Revista Ciencia en Desarrollo. Vol. 15 Num. 2. pp. 186 - 196
julio - diciembre 2024

https://doi.org/10.19053/uptc.01217488.v15.n2.2024.17076

Artículo de investigación

Advanced oxidation technology using Fe^0/H_2O_2 as an effective treatment to recycle industrial wastewater for irrigation of s crops.

Tecnología de oxidación avanzada utilizando Fe^0/H_2O_2 como tratamiento eficaz para reciclar aguas residuales industriales para riego de cultivos.

Paola Tatiana Valencia Carrasquilla [1] ✉, Jhon Sebastián Hernández [1], Mariana Alejandra Gil Agudelo [1] y Julie Joseane Murcia Mesa [1]

[1]Catalysis Group, School of Chemical Sciences, Pedagogical and Technological University of Colombia UPTC, Avenida Central del Norte, Tunja, Boyacá, Colombia

Recepción: 13-jun-2023 **Aceptado:** 15-abril-2024 **Publicado:** 23-julio-2024
Cómo citar: Valencia Carrasquilla, P. T., Hernandez Niño, J. S., Gil Agudelo, M. A., & Murcia Mesa, J. J. (2024). Oxidación avanzada usando Fe0/H2O2 como tratamiento efectivo para reciclar aguas residuales industriales para riego de cultivos. Ciencia en Desarrollo, 15(2). https://doi.org/10.19053/uptc.01217488.v15.n2.2024.17076

Abstract

This study focused on the development of a new Phenton treatment of water effluent from a local industrial park and dyeing industry. Different advanced oxidation technologies (AOTs) such as heterogeneous photocatalysis, photo-Fenton and UV-Vis/H_2O_2 using $FeSO_4$ and pure iron were evaluated. To develop this study, water samples were tested before and after each treatment. In general, the amount of chlorides, nitrates, hydrocarbons, heavy metals, TOC and bacteria decreased significantly after AOTs. Photo-Fenton and UV-Vis/H_2O_2/TiO_2 showed the best performance in the treatment of dyeing industry and industrial wastewater, respectively. Photo-Fenton mineralized 100% of the dyes, reduced total coliforms by 99%, eliminated 76% of the TOC and 60% of the heavy metals tested. Interestingly, the use of ferrous metal in the Photo-Fenton treatment was found to achieve similar results. This means that wastewater can be treated with benign chemicals. Treated wastewater was evaluated as a potential water source for irrigation of Lolium perenne, a conventional forage crop. In general, the physical characteristics of Lolium perenne, such as leaf and canopy length and width, were not significantly altered after irrigation with treated wastewater. Similar results were obtained using treated tap water as a reference. Trace amounts of metals remaining from the treatment were detected in the grass and soil. However, the concentration of Cd, Cr, Cu and Zn was very similar to that of tap water. Considering these results, the use of non-toxic zero-valent iron metal and hydrogen peroxide in a photo-Fenton reaction is a pilot plant scalable alternative oxidative treatment technology for recycling industrial wastewater in agricultural activities.

Keywords: Textile wastewater, industrial estate effluents, AOTs, irrigation, *Lolium perenne*.

CC BY NC ND
E-ISSN: 2462-7658

1 Introduction

Global water pollution is primarily attributed to wastewater discharges from various industrial sectors, particularly textiles and industrial parks. These industries release large quantities of organic and inorganic pollutants that affect aquatic ecosystems, in addition to agricultural activities, which use significant amounts of clean water for irrigation and pose risks when using untreated wastewater. This practice leads to the transfer of contaminants to crops and consequently to the food chain [1]. For example, in Colombia and other Latin American countries, Lolium perenne is the main crop used to feed animals for meat production [2]. It has been shown that irrigation with untreated wastewater leads to the transfer of heavy metals such as Cd, Pd, Cr, Zn, Fe and Mn to crops, in addition to pathogenic microorganisms such as *E. coli, Salmonella spp* and fungi. Therefore, the accumulated contaminants in crops are transferred to animals and then to humans who consume them, posing a serious risk to public health [3].

Most organic contaminants in industrial wastewater are characterized by their stability and complex molecular structures. Similarly, inorganic contaminants present in lower concentrations are also resistant to removal by conventional chemical and biological treatment methods, including filtration and coagulation. These techniques are primarily designed to remove solid contaminants, making them less effective against certain types of contaminants [4]. Therefore, the implementation of Advanced Oxidation Technologies (AOTs) is proposed for the effective removal and degradation of these contaminants in wastewater.

Numerous studies have used AOTs, including heterogeneous photocatalysis based on TiO_2, H_2O_2/UV-Vis, and Photo-Fenton, for the degradation of organic pollutants and the removal of heavy metals such as Hg, As, Cu, Cr, and Zn, as well as for the inactivation of bacteria [5, 6, 7]. These studies highlight the efficiency of these technologies due to their ability to generate highly oxidizing species known as hydroxyl radicals (OH) in the presence of light, which are capable of mineralizing organic contaminants, neutralizing odors, and precipitating heavy metals [7]. Each method has its own characteristics: TiO_2 is effective in removing organic pollutants, but its performance decreases with dyes at high concentrations due to catalyst poisoning; however, it is successful in removing heavy metals by photo deposition on the catalyst surface [8]. On the other hand, the H_2O_2/UV-Vis system excels in wastewater disinfection, although its oxidant generation rate limits its effectiveness in mineralizing other pollutants [9]. Finally, the Photo-Fenton process is widely used for the degradation of complex organic pollutants such as dyes, where the synergy with hydrogen peroxide leads to an increased production of hydroxyl radicals, which react with inorganic components to form water-insoluble compounds [10]. The reaction mechanism of the latter process is explained in the following paragraphs.

In 2007, the Photo-Fenton process was applied by Haber and Wisen, who claim that a pH < 3 is ideal for generating a kinetically favorable chain reaction. Conventionally, this process is carried out using iron salts such as $FeSO_4$, along with the addition of H_2O_2 (Equations 1-3) [11].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH + H^{+} \quad (2)$$

$$RH + OH \rightarrow \text{subproducts} + H_2O \quad (3)$$

However, this process has some drawbacks due to the addition of reagents to acidify and basify the treated water, especially considering that the pH must be between 6.0 and 9.0 for crop irrigation. Therefore, it is proposed to develop the process at neutral pH, using commercial steel wool as a source of valent iron and adding H_2O_2 to generate hydroxyl radicals (Equations 4-6) [12].

$$Fe^{0} + H_2O_2 \rightarrow Fe^{2+} + 2HO^{-} \quad (4)$$

$$Fe^{2+} + H_2O_2 + \rightarrow Fe^{3+} + OH + HO^{-} \quad (5)$$

$$OH + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} \quad (6)$$

In the field of water treatment, numerous scientific studies have focused on the development of AOTs. These technologies have proven to be effective in degrading and eliminating various contaminants present in wastewater, as evidenced by the research of Martínez and Brillas [13], who documented the ability of AOTs to significantly reduce the levels of persistent organic compounds and pathogenic microorganisms in treated water. However, despite the progress made in the removal of individual contaminants, there is a notable lack of studies addressing the applications and post-treatment effects of these technologies.

Specifically, most studies of AOTs have focused on limited control parameters to assess the quality of post-treatment effluent [14, 15] , as noted by Chen et al. [16] in their review of methodologies for assessing the quality of water treated by AOTs. These studies tend to prioritize the removal of specific contaminants, but do not delve into a comprehensive assessment of the resulting water quality, leaving a significant gap in understanding the residual impacts of these treatments. Furthermore, even in cases where post-treatment applications are considered, phototoxicity analysis often remains qualitative rather than quantitative, limiting the ability to accurately assess the risks associated with the use of treated water in different contexts, as highlighted by the work of Fernández and Pérez [17].

Therefore, there is a need for more comprehensive studies that not only focus on contaminant removal, but also evaluate the quality of the treated water for specific applications. In this regard, the present research addresses this need by complying with more than 30 parameters required by local regulations. These parameters include in situ irrigation of Lolium perenne from seed to growth for two months, followed by phytotoxicity analysis of both the plant and the soil.

The selection of Lolium perenne as a bioindicator organism allows a detailed evaluation of the potential toxic effects of treated water in an agricultural context, which is crucial to determine the viability of using this water for crop irrigation. Previous studies, such as those conducted by Lin et al [18], have demonstrated the importance of using bioindicators to assess the environmental impact of treated water, highlighting the need for quantitative analyses to obtain accurate and reliable results. Therefore, this research not only contributes to the field of water treatment through the implementation of AOTs, but also addresses one of the main limitations identified in the literature by providing a comprehensive evaluation of the quality of post-treatment water and its suitability for agricultural applications.

By addressing this gap, this study advances the understanding of residual effects of water treatment technologies, promoting their optimization and adaptation for sustainable applications. The implementation of a rigorous and quantitative analytical approach to evaluate the quality of treated water and its impact on agricultural crops will significantly contribute to the development of safer and more effective practices in water resource management, in line with sustainability and environmental protection goals.

2 Experimental work

The experimental work of this research was carried out in 4 main stages, which are described in detail below:

2.1 Wastewater sampling and physicochemical analysis

Wastewater sampling was performed according to the procedures described in the Standard Methods for Examination of Water and Wastewater (SMEWW) [19]. Sample analyses were performed both before and after application of the AOTs under study. To ensure the reliability and reproducibility of the results, all analyses were performed in triplicate. The specific methods used in these analyses are described below.

Microbiological analyses: The quantification of microorganisms was performed using the SMEWW 9222 method [19]. This method consisted of filtering 100 mL of the water sample through a sterile nitrocellulose membrane, followed by placing the filtered sample on a Petri dish containing Merck Chromocult Agar as the culture medium. This agar facilitated the simultaneous identification of four types of bacteria after 24 hours of incubation: *E. coli, Salmonella spp. and Citrobacter freundii*.

Hydrocarbons: These analyses were developed using the SM 5520-F method [19]. The method involves liquid-liquid extraction of fats and oils using n-hexane, followed by adsorption of the extract on silica gel.

Determination of metals: For the analysis of metals such as Cd, Zn, Cr, Fe, Cu, Ni, Na, and Pb, the SMEWW method 3111B [19] was used, which generally involves acid digestion. In this process, 1mL HCl and 3mL HNO_3 were added to 50 mL Milli-Q water. This mixture, combined with the plant, soil, or wastewater sample, was then heated with constant stirring at 300 rpm until evaporation occurred. The residue was then redissolved in 25mL of Milli-Q water for analysis. The final solution was analyzed using a SHIMADZU AA-7000 spectrometer equipped with a dual-flame furnace system using an acetylene-air flame.

Residual total chlorine: The analysis was performed using a RCYAGO digital water quality analyzer, which includes an electrotester for pH and chlorine measurements [20].

Total Organic Carbon: The Analytikjena multi N/C 2100 instrument was used for this analysis according to method 5310 B [19]. First, total carbon (TC) was measured in 200μL of each sample using a combustion tube, where pyrolysis and oxidation were facilitated by a gas flow with a palladium catalyst. Subsequently, 200μL of the sample was introduced into the total inorganic carbon (TIC) reactor and CO_2 production was detected using a non-dispersive infrared absorption (NDIR) detector. The TOC concentration was then determined as the proportional carbon concentration in the sample.

Nitrates: Analyzed by HACH method 8039, adapted from SM 4500 NO_3^- E [21] at 500 nm wavelength.

Sulfates: Measured by HACH method 8051, based on SM 4500 SO_4^{2-} E [22], at 450nm in a UV-Vis spectrophotometer DR 6000.

2.2 Evaluation of the efficacy of AOTs in the treatment of wastewater samples

In the laboratory, AOTs treatments were developed using a cylindrical stirred tank reactor (STR) placed under a 300 W Osram Ultravitalux lamp. This setup provided a light intensity of 30 W/m² to the 250 mL of wastewater contained in the reactor. Each treatment was performed for 4 hours at a stirring speed of 300rpm under ambient conditions at 22°C.

In addition, two blank tests were conducted in parallel with the AOTs treatments using UV-Vis light. Blank test 1 involved the photolysis of water without any added reagents, establishing a baseline for the evaluation of the photocatalytic process. On the other hand, blank test 2 was developed using $FeSO_4$*7H_2O (MCKENNA GROUP S.A.S) without hydrogen peroxide. For this test, the water was first acidified with HCl and then adjusted to a pH suitable for crop irrigation with NaOH.

After blank tests, the AOTs were used to treat 250mL wastewater samples. The experimental conditions for these reactions, including the use of UV-Vis light, are outlined below:

- **Heterogeneous photocatalysis:** It was carried out using the parameters described above, with 1 g/L of commercial TiO_2 (Sigma-Aldrich; crystalline phase anatase; JCPDS: 21-1272) as photocatalyst.

- **UV-Vis/H_2O_2** The peroxide concentration was 0.07 M, which was selected based on previous efficacy studies [23].

- **Photo-Fenton treatment 1:** 1 g/L $FeSO_4$, 0.07 M H_2O_2 and acidic pH < 3 were used. The pH was then adjusted to 7 by adding NaOH solution.

- **Photo-Fenton - Treatment 2:** In order to avoid the addition of reactants to acidify and basify the wastewater, a different source of iron was chosen, so 1 g/L of commercial steel wool (Fe^0) and 0.07M H_2O_2 solution were used in this treatment, which was carried out at natural pH.

Finally, the AOT that showed the highest effectiveness in removing the pollutant from the wastewater samples at the laboratory scale was evaluated in a pilot plant scale reactor. A patented device was used for these tests [24]. These processes were developed for 7 hours, under sunlight, and the operating parameters were flow rate of 0.5 L/s, velocity of 0.5 m/s, reactor length of 22.5 m, and residence time of 36 s. The water treated at the pilot plant level was used for the irrigation crop tests described below.

2.3 Lolium perenne crop irrigation with treated wastewater

The irrigation protocol was adapted from the methodology reported by Zedník et al [25]. The process of irrigation and planting is described as follows:

- Three different plastic containers were used for the *Lolium perenne* crop: (i) blank crop irrigated only with tap water (human consumption quality level); (ii) crop irrigated with treated dyeing industry effluent and (iii) crop irrigated with treated industrial estate effluent.

- For soil preparation, 1.6 kg of arable land was fertilized by adding 250 mg of Anasac (Anafert).

- After soil preparation, 2.5 g of Lolium perenne seeds were sown at a depth of 15 cm.

- Then the plants were watered daily in the morning between 8:00 and 9:00 am for 60 days.

- Finally, after the growth of *Lolium perenne*, phytotoxicity analysis was developed. The irrigation protocol was adapted from the methodology reported by Zedník et al. [25]. The process of irrigation and planting is described as follows:

2.4 Determination of residual and/or phytotoxicity

To evaluate potential residual or toxicity in the crop after irrigation, daily qualitative assessments of grass characteristics were made. These assessments focused on leaf color and measurements of leaf height, width, and root growth. In addition, the adsorption of heavy metals in leaves and soil after irrigation was quantified using atomic absorption spectrophotometry (AA) according to the method described in section 2.1, with the addition of 2 mL H_2O_2 and 1 g samples of soil or plant leaves.

3 Results and discussion

3.1 Staining of industrial effluents treated with AOTs.

Table 1 summarizes the results obtained before and after the treatment of wastewater samples coming from the dyeing industry by different AOTs, this table also includes a comparison with the maximum permissible limits in the Colombian regulations for wastewater recycling applied to crop irrigation for animal feeding. TOC and total coliform content are not required parameters in the local regulations; however, it is very important to determine the value of this analysis to have a better idea of the quality of the wastewater after treatment.

Table 1: Results of dyeing industry effluents before and after AOTs application.

Water quality control parameter	Units	Maximum permissible limit	Start Wastewater Sample	AOTs						
				STR						Pilot plant
				Blank 1	UV-Vis/TiO_2	UV-Vis/H_2O_2	Blank 2	Photo-Fenton (1)	Photo-Fenton (2)	Photo-Fenton (2)
pH	pH Value	6.0 – 9.0	6.5	6.8	6.85	6.6	3-7*	3-7*	6.55	6.55
Conductivity	µS/Cm	1500	26000	ND	ND	ND	ND	ND	4800	5400
Total hydrocarbons	mg/L	1	3.7	ND	ND	<2	ND	<3	<2	<2
Chlorides		300	4695	ND	ND	4248	ND	ND	1726	1875
Sulfates		500	780	ND	ND	600	ND	1560	400	510
Sodium		200	1522	ND	ND	ND	ND	4476	ND	ND
Cadmium		0	0.13	0.11	0.04	0.04	0	0.01	0.03	0.1
Zinc		3	12.9	9.14	4.03	6.02	2.4	9.05	2	3
Nickel		0.2	0.73	0.35	0.19	0.31	0.65	0.63	0.33	0.4
Chromium		0.1	1.2	1	0.6	1.03	0.92	0.87	0.61	0.7
Copper		1	1.3	1	0.07	0.03	0.21	0.6	0.2	0.41
Iron		5	5.32	3.22	2.33	2.21	38	25.4	33.15	59.1
Total residual chlorine		< 1.0	>3	ND	ND	>3	ND	>3	>3	>3
Nitrates		5	35	ND	ND	ND	ND	1.2	1	1.9
TOC		NR	2940	2240	2000	2200	1720	188	700	742
Total coliforms	CFU/ 100 mL	NR	$2.6x10^6$	$2.5x10^5$	$5.8x10^3$	$5.0x10^3$	$2.0x10^2$	$1.3x10^2$	$1.03x10^2$	$1.09x10^2$

* These values correspond to the pH obtained after photo-Fenton treatment (3.0) and after neutral pH adjustment for crib rinsing.

In general, as shown in Table 1, the initial sample has values that exceed the regulations in several quality control parameters such as: total hydrocarbons, chlorides, total residual chlorine, nitrates and heavy metals (Na, Cd, Zn, Ni, Cr, Co and Fe).

3.1.1 AOTs using lab-scale STR (Table 1)

Blank test 1: In this analysis, a slight increase in pH was observed, probably due to the reduction of H^+ ions through reactions with other species, such as hydroxyl radicals, produced during photolysis. The concentrations of heavy metals showed a slight decrease after 4 hours of exposure to UV-Vis light, possibly due to oxidation processes leading to the formation of metal hydroxides and oxides [3], which were subsequently removed by ultrafiltration. The decrease in TOC concentration is mainly due to the action of hydroxyl radicals generated by water photolysis and photosensitization of organic compounds under UV-Vis light [26]. In addition, there was a significant reduction in total coliform bacteria (90.38%) as a result of the bactericidal effects of UV-Vis radiation on the DNA of bacterial cells [27].

Heterogeneous photocatalysis: During this process, the pH increased from 6.50 to 7.00due to the generation of H^+ ions, an increase in pH was observed in the experiments conducted. This increase could be due to the formation of hydroxyl radicals that react with the H^+ ions, neutralizing them and thus influencing the rise in pH of the water sample. This treatment reduced TOC to 32%, significantly less than the 60-70% reductions reported in other studies. This reduction can be attributed to the poisoning of the semiconductor, likely caused by a combination of contaminants in the water. Dyes, ions, and metals present can interact with the photocatalyst, resulting in deactivation. Chlorides, heavy metals, and complex organic molecules contribute to this effect. The cumulative effect of these contaminants inhibits the photocatalytic activity, resulting in the observed lower TOC reduction [28]. This treatment proved to be effective in eliminating 99.7% of the total coliforms, similar to previous works [29], the elimination of bacteria is due to the damage in the cell membrane and cellular components such as proteins and nucleic acids [30] caused by the oxidant reactive species (ROS). On the other hand, the removal of heavy metals observed after the treatment is mainly due to their photoreduction on the semiconductor surface [31].

UV-Vis/H_2O_2: After this treatment, significant reductions in wastewater parameters were observed, including total hydrocarbons, chlorides, heavy metals, sulfates, and total coliforms. The pH level remained within the limits allowed by local regulations. In addition, the hydrocarbon concentration decreased due to the interaction of hydroxyl radicals (from H_2O_2 photolysis) with aromatic rings [32]. This interaction facilitated the cleavage of carbon-carbon bonds and subsequent oxidation leading to CO_2 formation, thus demonstrating hydrocarbon removal via dye degradation.

The chlorides in the wastewater sample come mainly from the NaCl used for color fixation; the chloride ion interacts with dye molecules to form chlorinated by-products, then the presence of H_2O_2 further leads to the formation of HClO and ClO^- species. Meanwhile, hydroxyl radicals interact with Cl^- ions to form HCl, which then reacts with H_2O_2 to form H_2O and gaseous Cl_2. This series of reactions explains the observed decrease in chloride concentration in the aqueous phase (Equations 7-9) [33].

$$\text{chlorined subproducts} + H_2O_2 \rightarrow HClO + ClO^- \quad (7)$$

$$Cl^- + OH \rightarrow HCl \quad (8)$$

$$HCl + H_2O_2 \rightarrow H_2O + Cl_2 \quad (9)$$

Some studies have suggested that chlorine ions may be insoluble and removed from the liquid phase by precipitation [34], however, this scenario seems less likely in the context of the present work due to the tendency of chlorine ions to precipitate or even solubilize salts, given the presence of metals in the sample, the salts can be dissociated. Consequently, the pH would change from basic to acidic, which was not observed at the end of the reaction.

On the other hand, the removal of heavy metals could be explained by the photolysis of water and H_2O_2, which improves the production of hydroxyl radicals to interact with the heavy metals present in the sample, leading to the formation of metallic oxides that can precipitate after the reaction, as stated in other studies [34].

In the case of sulfate ions, a decrease of almost 23% was observed after the treatment, which can be due to the simultaneous reduction of metals in the aqueous phase; it is because these ions are oxidized by reaction with H_2O_2 and OH radicals, subsequently interacting with dissolved metals to produce precipitation in the form of salts, these results are in agreement with different authors [35].

Furthermore, the coliform removal efficiency observed was 99.8%; this result is not optimal compared to previous studies where 100% inactivation was achieved [36], in this work the lower efficiency may be due to the presence of 75% TOC concentration, in this case the organic matter can act as a protective shield for the bacterial cell wall during the AOT treatment [37]. Moreover, in this work, 25% of TOC removal was observed after the treatment, which is higher than some results reported by other authors using lower concentration of H_2O_2 [38].

Blank test 2: This treatment was carried out by using only $FeSO_4$*$7H_2O$ in the reaction medium, the pH was acidified to avoid the precipitation of this salt and to ensure the reaction yield. The results obtained showed a decrease in the content of metals such as Cd, Zn and Cu, a reduction in the TOC concentration of 46% and a 99% elimination of total coliforms. These results can be attributed to the use of $FeSO_4$*$7H_2O$, which is commonly used as a biological coagulant that reacts with environmental contaminants to convert them into their insoluble forms [39]. In addition, the presence of UV-Vis light and Fe^{2+} enhances the oxidation of organic matter as well as the opening of aromatic rings, thus explaining the decrease in TOC concentration [40]. However, the percentage of coliform elimination is not consistent with other studies [41], as they suggest that coagulation treatments are not effective in eliminating bacteria. Therefore, this elimination percentage is attributed to hydroxyl radicals formed by the action of UV-Vis light.

Photo-Fenton, treatment 1: Considering the results obtained, it is evident that the best treatment for heavy metals removal was UV-Vis/H_2O_2, and since the highest inactivation of total coliforms and TOC concentration was obtained in the blank test 2, it was decided to combine these two treatments to carry out the photo-Fenton treatment 1. This treatment presents the highest effectiveness in the removal of total coliforms due to the acidic conditions in the reaction medium; under these conditions, the concentration of hydronium ions increases and, with the help of ROS, it was possible to damage the cellular structure and function [27]. Nevertheless, the remaining percentage of bacteria has been identified as **Aeromonas hydrophila** [42], based on other studies, which thrives in saline environments and may have a detrimental effect on human lungs [43]. On the other hand, the TOC concentration decreased by 94% and 100% dye degradation was observed, therefore the results are consistent with each other and give better results than other studies where 98% dye degradation [44] and 80% TOC removal [45] were achieved, this discrepancy may be attributed to the fact that those studies may have used concentrations of 0.1 g/L of the iron precursor, whereas in this study 1 g/L was used.

On the other hand, it was observed that Photo-Fenton 1 is not an effective method to remove heavy metals, as pointed out by some authors [46]; in fact, the results obtained in this treatment are quite similar to the blank test 1, where only UV-Vis light was used.

The total hydrocarbon content was almost the same after photo-Fenton, treatment 1, indicating that these compounds are not completely degraded by this treatment. The SO_4^{2-} ions in the iron sulfate react in the acidic medium (i.e., pH 3.0 after HCl addition) with the hydroxyl radicals to form SO_4^{2-}, which can also react with H_2O_2 to form sulfate ions again (Eqs. 10-11) [47]. During this reaction, the sulfate ions consume part of the H_2O_2 content, thus reducing the availability of this reactive for the generation of hydroxyl radicals in the reaction medium, which can explain the lower effectiveness of the treatment in hydrocarbon degradation.

$$HSO_4^- + HO \rightarrow SO_4^- + H_2O \quad (10)$$

$$SO_4^- + H_2O_2 \rightarrow SO_4^- + H^+ + HO_2 \quad (11)$$

Photo-Fenton, treatment 2: The concentrations of total hydrocarbons, chlorides, sulfates, Cd, Zn, Cu, Cr, Ni and nitrates decreased significantly. However, the TOC concentration increased almost sixfold compared to Photo-Fenton 1. In addition, the removal of total coliforms did not show a significant difference due to the formation of sludge that prevents UV-Vis interaction with the effluent (Equation 12) [48]. Nevertheless, the iron concentration was found to be almost six times higher than allowed by local regulations, which will be advantageous during the irrigation phase of the crop, which will be explained in detail in the next sections.

$$4Fe^0 + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3 \quad (12)$$

On the other hand, the removal of total hydrocarbons is attributed to the presence of excess iron, which plays a role in the opening of the aromatic ring [49]. The concentration of sulfates decreases due to the interaction between Fe^{3+} and these ions, leading to their subsequent precipitation [50]. However, there are no studies that provide an explanation for the removal of chlorides and nitrates with this treatment, with the majority claiming that it is not effective [51].

The effectiveness of this process is innovative compared to the conventional use of semiconductors or supported metals, iron nanoparticles, and/or a prior treatment such as coagulation or flocculation, where good results are obtained, such as 90% dye degradation, 65% TOC removal, 98% bacteria elimination, and removal of heavy metals in different percentages [52, 53, 54]. In contrast, in the present study, 99.99% total coliform removal, 100% dye degradation, 77% TOC removal, and effective removal of heavy metals and ions were achieved.

Even the excess of iron present in the treated wastewater, it is possible to conclude that Photo-Fenton 2 led to overcome the main disadvantages observed in the application of conventional Photo-Fenton, for this reason this treatment was selected to be tested at pilot plant scale, this procedure focused on the treated dyeing wastewater recycling as explained in detail below.

3.1.2 Photo-Fenton 2 Treatment Tested at Pilot Plant Level.

Considering that the Photo-Fenton 2 has the highest efficacy in the treatment of colored wastewater, this AOT was selected to test it at the pilot plant level, and the results obtained from this test are also included in Table 1. As can be seen in this table, the effectiveness of this treatment remains almost constant at STR and pilot plant level, thus showing the effectiveness of these treatments at different volumes of water and under environmental or laboratory conditions. From the results obtained, it is possible to conclude that this AOT is a good alternative for the treatment and recovery of colored wastewater, thus achieving values of quality control parameters according to Colombian regulations for crop irrigation of *Lolium Perenne*.

3.2 Industrial area effluents treated by AOTs.

Wastewater treatment results from an industrial park are shown in Table 2. The data indicates that parameters such as conductivity, total hydrocarbons, total residual chlorine and nitrates exceed local regulatory standards. Several AOTs were systematically evaluated and TiO_2 was found to be effective in metal removal while H_2O_2 was effective in TOC reduction. Based on these results, a combined treatment approach was adopted, allowing the treated water to be reused for agricultural irrigation.

The combination of AOTs used proved to be synergistic in the treatment of water contaminants. By enhancing the generation of hydroxyl radicals, it is possible to enhance the oxidation of organic matter, inactivate total coliforms, and aid in the removal of heavy metals and ions. Comparatively, while previous research using a similar methodology achieved an 80% removal of TOC [55] and a 90% bacterial elimination rate [56], the current study has realized an elimination rate of 99% and removal of 56% of TOC concentration. Such discrepancies can be attributed to the complex nature of the real water samples analyzed, especially the presence of contaminants such as chloride ions, which can modulate the treatment efficacy.

Table 2 also presents the results obtained by the application of UV-Vis/H_2O_2/TiO_2 at STR and at pilot plant level, as it can be observed that the effectiveness of these AOTs slightly decreases at pilot plant scale, which is mainly due to the real conditions in which these treatments were carried out, and mainly because under environmental conditions the light intensity can vary during the day, leading to a decrease in the overall effectiveness of the treatment.

Considering the results obtained, the polluted wastewater treated by Photo-Fenton 2 and the industrial park wastewater treated by UV-Vis/H_2O_2/TiO_2 were selected as water sources for crop irrigation. The results obtained in the vegetable species after prolonged irrigation with these treated effluents are presented in the following section.

3.3 Recirculation of treated wastewater for irrigation of *Lolium perenne* crops.

As explained in the experimental section, treated wastewater was used to irrigate *Lolium perenne*, a grass species commonly used for animal feed. The observation protocols included daily irrigation for 8 weeks. Leaf length and width were measured with a ruler. Root length was measured from the base to the tip after the plants were carefully removed from the soil. Heavy metal residues were determined by analyzing soil and plant samples using atomic absorption spectroscopy.

Tap water was used as a control for the irrigation process, along with the two treated wastewater samples. Qualitatively, no significant difference was observed between the wastewater treated and untreated with AOTs, which is consistent with other studies suggesting that irrigation with treated water does not hinder crop development, but rather accelerates its growth [55, 56]. However, a difference in root length was observed with the TiO_2/H_2O_2/UV-Vis treatment, possibly due to the amount of organic matter present after the process.

Figures 1 and 2 show images of the Lolium perenne plant after irrigation with the treated wastewater. On the one hand, a loss of coloration is observed in the crop irrigated with the Photo-Fenton 2 treatment, and on the other hand, necrosis is observed in the crop irrigated with the TiO_2/H_2O_2/UV-Vis treatment. This behavior is attributed to the excess of H_2O_2 present in the aqueous phase after each treatment. Some studies suggest that concentrations above 0.03M of this chemical have adverse effects [57], including reduced biomass and changes in protein and chlorophyll content [58].

Figure 1: *Lolium perenne* crop irrigated with dyeing industry effluent treated with Photo-Fenton 2. Left: *Lolium perenne* plant and right: *Lolium perenne* leaf.

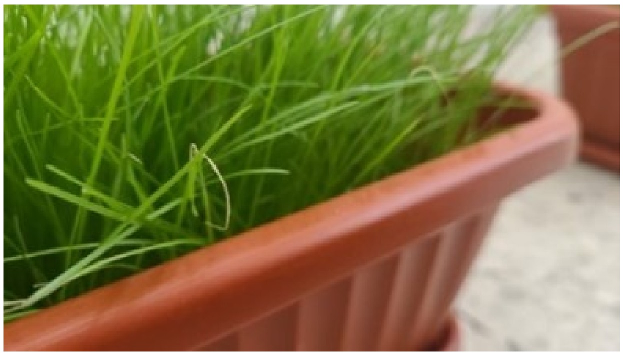

Figure 2: *Lolium perenne* crop irrigated with industrial effluent treated with UV-Vis/H_2O_2/TiO_2, after 5 weeks of irrigation.

On the other hand, even that after irrigation of *Lolium perenne* some discoloration was observed during the first weeks, the grass irrigated with coloring industrial effluents treated by Photo-Fenton 2 recovers its color (Figure 3), it is probably due to the presence of an excess of iron in the water, coming from the steel wool used in the treatment. In this treatment, the heavy metal Fe is above the local regulations (Table 1), however, it is an advantage for the vegetable species because the irrigation with this type of treated wastewater in the presence of iron excess increases the foliar area, chlorophyll concentration, and improves the growth and yield of the crop [59].

On the other hand, this treated wastewater presents a high conductivity due to the presence of dissolved ions, this affects the salinity of the soil reducing the absorption of nutrients for a hormonal change in the root plant. The excess of Fe can contribute to the regulation of the salinity problem, besides promoting the activity of antioxidant enzymes that are responsible of the ROS elimination, improving the defense mechanisms against salinity [60]. For all these reasons, the *Lolium perenne* crop can recover its vitality after irrigation with the water treated by Photo-Fenton 2, in the case of the other water source, the iron content is very low, thus wasting the advantages of this micronutrient in the crop.

3.3.1 Heavy Metal Residues

Some metals such as Cd, Cr, Cu, Fe and Zn are essential micronutrients for the plant, nevertheless in high concentration can affect

Table 2: Results of industrial park effluents before and after AOTs application.

Water quality control parameter	Units	Maximum permisible limit	Start Wastewater Sample	AOTs					
				STR					Pilot plant
				Blank	Photo-fenton (1)	UV-Vis/TiO_2	UV-Vis/H_2O_2	UV-Vis/H_2O_2/TiO_2	UV-Vis/H_2O_2/TiO_2
pH	pH Value	6.0 – 9.0	7.4	8.6	7.55	8.4	8.6	8.9	8.52
Conductivity	µS/Cm	1500	1935	ND	ND	ND	ND	1069	754
Total hydrocarbons	mg/L	1	13.3	ND	ND	ND	ND	<2	<2
Chlorides		300	212.4	ND	ND	ND	ND	148	99
Sulfates		500	152	ND	ND	ND	ND	41	35
Cadmium		0	$6x10^{-3}$	< DL	ND	< DL	< DL	< DL	< DL
Zinc		3	12.2	8.5	2.24	5.4	6.51	0.33	0.8
Copper		1	0.15	0.14	0.18	0.104	0.14	0.1	0.15
Chromium		0.1	0.6	0.62	0.52	0.23	0.56	0.391	0.32
Iron		5	4.74	4.1	59.62	1.22	2.73	0.02	1.54
Nickel		0.2	1.52	1.3	0.57	1.2	1.25	0.02	0.55
Lead		5	5.84	2.9	0.5	0.7	1	0.27	0.67
Total residual chlorine		<1.0	>3	ND	0.49	ND	ND	>3	>3
Nitrates		5	13.2	ND	ND	ND	ND	5.3	9.15
TOC		NR	81.5	73	ND	51.5	59	38.1	20.3
Total coliforms	CFU/ 100mL	NR	$4.3x10^4$	$1.2x10^3$	ND	ND	ND	200	100

Table 3. Physical characteristics of Lolium perenne crop after 8 weeks of irrigation with different treated water sources.

Physical characteristic	Tap water	Staining industry effluents treated by Photo-Fenton 2	Industrial area effluents treated by UV-Vis/H_2O_2/TiO_2
Leaf length (cm)	20.0	22.0	19.7
Leaf width (cm)	0.10	0.09	0.14
Root length (cm)	2.00	2.70	4.30

the biological and physiological functions of crops. These metals in excess can produce several diseases such as: chlorosis, growth inhibition, browning of the roots; besides, can affect the photosynthesis procedure, absorption and transport of several nutrients, and finally the death of the plant [61]. However, in the present work, necrosis was observed only in the water coming from the industrial area treated by UV-Vis/H_2O_2/TiO_2.

Considering that *Lolium perenne* is mainly used for animal feed, the residual content of heavy metals in the treated wastewater is a limiting factor for this water recycling. The metal contents in the grass blade and in the cultivation soil are reported in Table 4. As it was reported in Table 1 and 2, after the treatments it was not possible to achieve the total elimination of the metals analyzed, but in different metals and other quality control parameters it was possible to comply with the national regulations for wastewater recycling in crop irrigation.

Figure 3: *Lolium perenne* crop irrigated with colored industrial wastewater treated with Photo-Fenton 2. The recovery color is visible after 3 days of irrigation.

Table 4. Physicochemical analysis of Lolium perenne leaves and cultivation soil after 8 weeks of irrigation with different treated water sources.

Substrate analyzed	Metal				pH		
		Tap water	Staining of industrial effluents treated by Photo-Fenton 2/H_2O_2	Industrial wastewater treated by UV-Vis/H_2O_2/TiO_2	Tap water	Staining of industrial effluents treated by Photo-Fenton (2)	Industrial wastewater treated by UV-Vis/H_2O_2/TiO_2
Leaf	Cd	0.040	0.034	0.040	ND		
	Cr	0.57	0.54	0.55			
	Cu	0.00	0.40	0.22			
	Fe	14.40	43.5	17.50			
	Zn	2.92	2.24	2.64			
Soil	Cd	0.08	0.08	0.060	7.23	6.30	6.20
	Cr	1.12	1.00	0.91			
	Cu	0.98	1.07	0.23			
	Fe	50.0	50.30	50.13			
	Zn	6.20	3.41	3.45			

Considering the results obtained from the previous table, a comparison was proposed with any regulation that specifies the permissible level of heavy metals in animal feed. However, the only regulation that provides this information is the European Union Regulation (EC) No. 1881/2006 [62]. This regulation specifically mentions metals such as Cd, Pb, As and Hg. In particular, it states that the maximum permissible level of Cd in meat for human consumption is 0.05 ppm. Based on the results of this study, we are approaching that threshold.

Given the research focus on irrigation of pastures with reclaimed water intended for animal consumption, particularly for milk and meat production, the results of this study were compared with analyses from Russia. In these Russian studies, post-irrigation results using untreated water showed concentrations of 6.3 ppm for Zn, 0.30 ppm for Cd, and 1.40 ppm for Cu [63]. Based on these metrics, it was determined that such concentrations can be considered toxic because of their multiple effects on human and animal health through the intricacies of the food chain.

4 Conclusions

The AOTs applied to industrial wastewater treatment have been effective in eliminating various pollutants and bacteria, resulting in compliance with many of the parameters required by government regulations for recycling treated wastewater in crop irrigation. Conventional Photo-Fenton by using iron sulfate and hydrogen peroxide under UV-Vis radiation, present some disadvantages related to the number of chemical compounds that is necessary to employ in the process. However, by using an alternative iron source such as commercial iron wool, it has been possible to overcome these disadvantages in the treatment of industrial wastewater.

Photo-Fenton (with iron wool) and the combination of UV-Vis/ H_2O_2 /TiO_2 were the best performers in the treatment of industrial wastewater from the textile industry and industrial park activities, respectively.

The use of industrial Wastewater treated with UV-Vis/H_2O_2/TiO_2 for the irrigation of Lolium perenne crop induces tissue necrosis, leading to the death of the plant.

The excess of iron content in the water coming from textile industry effluents after Photo-Fenton treatment contributes significantly to the defense mechanism of the Lolium Perenne crop, thus recovering the coloration and vitality of the plant after continuous irrigation. In addition, this treatment represents an ecological and low-cost alternative for the recovery and recycling of Wastewater, avoiding the use of chemical compounds.

Acknowledgements

This work was funded by the Ministerio de Ciencia, Tecnología e Innovación - Minciencias, Ministerio de Salud y Protección Social, Project 110991891727 and the Universidad Pedagógica y Tecnológica de Colombia (UPTC) Project SGI 3393 and SGI 3502.

Ethical implications

This study complied with national and international regulations and was approved by the Dexa Diab Research Ethics Committee. Being a risk-free study by Resolution 8430 of 1993, was exempted from informed consent by the Ethics Committee, however, all patients evaluated by the clinical team signed their respective consent informed authorizing the procedure.

Authors contribution statement

The authors confirm contribution to the paper as follows: study conception and design: Paola Tatiana Valencia Carrasquilla, Jhon Sebastián Hernández, Mariana Alejandra Gil Agudelo, Julie Joseane Murcia Mesa; data collection: Paola Tatiana Valencia Carrasquilla and Mariana Alejandra Gil Agudelo; analysis and interpretation of results: Paola Tatiana Valencia Carrasquilla, Jhon Sebastián Hernández, Mariana Alejandra Gil Agudelo; draft manuscript preparation: Paola Tatiana Valencia Carrasquilla, Jhon Sebastián Hernández, Mariana Alejandra Gil Agudelo, Julie Joseane Murcia Mesa. All authors reviewed the results and approved the final version of the manuscript.

Declaration of source of founds

This work was funded by the Ministerio de Ciencia, Tecnología e Innovación - Minciencias, Ministerio de Salud y Protección Social, Project 110991891727 and the Universidad Pedagógica y Tecnológica de Colombia (UPTC) Project SGI 3393 and SGI 3502. This research did not receive any specific grant from funding agencies in the public, commercial, or nonprofit sectors. Conflicts of interest The authors declare that there is no conflict of interest regarding the publication. of this article.

Conflicts of interest

The authors declare that there is no conflict of interest regarding the publication. of this article

References

[1] N. Bougdour, R. Tiskatine, I. Bakas, and A. Assabbane, "Textile Wastewater Treatment by Peroxydisulfate/Fe(II)/UV: Operating Cost Evaluation and Phytotoxicity Studies," Chem. Africa, vol. 3, no. 1, pp. 153–160, 2020, doi: 10.1007/s42250-019-00094-7.

[2] L. Villalobos and J. M. Sánchez, "Agronomic and nutritional evaluation of perennial tetraploid ryegrass-based pastures (Lolium perenne) in dairy farms on the highlands of Costa Rica. II. Nutritional value.," Agron. Costarric., vol. 34, no. 1, pp. 43–52, 2010.

[3] S. Khalid et al., "A Review of Environmental Contamination and Health Risk Assessment of Wastewater Use for Crop Irrigation with a Focus on Low and High-Income Countries," International Journal of Environmental Research and Public Health, vol. 15, no. 5. 2018. doi: 10.3390/ijerph15050895.

[4] S. G. Cetinkaya, M. H. Morcali, S. Akarsu, C. A. Ziba, and M. Dolaz, "Comparison of classic Fenton with ultrasound Fenton processes on industrial textile wastewater," Sustain. Environ. Res., vol. 28, no. 4, pp. 165–170, 2018, doi: https://doi.org/10.1016/j.serj.2018.02.001.

[5] G. Gopalakrishnan, R. B. Jeyakumar, and A. Somanathan, "Challenges and Emerging Trends in Advanced Oxidation Technologies and Integration of Advanced Oxidation Processes with Biological Processes for Wastewater Treatment," Sustainability, vol. 15, no. 5. 2023. doi: 10.3390/su15054235.

[6] M. Bansal, "Textile Wastewater Treatment Using Sustainable Technologies: Advanced Oxidation and Degradation Using Metal Ions and Polymeric Materials BT - Advanced Oxidation Processes in Dye-Containing Wastewater: Volume 1," S. S. Muthu and A. Khadir, Eds., Singapore: Springer Nature Singapore, 2022, pp. 189–217.

[7] A. R. Lado Ribeiro, N. F. F. Moreira, G. Li Puma, and A. M. T. Silva, "Impact of water matrix on the removal of micropollutants by advanced oxidation technologies," Chem. Eng. J., vol. 363, pp. 155–173, 2019, doi: https://doi.org/10.1016/j.cej.2019.01.080

[8] R. Kavitha, P. M. Nithya, and S. Girish Kumar, "Noble metal deposited graphitic carbon nitride based heterojunction photocatalysts," Appl. Surf. Sci., vol. 508, p. 145142, 2020, doi: https://doi.org/10.1016/j.apsusc.2019.145142.

[9] F. R. Lima, P. de Souza Costa Sobrinho, L. de Oliveira Ferreira Rocha, and P. Mendes de Souza, "Modeling of Listeria innocua, Escherichia coli, and Salmonella Enteritidis inactivation in milk treated by gamma irradiation," Brazilian J. Microbiol., vol. 54, no. 2, pp. 1047–1054, 2023, doi: 10.1007/s42770-023-00931-5.

[10] S. Bolisetty, M. Peydayesh, and R. Mezzenga, "Sustainable technologies for water purification from heavy metals: review and analysis," Chem. Soc. Rev., vol. 48, no. 2, pp. 463–487, 2019, doi: 10.1039/C8CS00493E.

[11] E. M. P. Cardoso, "Lymphocytes in the liver and hepatic iron toxicity: human and animal models of iron overload," 2000.

[12] P. B. Ramos, P. Vitale, G. P. Barreto, F. Aparicio, M. de los Á. Dublan, and G. N. Eyler, "Treatment of real non-biodegradable wastewater: Feasibility analysis of a zero-valent iron/H2O2 process," J. Environ. Chem. Eng., vol. 8, no. 4, p. 103954, 2020, doi: https://doi.org/10.1016/j.jece.2020.103954.

[13] C. A. Martínez-Huitle and E. Brillas, "Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review," Appl. Catal. B Environ., vol. 87, no. 3, pp. 105–145, 2009, doi: https://doi.org/10.1016/j.apcatb.2008.09.017.

[14] H. A. Casierra-Martinez, C. A. Madera-Parra, X. M. Vargas-Ramírez, A. Caselles-Osorio, and W. A. Torres-López, "Diclofenac and carbamazepine removal from domestic wastewater using a Constructed Wetland-Solar Photo-Fenton coupled system," Ecol. Eng., vol. 153, p. 105699, 2020, doi: https://doi.org/10.1016/j.ecoleng.2019.105699.

[15] F. Hosseini, A. A. Assadi, P. Nguyen-Tri, I. Ali, and S. Rtimi, "Titanium-based photocatalytic coatings for bacterial disinfection: The shift from suspended powders to catalytic interfaces," Surfaces and Interfaces, vol. 32, p. 102078, 2022, doi: https://doi.org/10.1016/j.surfin.2022.102078.

[16] D. Chen et al., "Photocatalytic degradation of organic pollutants using TiO2-based photocatalysts: A review," J. Clean. Prod., vol. 268, p. 121725, 2020, doi: https://doi.org/10.1016/j.jclepro.2020.121725.

[17] G. Ren et al., "Recent Advances of Photocatalytic Application in Water Treatment: A Review," Nanomaterials, vol. 11, no. 7. 2021. doi: 10.3390/nano11071804.

[18] L. Lin, W. Jiang, L. Chen, P. Xu, and H. Wang, "Treatment of Produced Water with Photocatalysis: Recent Advances, Affecting Factors and Future Research Prospects," Catalysts, vol. 10, no. 8. 2020. doi: 10.3390/catal10080924.

[19] E. Baird, Rodger; Eaton, Andrew; Rice, "Standart Methods for the examination of water and wastewater.," 2017.

[20] Digilife, "pH + chlorine tester for swimming pool & spa." [Online]. Available: http://digilifeweb.com/PH-Chlorine-Tester

[21] HACH, "Nitrate, cadmium reduction method," 2018, pp. 1–8.

[22] HACH, "USEPA SulfaVer 4 method." [Online]. Available: https://co.hach.com/sulfaver-4-sulfate-reagent-powder-pillows-25-ml-pk-1000/product?id=53559618642

[23] M. Jiménez-Tototzintle, I. Oller, A. Hernández-Ramírez, S. Malato, and M. I. Maldonado, "Remediation of agro-food industry effluents by biotreatment combined with supported TiO2/H2O2 solar photocatalysis," Chem. Eng. J., vol. 273, pp. 205–213, 2015, doi: https://doi.org/10.1016/j.cej.2015.03.060.

[24] J. R. H. Murcia, Julie; Rojas, Wilson; Cubillos, "Planta para el tratamiento de aguas residuales con función dual floculación y fotocatálisis." [Online]. Available: http://www.uptc.edu.co/facultades/f_ciencias/pregrado/quimica/inf_adicional/investigacion/gc/patents

[25] E. Hyánková, M. Kriška Dunajský, O. Zedník, O. Chaloupka, and M. Pumprlová Němcová, "Irrigation with Treated Wastewater as an Alternative Nutrient Source (for Crop): Numerical Simulation," Agriculture, vol. 11, no. 10. 2021. doi: 10.3390/agriculture11100946.

[26] P. L. S. Florez, S. A. lves, P. L. Weinert, and E. R. L. Tiburtius, "Assessment of UV-Vis LED-assisted Photo-Fenton Reactor for Atrazine Degradation in Aqueous Solution," Orbital Electron. J. Chem., vol. 13, no. 2 SE-FULL PAPERS, Jun. 2021, [Online]. Available: https://periodicos.ufms.br/index.php/orbital/article/view/15624

[27] E. Vitzilaiou, A. M. Kuria, H. Siegumfeldt, M. A. Rasmussen, and S. Knøchel, "The impact of bacterial cell aggregation on UV inactivation kinetics," Water Res., vol. 204, p. 117593, 2021, doi: https://doi.org/10.1016/j.watres.2021.117593.

[28] T. Triquet, C. Tendero, L. Latapie, M.-H. Manero, R. Richard, and C. Andriantsiferana, "TiO2 MOCVD coating for photocatalytic degradation of ciprofloxacin using 365 nm UV LEDs - kinetics and mechanisms," J. Environ. Chem. Eng., vol. 8, no. 6, p. 104544, 2020, doi: https://doi.org/10.1016/j.jece.2020.104544.

[29] M. A. Gil, J. J. Murcia, M. Hernández-Laverde, N. Morante, D. Sannino, and V. Vaiano, "Ag/Cr-TiO2 and Pd/Cr-TiO2 for Organic Dyes Elimination and Treatment of Polluted River Water in Presence of Visible Light," Nanomaterials, vol. 13, no. 16. 2023. doi: 10.3390/nano13162341.

[30] R. Alexpandi et al., "Tocopherol-assisted magnetic Ag-Fe3O4-TiO2 nanocomposite for photocatalytic bacterial-inactivation with elucidation of mechanism and its hazardous level assessment with zebrafish model," J. Hazard. Mater., vol. 442, p. 130044, 2023, doi: https://doi.org/10.1016/j.jhazmat.2022.130044.

[31] A. Shoneye, J. Sen Chang, M. N. Chong, and J. Tang, "Recent progress in photocatalytic degradation of chlorinated phenols and reduction of heavy metal ions in water by TiO2-based catalysts," Int. Mater. Rev., vol. 67, no. 1, pp. 47–64, Jan. 2022, doi: 10.1080/09506608.2021.1891368.

[32] A. Kakoria, S. Sinha-Ray, and S. Sinha-Ray, "Industrially scalable Chitosan/Nylon-6 (CS/N) nanofiber-based reusable adsorbent for efficient removal of heavy metal from water," Polymer (Guildf)., vol. 213, p. 123333, 2021, doi: https://doi.org/10.1016/j.polymer.2020.123333.

[33] B. Yang et al., "Dye mineralization under UV/H2O2 promoted by chloride ion at high concentration and the generation of chlorinated byproducts," Sci. Total Environ., vol. 857, 2023, doi: 10.1016/j.scitotenv.2022.159453.

[34] M. Iqbal et al., "Using Combined UV and H2O2 Treatments to Reduce Tannery Wastewater Pollution Load," Polish J. Environ. Stud., vol. 28, no. 5, pp. 3207–3213, 2019, doi: 10.15244/pjoes/92706.

[35] K. Tian, L. Hu, L. Li, Q. Zheng, Y. Xin, and G. Zhang, "Recent advances in persulfate-based advanced oxidation processes for organic wastewater treatment," Chinese Chem. Lett., vol. 33, no. 10, pp. 4461–4477, 2022, doi: https://doi.org/10.1016/j.cclet.2021.12.042.

[36] R. P. Cavalcante, J. A. Malvestiti, J. P. D. Júnior, and R. F. Dantas, "Modeling carbonate/bicarbonate and nitrate disturbance during secondary effluent disinfection by UV/H2O2 and UV/ozone," Water Sci. Technol., vol. 86, no. 11, pp. 2943–2962, Nov. 2022, doi: 10.2166/wst.2022.376.

[37] C. Pironti et al., "Comparative analysis of peracetic acid (PAA) and permaleic acid (PMA) in disinfection processes," Sci. Total Environ., vol. 797, p. 149206, 2021, doi: https://doi.org/10.1016/j.scitotenv.2021.149206.

[38] Y. Xiang, M. Gonsior, P. Schmitt-Kopplin, and C. Shang, "Influence of the UV/H2O2 Advanced Oxidation Process on Dissolved Organic Matter and the Connection between Elemental Composition and Disinfection Byproduct Formation," Environ. Sci. Technol., vol. 54, no. 23, pp. 14964–14973, Dec. 2020, doi: 10.1021/acs.est.0c03220.

[39] N. A. Mohamad et al., "Copperas as Iron-Based Coagulant for Water and Wastewater Treatment: A Review," Biointerface Res. Appl. Chem., vol. 12, pp. 4155–4176, Jun. 2022, doi: 10.33263/BRIAC123.41554176.

[40] A. Eslami et al., "Periodate activation by concurrent utilization of UV and US for the degradation of para-nitrophenol in water: A synergistic approach," Korean J. Chem. Eng., vol. 40, no. 4, pp. 882–891, 2023, doi: 10.1007/s11814-022-1247-4.

[41] I. T. Tomasi, C. A. Machado, R. A. R. Boaventura, C. M. S. Botelho, and S. C. R. Santos, "Tannin-based coagulants: Current development and prospects on synthesis and uses," Sci. Total Environ., vol. 822, p. 153454, 2022, doi: https://doi.org/10.1016/j.scitotenv.2022.153454.

[42] B. Lange, M. Strathmann, and R. Oßmer, "Performance validation of chromogenic coliform agar for the enumeration of Escherichia coli and coliform bacteria," Lett. Appl. Microbiol., vol. 57, no. 6, pp. 547–553, Dec. 2013, doi: https://doi.org/10.1111/lam.12147.

[43] A. Sadique et al., "Dynamics, Diversity, and Virulence of Aeromonas spp. in Homestead Pond Water in Coastal Bangladesh," Frontiers in Public Health , vol. 9. 2021. [Online]. Available: https://www.frontiersin.org/articles/10.3389/fpubh.2021.692166

[44] M. Ashrafivala, S. B. Mousavi, S. Zeinali Heris, M. Heidari, M. Mohammadpourfard, and H. Aslani, "Investigation of H2O2/UV advanced oxidation process on the removal rate of coliforms from the industrial effluent: A pilot-scale study," Int. J. Hydrogen Energy, vol. 47, no. 78, pp. 33530–33540, 2022, doi: https://doi.org/10.1016/j.ijhydene.2022.07.231.

[45] H. Ghazzaf, B. Nechchadi, A. Jouali, A. Salhi, M. El Krati, and S. Tahiri, "Synthesis of heterogeneous photo-Fenton catalyst from iron rust and its application to degradation of Acid Red 97 in aqueous medium," J. Environ. Chem. Eng., vol. 10, no. 3, p. 107570, 2022, doi: https://doi.org/10.1016/j.jece.2022.107570.

[46] S. Guo, W. Yang, L. You, J. Li, J. Chen, and K. Zhou, "Simultaneous reduction of Cr(VI) and degradation of tetracycline hydrochloride by a novel iron-modified rectorite composite through heterogeneous photo-Fenton processes," Chem. Eng. J., vol. 393, p. 124758, 2020, doi: https://doi.org/10.1016/j.cej.2020.124758.

[47] H. S. Dossary, F. I. Alghunaimi, and Y. C. Choi, "Produced Water Reuse for Drilling and Completion Fluids Using Ion Exchange Resins," Abu Dhabi International Petroleum Exhibition & Conference. p. D011S007R003, Nov. 15, 2021. doi: 10.2118/207543-MS.

[48] E. Ortega-Gómez, M. M. B. Martín, B. E. García, J. A. S. Pérez, and P. F. Ibáñez, "Wastewater disinfection by neutral pH photo-Fenton: The role of solar radiation intensity," Appl. Catal. B Environ., vol. 181, pp. 1–6, 2016, doi: https://doi.org/10.1016/j.apcatb.2015.06.059.

[49] Ö. Tuna and E. B. Simsek, "Enhanced visible-light-assisted peroxymonosulfate activation of low-cost perovskite CaFe2O4 for tartrazine degradation: Experimental design modelling," Mater. Res. Bull., vol. 159, p. 112090, 2023, doi: https://doi.org/10.1016/j.materresbull.2022.112090.

[50] M. Tariq et al., "Removal of Rhodamine B dye from aqueous solutions using photo-Fenton processes and novel Ni-Cu@MWCNTs photocatalyst," J. Mol. Liq., vol. 312, p. 113399, 2020, doi: https://doi.org/10.1016/j.molliq.2020.113399.

[51] A. H. Jagaba et al., "Effect of Environmental and Operational Parameters on Sequential Batch Reactor Systems in Dye Degradation BT - Dye Biodegradation, Mechanisms and Techniques: Recent Advances," S. S. Muthu and A. Khadir, Eds., Singapore: Springer Singapore, 2022, pp. 193–225.

[52] J. Tejera, R. Miranda, D. Hermosilla, I. Urra, C. Negro, and Á. Blanco, "Treatment of a Mature Landfill Leachate: Comparison between Homogeneous and Heterogeneous Photo-Fenton with Different Pretreatments," Water, vol. 11, no. 9. 2019. doi: 10.3390/w11091849.

[53] B. Yang, P. Zhou, X. Cheng, H. Li, X. Huo, and Y. Zhang, "Simultaneous removal of methylene blue and total dissolved copper in zero-valent iron/H2O2 Fenton system: Kinetics, mechanism and degradation pathway," J. Colloid Interface Sci., vol. 555, pp. 383–393, 2019, doi: https://doi.org/10.1016/j.jcis.2019.07.071.

[54] V. Manikandan et al., "Influence of CoOx surface passivation and Sn/Zr-co-doping on the photocatalytic activity of Fe2O3 nanorod photocatalysts for bacterial inactivation and photo-Fenton degradation," Chemosphere, vol. 337, p. 139255, 2023, doi: https://doi.org/10.1016/j.chemosphere.2023.139255.

[55] J. Suave, H. J. José, and R. de F. P. M. Moreira, "Photocatalytic degradation of polyvinylpyrrolidone in aqueous solution using TiO2/H2O2/UV system," Environ. Technol., vol. 39, no. 11, pp. 1404–1412, Jun. 2018, doi: 10.1080/09593330.2017.1330365.

[56] R. B. Aranciaga Pajuelo, J. P. Vargas Lopez, C. Castaneda Olivera, J. L. Jave Nakayo, E. G. Benites Alfaro, and C. F. Cabrera Carranza, "Inactivation of Antibiotic Resistant Bacteria in Hospital Wastewater by Tio2/h2o2 Photocatalysis," Chem. Eng. Trans., vol. 86, pp. 853-858 SE-Research Articles, Jun. 2021, doi: 10.3303/CET2186143.

[57] N. Nurnaeimah et al., "The Effects of Hydrogen Peroxide on Plant Growth, Mineral Accumulation, as Well as Biological and Chemical Properties of Ficus deltoidea," Agronomy, vol. 10, no. 4. 2020. doi: 10.3390/agronomy10040599.

[58] D. Li, F. Chen, and J. Han, "A study of the treatment of high-salt chromium-containing wastewater by the photocatalysis-constructed wetland combination method," Water Sci. Technol., vol. 80, no. 10, pp. 1956–1966, Jan. 2020, doi: 10.2166/wst.2020.017.

[59] S. Sharma et al., "Foliar application of organic and inorganic iron formulation induces differential detoxification response to improve growth and biofortification in soybean," Plant Physiol. Reports, vol. 24, no. 1, pp. 119–128, 2019, doi: 10.1007/s40502-018-0412-6.

[60] D. K. Tripathi et al., "Acquisition and Homeostasis of Iron in Higher Plants and Their Probable Role in Abiotic Stress Tolerance ," Frontiers in Environmental Science , vol. 5. 2018. [Online]. Available: https://www.frontiersin.org/articles/10.3389/fenvs.2017.00086

[61] D. Goyal et al., "Effect of Heavy Metals on Plant Growth: An Overview BT - Contaminants in Agriculture: Sources, Impacts and Management," M. Naeem, A. A. Ansari, and S. S. Gill, Eds., Cham: Springer International Publishing, 2020, pp. 79–101.

[62] I. Barrientos, I. Chamorro, C. Zambrano, M. Pérez, N. González, and A. K. Carrascal, "Presencia de metales pesados y calidad microbiológica de concentrados para la alimentación porcina en cuatroregiones colombianas ," Revista de Investigaciones Veterinarias del Perú , vol. 29. scielo , pp. 774–781, 2018.

[63] N. Kuramshina et al., "Heavy metals content in meat and milk of Orenburg region of Russia.," Int. J. Pharm. Res., vol. 11, no. 1, pp. 1031–1035, Jan. 2019, [Online]. Available: https://login.biblio.uptc.edu.co/login?url=https://search.ebscohost.com/login.aspx?direct=true&db=asn&AN=139070103&lang=es&site=ehost-live&scope=site