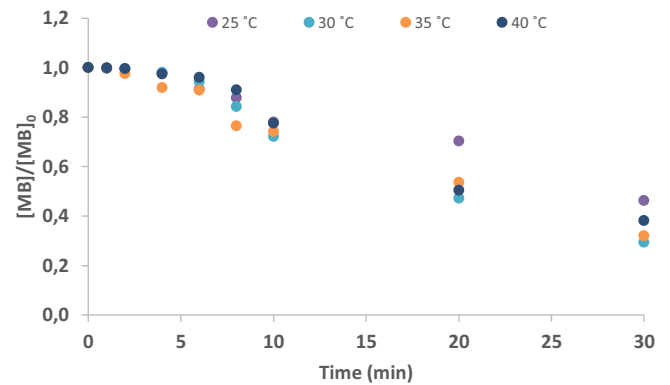


Fig. 5. Effect of temperature on the degradation of methylene blue by Fe³⁺ EDDS using Fe²⁺ = 20 mg/L; H₂O₂ = 90 mg/L; Fe:EDDS = 1:1.5; pH = 7.

Table 1
One-sample test

Test value = 0						
T	df	Sig. (2-tailed)	Mean difference	95% Confidence interval of the difference		
				Lower	Upper	
25°C	14.183	8	0.000	0.85622	0.7170	0.9954
30°C	9.299	8	0.000	0.80538	0.6057	1.0051
35°C	10.188	8	0.000	0.79619	0.6160	0.9764
40°C	10.667	8	0.000	0.83348	0.6533	1.0137

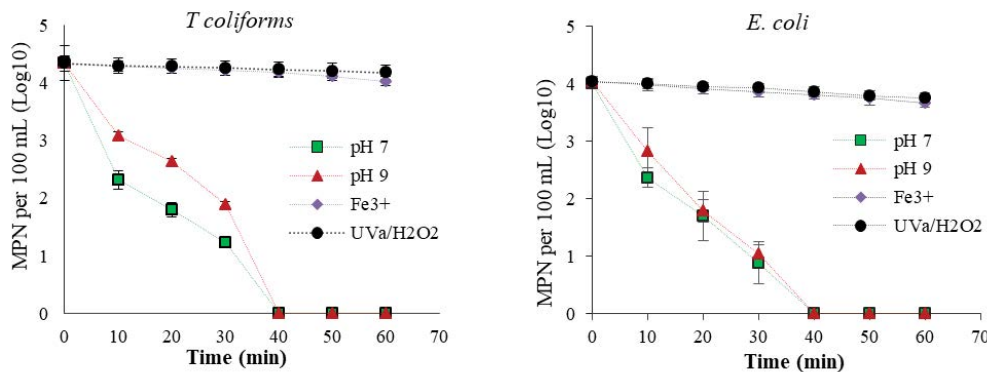


Fig. 6. Disinfection of secondary effluents at pH of 7 and 9 (Fe³⁺ = 5 mg/L; H₂O₂ = 90 mg/L; Fe:EDDS = 1:1.5).

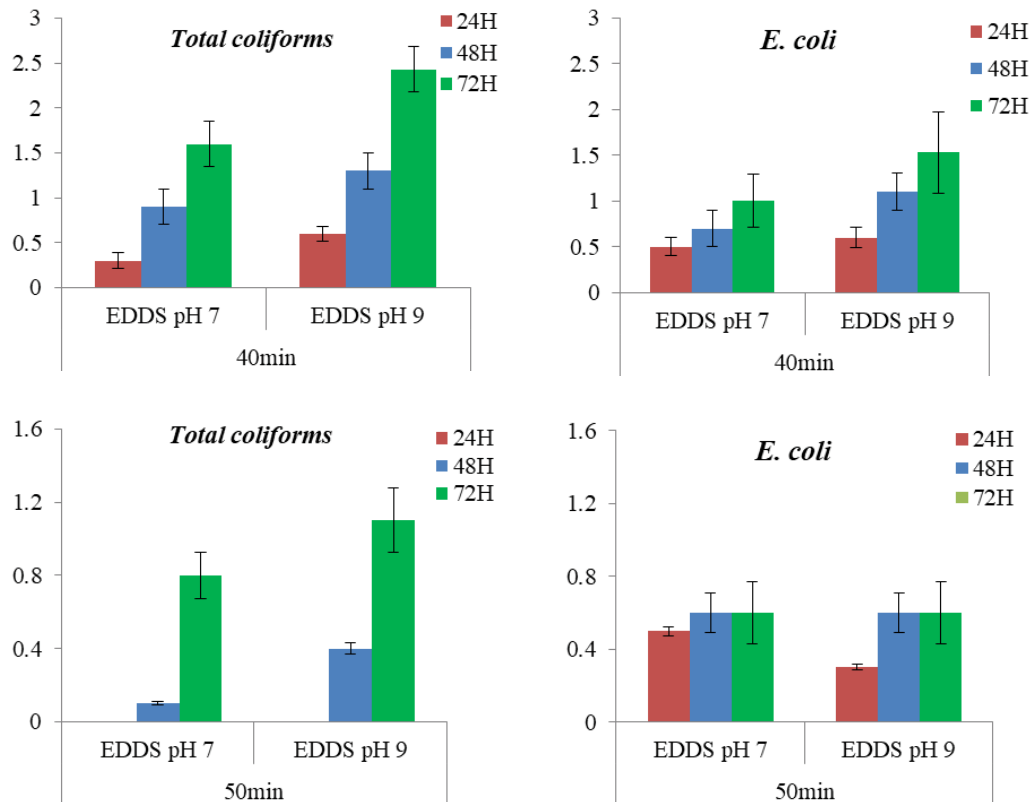


Fig. 7. Microbial regrowth after treatment with photo-Fenton ($\text{Fe}^{3+} = 5 \text{ mg/L}$; $\text{H}_2\text{O}_2 = 90 \text{ mg/L}$; $\text{Fe}:\text{EDDS} = 1:1.5$).

on the cellular membrane due to the external generation of OH^\bullet ; the damages initiated by a source of radiation – in our case, UVA; and the internal photo-Fenton process as a result of diffusion of H_2O_2 and iron into the cell of the organism. Some other studies have shown that amino polycarboxylic acid chelates (EDTA, EDDS, etc.) initiate changes in ligands to bring about changes in outer membrane absorptivity which results to changing the internal chemical and physical conditions of the cell, leading eventually to cell death [41]. This alteration can be credited to the coordination of cations such as Mg^{2+} and Ca^{2+} which confer electrostatic stability on the different parts of the lipopolysaccharides found on the surface of the outer membrane [27].

The microbial regrowth is another factor which was used to assess the performance of Fe^{3+} EDDS in the treatment of the secondary effluent. Some effluents have pH values which are higher than 7; therefore, it is very important to carry out the disinfection of these effluents at pH values of 7 and above to determine the process efficiency. It is noteworthy that at pH of 7 and above, there was high iron precipitation, with the result being reduced efficiency [42]. The same applied to the regrowth observed here. Increasing iron precipitation led to less damage on the microbial cell as the pH increased (Fig. 7). Therefore, higher regrowth was recorded as the pH increased toward alkalinity. In this system, it was also discovered that despite complete disinfection of microorganisms after 30 min of irradiation, implying that some microorganisms which were not seen after 30 min of disinfection were only partially injured and were reactivated after some time [43].

4. Conclusion

In this study, the Fe^{3+} EDDS system was investigated to ascertain the suitable $\text{Fe}:\text{L}$ ratio, effect of pH on iron precipitation, effect of temperature on the decolorization of MB, and the ability of Fe^{3+} EDDS to disinfect a secondary effluent in the photo-Fenton process. The results of the experiments reveal that an iron–Ligand ratio of 1:1.5 is needed for the effective performance of the Fe^{3+} EDDS system. The pH of the solution also affects the performance of the iron Fe^{3+} EDDS system, with high iron precipitation experienced at higher pH levels. When the pH of the solution increased, the rate at which the Fe^{3+} EDDS performed in the photo-Fenton process decreased. Decrease in efficiency of MB decolorization was experienced with increase in temperature. This shows that an increase in temperature brought about an increase in iron precipitation, thereby decreasing the effectiveness of the system. EDDS can be considered a feasible option to carry out treatment of wastewater effluents in the pH ranges between 4 and 9. Since the application of this method on a full scale basis is the focus of this work, it is recommended that the system be applied in systems which require the use of a natural source of radiation (sunlight) instead of UV light from electrical sources.

Acknowledgments

This work is supported by the Tertiary Education Fund (TETFund-Nigeria), the National Council of Scientific and Technological Development (CNPq) [308914/2017-1] and

[424395/2016-9] and the São Paulo Research Foundation (FAPESP) [2014/17774-1].

References

- [1] L. Rizzo, S. Malato, D. Antakyali, V.G. Beretsou, M.B. Đolić, W. Gernjak, E. Heath, I. Ivancev-Tumbas, P. Karaolia, A.R. Lado Ribeiro, G. Mascolo, C.S. McArdell, H. Schaar, A.M.T. Silva, D. Fatta-Kassinos, Consolidated vs new advanced treatment methods for the removal of contaminants of emerging concern from urban wastewater, *Sci. Total Environ.*, 655 (2019) 986–1008.
- [2] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, *Sci. Total Environ.*, 473–474 (2014) 619–641.
- [3] The Swis Federal Council, Waters Protection Ordinance (WPO), Vol. 2011, 2018, pp. 1–70.
- [4] L. Clarizia, D. Russo, I. Di Somma, R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: a review, *Appl. Catal., B*, 209 (2017) 358–371.
- [5] B.S. Souza, R.F. Dantas, M. Agulló-Barceló, F. Lucena, C. Sans, S. Esplugas, M. Dezotti, Evaluation of UV/H₂O₂ for the disinfection and treatment of municipal secondary effluents for water reuse, *J. Chem. Technol. Biotechnol.*, 88 (2013) 1697–1706.
- [6] R.C. Martins, R.F. Dantas, C. Sans, S. Esplugas, R.M. Quinta-Ferreira, Ozone/H₂O₂ performance on the degradation of sulfamethoxazole, *Ozone Sci. Eng.*, 37 (2015) 509–517.
- [7] L.P. Glugoski, P.D.J. Cubas, S.T. Fujiwara, Reactive Black 5 dye degradation using filters of smuggled cigarette modified with Fe³⁺, *Environ. Sci. Pollut. Res.*, 24 (2017) 6143–6150.
- [8] S. Shekoohtyan, S. Rtimi, G. Moussavi, S. Giannakis, C. Pulgarin, Enhancing solar disinfection of water in PET bottles by optimized in-situ formation of iron oxide films. From heterogeneous to homogeneous action modes with H₂O₂ vs. O₂ – Part 1: iron salts as oxide precursors, *Chem. Eng. J.*, 358 (2019) 211–224.
- [9] L. Narayanasamy, T. Murugesan, Degradation of Alizarin Yellow R using UV/H₂O₂ advanced oxidation process, *Environ. Prog. Sustainable Energy*, 33 (2014) 482–489.
- [10] B. Bethi, S.H. Sonawane, B.A. Bhanvase, S.P. Gumfekar, Nanomaterials-based advanced oxidation processes for wastewater treatment: a review, *Chem. Eng. Process. Process Intensif.*, 109 (2016) 178–189.
- [11] L. Victoria, S. Murillo, A. Schärer, S. Giannakis, S. Rtimi, C. Pulgarin, Iron-coated polymer films with high antibacterial activity under indoor and outdoor light, prepared by different facile pre-treatment and deposition methods, *Appl. Catal., B*, 243 (2019) 161–174.
- [12] E. Ortega-Gómez, M.M. Ballesteros Martín, B. Esteban García, J.A. Sánchez Pérez, P. Fernández Ibáñez, Solar photo-Fenton for water disinfection: an investigation of the competitive role of model organic matter for oxidative species, *Appl. Catal., B*, 148–149 (2014) 484–489.
- [13] J. Rodríguez-Chueca, M.I. Polo-López, R. Mosteo, M.P. Ormad, P. Fernández-Ibáñez, Disinfection of real and simulated urban wastewater effluents using a mild solar photo-Fenton, *Appl. Catal., B*, 150–151 (2014) 619–629.
- [14] K. Kuma, S. Nakabayashi, K. Matsunaga, Photoreduction of Fe(III) by hydroxycarboxylic acids in seawater, *Water Res.*, 29 (1995) 1559–1569.
- [15] R. Takahashi, N. Fujimoto, M. Suzuki, T. Endo, Biodegradabilities of ethylenediamine-N,N'-disuccinic acid (EDDS) and other chelating agents, *Biosci. Biotechnol. Biochem.*, 61 (1997) 1957–1959.
- [16] L. Chen, T. Liu, C. Ma, Metal complexation and biodegradation of EDTA and S,S-EDDS: a density functional theory study, *J. Phys. Chem. A*, 114 (2010) 443–454.
- [17] W. Huang, M. Brigante, F. Wu, C. Mousty, K. Hanna, G. Mailhot, Assessment of the Fe(III)-EDDS complex in Fenton-like processes: from the radical formation to the degradation of bisphenol A, *Environ. Sci. Technol.*, 47 (2013) 1952–1959.
- [18] S. Papoutsakis, F.F. Brites-Nóbrega, C. Pulgarin, S. Malato, Benefits and limitations of using Fe(III)-EDDS for the treatment of highly contaminated water at near-neutral pH, *J. Photochem. Photobiol., A*, 303–304 (2015) 1–7.
- [19] Y. Wu, M. Passananti, M. Brigante, W. Dong, G. Mailhot, Fe(III)-EDDS complex in Fenton and photo-Fenton processes: from the radical formation to the degradation of a target compound, *Environ. Sci. Pollut. Res.*, 21 (2014) 12154–12162.
- [20] Y. Zhang, N. Klamerth, P. Chelme-Ayala, M. Gamal El-Din, Comparison of nitrilotriacetic acid and [S,S]-ethylenediamine-N,N'-disuccinic acid in UV-Fenton for the treatment of oil sands process-affected water at natural pH, *Environ. Sci. Technol.*, 50 (2016) 10535–10544.
- [21] T. Lehoczi, É. Józsa, K. Osz, Ferrioxalate actinometry with online spectrophotometric detection, *J. Photochem. Photobiol., A*, 251 (2013) 63–68.
- [22] S. Goldstein, J. Rabani, The ferrioxalate and iodide-iodate actinometers in the UV region, *J. Photochem. Photobiol., A*, 193 (2008) 50–55.
- [23] Y. Chen, N. Li, Y. Zhang, L. Zhang, Novel low-cost Fenton-like layered Fe-titanate catalyst: preparation, characterization and application for degradation of organic colorants, *J. Colloid Interface Sci.*, 422 (2014) 9–15.
- [24] A. De Luca, Fenton and Photo-Fenton Like at Neutral pH for the Removal of Emerging Contaminants in Water and Wastewater Effluents, Ph.D. Thesis, Universitat De Barcelona, 2016, 198 p. Available at: http://diposit.ub.edu/dspace/bitstream/2445/106497/1/Antonella%20De%20Luca_THESIS.pdf
- [25] C. Lei, Y. Sun, D.C.W. Tsang, D. Lin, Environmental transformations and ecological effects of iron-based nanoparticles, *Environ. Pollut.*, 232 (2018) 10–30.
- [26] F. Gozzi, A. Machulek, V.S. Ferreira, M.E. Osugi, A.P.F. Santos, J.A. Nogueira, R.F. Dantas, S. Esplugas, S.C. de Oliveira, Investigation of chlorimuron-ethyl degradation by Fenton, photo-Fenton and ozonation processes, *Chem. Eng. J.*, 210 (2012) 444–450.
- [27] S. Nahim-Granados, I. Oller, S. Malato, J.A. Sánchez-Pérez, M.I. Polo-Lopez, Commercial fertilizer as effective iron chelate (Fe³⁺-EDDHA) for wastewater disinfection under natural sunlight for reusing in irrigation, *Appl. Catal., B*, 253 (2019) 286–292.
- [28] G.E. Budnick, R.T. Howard, D. Mayo, Comparison of Colilert-18 to the mTEC Agar Method for the Enumeration of *Escherichia coli* in Recreational Waters, American Society of Microbiologists Annual Convention, Connecticut, 2001.
- [29] US EPA, Guidelines Establishing Test Procedures for the Analysis of Pollutants; Analytical Methods for Biological Pollutants in Ambient Water, Vol. 66, 2003, pp. 24–42. Available at: <https://www.idexx.com/resource-library/water/water-reg-article5AP.pdf>
- [30] S.G. Michael, I. Michael-Kordatou, V.G. Beretsou, T. Jäger, Solar photo-Fenton oxidation followed by adsorption on activated carbon for the minimisation of antibiotic resistance determinants and toxicity present in urban wastewater, *Appl. Catal., B*, 244 (2019) 871–880.
- [31] United States Environmental Protection Agency, Analytical Methods Approved for Compliance Monitoring under the Revised Total Coliform Rule, 2017.
- [32] E. Fox, Microbiology Methods for Drinking Water Laboratories Origins of Drinking Water Bacteriological Testing, Conference Proceedings, London. Available at: https://cdn.ymaws.com/www.vwea.org/resource/resmgr/Conference_Proceedings/2016/LPC/5_Microbiology_Methods_for_.pdf
- [33] S.I. Niemela, J.V. Lee, C.R. Fricker, A comparison of the International Standards Organisation reference method for the detection of coliforms and *Escherichia coli* in water with a defined substrate procedure, *J. Appl. Microbiol.*, 95 (2003) 1285–1292.
- [34] ISO 6332, Water Quality - Determination of Iron - Spectrometric Method Using 1,10-Phenanthroline, 1988.
- [35] Y. Sun, J.J. Pignatello, Chemical treatment of pesticide wastes, evaluation of iron(III) chelates for catalytic hydrogen peroxide oxidation of 2,4-D at circumneutral pH, *J. Agric. Food Chem.*, 40 (1992) 322–327.

- [36] A. De Luca, R.F. Dantas, S. Esplugas, Assessment of iron chelates efficiency for photo-Fenton at neutral pH, *Water Res.*, 61 (2014) 232–242.
- [37] V.D. Masliy, A.V. Selyukov, Applying hydrogen peroxide for oxidizing underground water iron, *Chem. Sustain. Dev.*, 17 (2009) 527–531.
- [38] M. Gar Alalm, A. Tawfik, S. Ookawara, Comparison of solar TiO₂ photocatalysis and solar photo-Fenton for treatment of pesticides industry wastewater: operational conditions, kinetics, and costs, *J. Water Process Eng.*, 8 (2015) 55–63.
- [39] C. Bouasla, F. Ismail, M.E.H. Samar, Effects of operator parameters, anions and cations on the degradation of AY99 in an aqueous solution using Fenton's reagent. Optimization and kinetics study, *Int. J. Ind. Chem.*, 3 (2012) 1–12, doi: 10.1186/2228-5547-3-15.
- [40] E. Ortega-Gómez, P. Fernández-Ibáñez, M.M. Ballesteros Martín, M.I. Polo-López, B. Esteban García, J.A. Sánchez Pérez, Water disinfection using photo-Fenton: effect of temperature on *Enterococcus faecalis* survival, *Water Res.*, 46 (2012) 6154–6162.
- [41] A. Bunesco, P. Besse-Hoggar, M. Sancelme, G. Mailhot, A.M. Delort, Fate of the nitrilotriacetic acid-Fe(III) complex during photodegradation and biodegradation by *Rhodococcus rhodochromus*, *Appl. Environ. Microbiol.*, 74 (2008) 6320–6326.
- [42] I. García-Fernández, S. Miralles-Cuevas, I. Oller, S. Malato, P. Fernández-Ibáñez, M.I. Polo-López, Inactivation of *E. coli* and *E. faecalis* by solar photo-Fenton with EDDS complex at neutral pH in municipal wastewater effluents, *J. Hazard. Mater.*, 372 (2018) 85–93.
- [43] S. Giannakis, M. Voumard, D. Grandjean, A. Magnet, L.F. De Alencastro, C. Pulgarin, Micropollutant degradation, bacterial inactivation and regrowth risk in wastewater effluents: influence of the secondary (pre)treatment on the efficiency of advanced oxidation processes, *Water Res.*, 102 (2016) 505–515.