

Review

The Grey–Taguchi Method, a Statistical Tool to Optimize the Photo-Fenton Process: A Review

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Abstract: Currently there is a growing concern about the presence of emerging contaminants (EC) in water bodies and their potential ecotoxicological effects. Pharmaceuticals, a type of EC, are widely distributed in the environment and their main entry is through wastewater from treatment plants, since these systems are not designed to remove EC. In this sense, the photo-Fenton process, an advanced oxidation process, has proven to be highly efficient in degrading new potentially harmful contaminants. However, this process is affected by multiple factors, which makes it necessary to implement a methodological strategy to optimize the photo-Fenton process. Within these, the Taguchi method provides robust and low-cost solutions with the least number of experiments, providing knowledge of the contribution of each of the factors studied to the response variable. In addition to the above, the Taguchi method can be coupled to a Grey relational analysis (Grey–Taguchi method), which will allow the optimization of more than one response variable at the same time. This paper discusses the parameters that affect the photo-Fenton process and the application of designs of experiments to optimize the process.

Keywords: advanced oxidation processes; emerging contaminants; Grey–Taguchi method; photo-Fenton; parameter optimization



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1. Introduction

Medications are allies of health, as they treat symptoms and diseases. Probably, in the current situation of the pandemic, we are more aware of their importance in everyday life. A drug is a chemically defined substance capable of modifying cellular activity in the body and therefore produces a biological, beneficial, or toxic effect depending on the dose supplied [1]. The traditional evaluation of the risks associated with the use of medications includes adverse effects after ingestion or application. However, it is not considered that, after use, the drug (in its unchanged form) and its degradation products (metabolites) end up in sewage networks and finally in wastewater treatment plants (WWTP). The latter end up incorporating these pollutants into the environment. The excretion of the non-metabolized active ingredient depends on the composition of the drug, the physical-chemical properties, and the idiosyncratic conditions of each individual to metabolize the active ingredient, which depends on age, sex, and health [1–3]. It is also important to consider topical medications whose excesses are removed from the body during bathing and go directly to wastewater.

In the case of drugs for veterinary use, the direct excretion of these substances produces soil contamination. Subsequently, the drugs and their metabolites are transported through the soil profile, until they reach the groundwater [4]. On the other hand, the poor disposal of expired drugs is another way in which they reach wastewater [5]. Of equal importance are hospital wastewater and those from the pharmaceutical industry since in the end, these waters reach municipal wastewater [6,7].

Due to the low removal efficiency of conventional wastewater treatment processes, drugs can have severe negative impacts on aquatic ecology, such as microbial resistance, disruption of the endocrine systems of aquatic organisms, and bioaccumulation in plants and animals [8–10]. These pollutants of pharmaceutical origin are globally known as emerging contaminants (EC), not necessarily because their presence in the environment is new, but because of their environmental interest. The EC list includes a wide variety of personal care products (shampoos, detergents, fragrances, creams, and protectors, among others), with the study of drugs in the environment being the most important. Pharmaceutical compounds in water bodies affect water quality by affecting drinking water supply, human health, and the ecosystem [10]. One of the main concerns arising from the presence of antibiotics in bodies of water is the appearance of resistance genes in bacteria [8]. In this sense, by 2050, 10 million deaths attributable to antibiotic resistance are expected, this being the main cause of death, surpassing oncological diseases [11].

The most investigated pharmacological groups in WWTP are analgesics and non-steroidal anti-inflammatory drugs, and antibiotics, followed by beta-blockers and antiepileptics, which represent up to 80% of the study frequency [12–14]. However, in recent years Ramírez-Morales et al. [14], determined the coefficient of danger associated with drugs. This indicator allows estimating which are the most dangerous compounds from an environmental point of view.

To degrade and remove EC residues, biological processes (activated sludge, trickling filters, aerobic and anaerobic bioreactors, membrane bioreactors, and artificial wetlands, among others) have been investigated due to their low cost, availability, and environmental friendliness [15–18]. However, these biological treatment processes lack effective removal of some non-biodegradable EC [19,20]. In this sense, advanced oxidation processes (AOP) are attractive options to remove persistent compounds such as pesticides and pharmaceutical products contained in wastewater [21,22]. These processes are characterized by the production of hydroxyl radicals ($\cdot OH$), which is a powerful non-selective oxidant (2.8 V vs. the standard hydrogen electrode, SHE) capable of oxidizing and mineralizing almost any organic molecule, producing CO_2 and inorganic anions [23,24]. Within AOP, the Fenton process involves the addition of iron (catalyst) and hydrogen peroxide for the generation of the hydroxyl radical. An improvement to this process involves the use of UV light in conjunction with hydrogen peroxide and iron salts to make the EC degradation process more efficient. In addition, the possibility of using sunlight in the photo-Fenton process implies an improvement in the process and environmental sustainability [19,25,26].

Various factors are involved in the removal of drugs by the photo-Fenton process: pH, the concentration of catalyst and hydrogen peroxide, temperature, reaction time, light intensity, and contaminant concentration, mainly. This makes it necessary to implement strategies to optimize the efficiency of the photo-Fenton process. In this sense, the design of experiments (DOE) has gained great interest, since it is a statistical tool that allows evaluating the simultaneous effect of more than one independent variable (factors) on one or more response variables. The DOE that have been most applied to the optimization of the photo-Fenton process are those based on a response surface (composite central design and Box-Behnken) [27–29]. However, this type of optimization technique is not appropriate when it is desired to evaluate the influence of more than four factors on the performance of a process, as is the case of the photo-Fenton process, since it considerably increases the number of experimental runs.

The Taguchi design is a multiparameter optimization technique that with a reduced number of experiments allows the optimization of a process, reducing costs [30]. In addition, the contribution of each factor to the performance of the process can be estimated [30,31]. The Taguchi design has been successfully applied in the optimization of the Fenton process (or Fenton-like) with a single response variable; being the removal of chemical oxygen demand, total organic carbon, or decrease in absorbance (in colored compounds) the objective parameters [27,32,33]. However, another variable to optimize (minimize) is the generation of sludge, a product of the application of iron in Fenton-like processes. Therefore, when

it is necessary to evaluate more than one response variable of the system (multi-objective optimization), it is possible to couple the Taguchi design to a Grey relational analysis (Grey–Taguchi method) (Figure 1). The Grey System Theory allows the solving of complicated interrelationships between multiple performance characteristics in an effective way. This allows the conversion of the optimization of multiple and complicated performance characteristics into a single variable (grey relational degree) [34,35]. This method emerged at the end of the 1980s and since then its application in various areas has grown almost exponentially (Figure 2A). Although the Grey–Taguchi method has been successfully applied in other areas (especially those related to manufacturing, Figure 2B) [36–39], its application in AOP optimization is limited. To our best knowledge, to date, there is no application of the Grey–Taguchi method to the optimization of the photo-Fenton process.

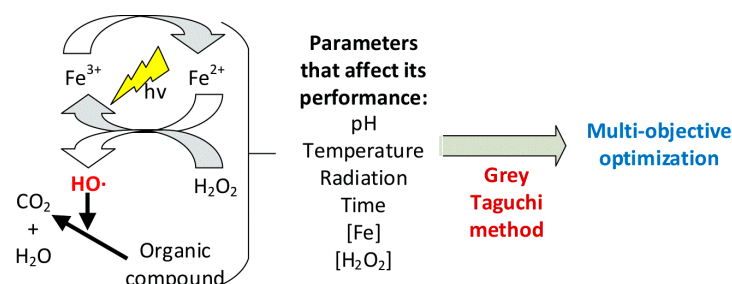


Figure 1. Gray-Taguchi method as a tool to optimize the photo-Fenton process in more than one response variable.

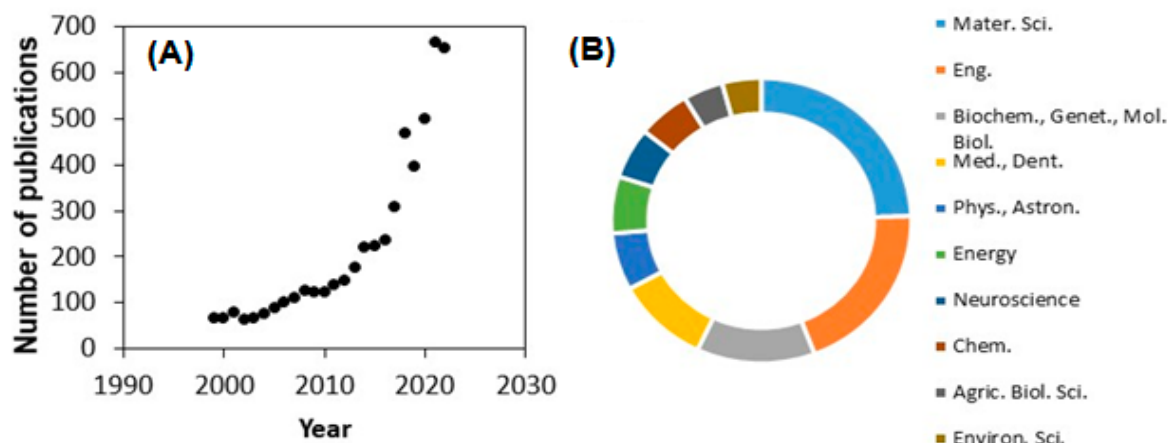


Figure 2. Evolution of the number of publications associated with the Grey–Taguchi method (A) and its application in each thematic area (B). The data were obtained from the period between 1999 and 2022 (<https://www.sciencedirect.com>; accessed on 8 November 2022). Mater. Sci. = Materials Science; Eng. = Engineering; Biochem., Genet., Mol. Biol. = Biochemistry, Genetics, and Molecular Biology; Med., Dent. = Medicine and Dentistry; Phys., Astron. = Physics and Astronomy; Energy = Energy; Neuroscience = Neuroscience; Chem. = Chemistry; Agric. Biol. Sci. = Agricultural and Biological Sciences; Environ. Sci. = Environmental Science.

In this review, the different methodological approaches that have been used for the optimization of this process are addressed, emphasizing the Grey–Taguchi method, as a useful novel tool for multi-objective optimization.

2. Advanced Oxidation Processes

AOP are based on the in situ generation of strong oxidants for the oxidation of organic compounds. This definition not only includes processes based on hydroxyl radicals ($\cdot OH$), the basis of most AOP but also processes based on other oxidizing species such as sulfate or chlorine radicals [40,41]. The $\cdot OH$ radical is the second most oxidizing chemical species, after fluorine (Table 1) this radical is a non-selective species and can oxidize complex mixtures of contaminants to their mineralization via hydroxylation or dehydrogenation [42]. Hydroxyl radicals are highly reactive species that attack most organic molecules with rate constants of the order of 10^6 – 10^9 L mol $^{-1}$ s $^{-1}$ [24]. Table 1 shows the standard reduction potentials for some oxidants generated in AOP.

Table 1. Standard reduction potential of some oxidants [43].

Redox Couple	Name	Reduction Reaction	E° (V vs. SHE)
F_2/F^-	Fluorine	$F_2(g) + 2H^+ + 2e^- \rightarrow 2HF$	3.05
$\cdot OH/H_2O$	Hydroxyl radical	$\cdot OH + H^+ + e^- \rightarrow H_2O$	2.81
$SO_4^{\cdot -}/SO_4^{2-}$	Sulfate radical	$SO_4^{\cdot -} + e^- \rightarrow SO_4^{2-}$	2.60
Fe^{6+}/Fe^{3+}	Ferrate	$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$	2.20
O_3/O_2	Ozone	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.08
$S_2O_8^{2-}/SO_4^{2-}$	Peroxodisulfate ion	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01
H_2O_2/H_2O	Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76
Mn^{7+}/Mn^{4+} (a)	Permanganate	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(s)} + 2H_2O$	1.67
$\cdot O_2H/H_2O$ (a)	Hydroperoxyl radical	$\cdot O_2H + 3H^+ + 3e^- \rightarrow 2H_2O$	1.65
Mn^{7+}/Mn^{2+} (b)	Permanganate	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51
$\cdot O_2H/H_2O_2$ (b)	Hydroperoxyl radical	$\cdot O_2H + H^+ + e^- \rightarrow H_2O_2$	1.44
$HClO/Cl^-$	Hypochlorous acid	$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.49
Cr^{6+}/Cr^{3+}	Dichromate	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.36
Cl_2/Cl^-	Chlorine	$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-$	1.36
Mn^{4+}/Mn^{2+}	Manganese dioxide	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.23
O_2/H_2O	Oxygen	$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
Br_2/Br^-	Bromine	$Br_{2(l)} + 2e^- \rightarrow 2Br^-$	1.06
ClO_2/ClO_2^-	Chlorite	$ClO_2 + e^- \rightarrow ClO_2^-$	0.95

Notes: (a) Weakly acidic or circumneutral medium; (b) Strongly acid medium.

Hydroxyl radicals are suitable within the group of strong oxidants since they have the following characteristics: (1) they do not generate additional residues; (2) they are non-toxic and have a very short shelf life; (3) They are not corrosive to equipment; and (4) They are usually produced using easy-to-handle assemblies [43]. AOP can be classified into two large groups: homogeneous and heterogeneous, distinguishing between those that operate with an external supply of energy and those that do not (Figure 3).

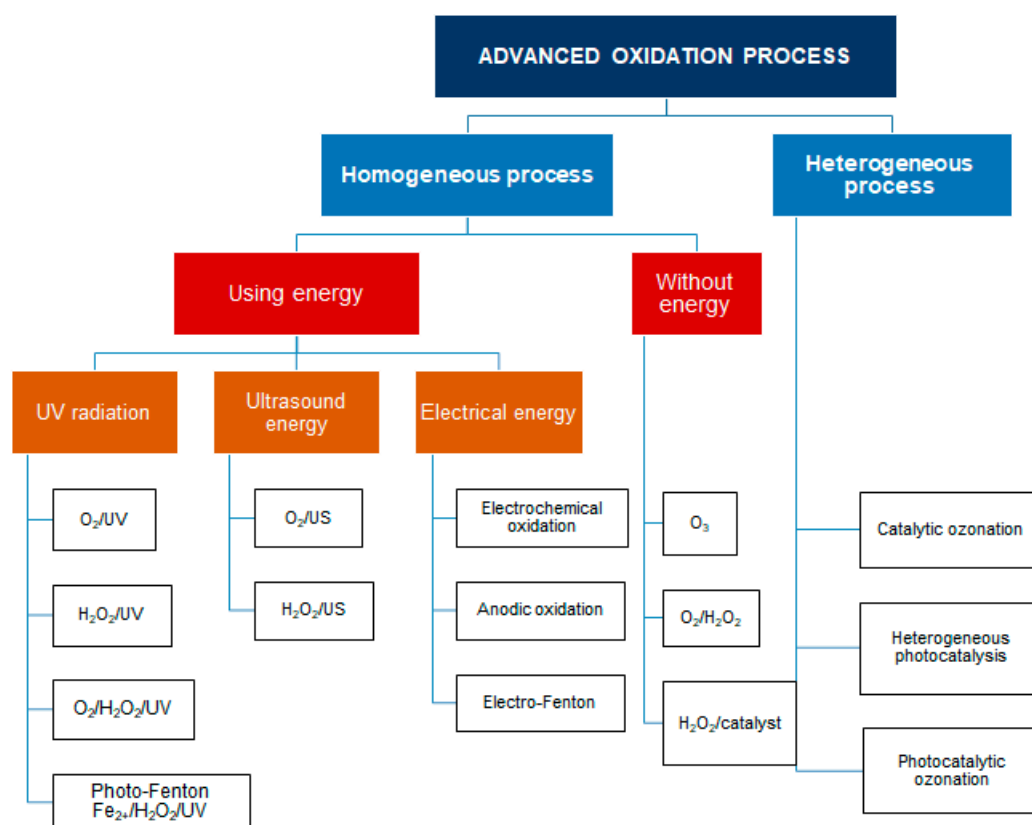


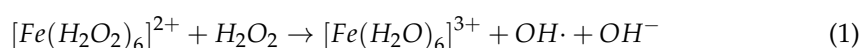
Figure 3. Classification of advanced oxidation processes [44].

Given the characteristics of the photo-Fenton process, it has become very important in recent years for the removal of emerging contaminants present in wastewater. In addition to its high efficiency and transformation rate of emerging pollutants, the photo-Fenton process can take advantage of natural sunlight, reducing the costs associated with its large-scale application [45].

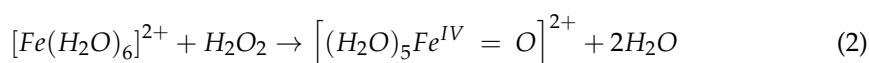
3. Fenton Process

The Fenton process was first described by H.J.H. Fenton in 1894, when he reported the decomposition of hydrogen peroxide (H_2O_2) by iron salts $[Fe(H_2O)_6]^{2+}$ in the oxidation of tartaric acid [46]. Although the Fenton reaction was discovered more than 120 years ago, it was not until the 1930s that its application to wastewater treatment became important, once its reaction mechanism was revealed.

In 1934, two mechanisms were proposed to describe the Fenton reaction. On the one hand, Haber and Weiss [47] proposed the following mechanism:

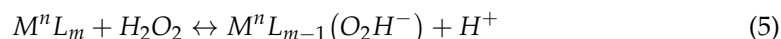
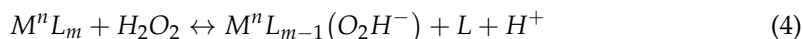
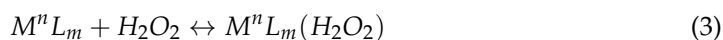


For this case, the authors suggest that $\cdot OH$ radicals are the intermediate oxidizing species formed. On the other hand, Bray and Gorin [48] proposed the following mechanism:

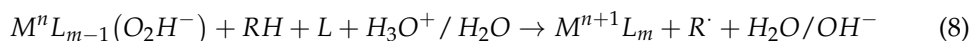
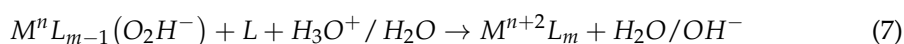
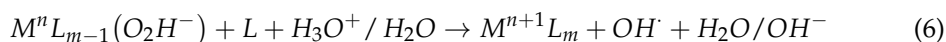


This last route refers to a high-valence intermediate $[(H_2O)_5Fe^{IV} = O]^{2+}$ as the oxidizing species. The debate about which of these mechanisms was correct lasted for decades, since both oxidizing species react in the same way with aliphatic compounds [49]. Despite this, at present, almost all studies assume that $\cdot OH$ radicals are the oxidizing species formed during the Fenton reaction (and Fenton-like reactions).

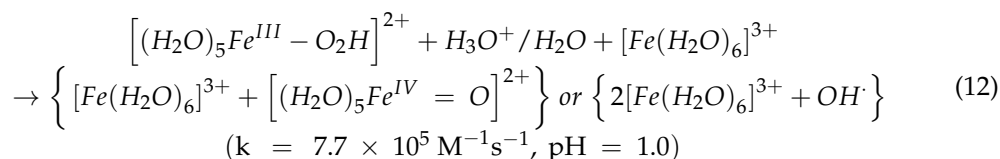
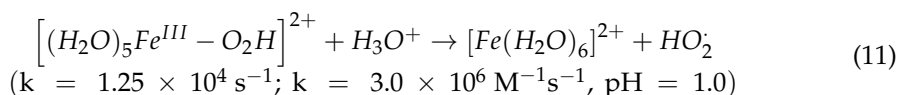
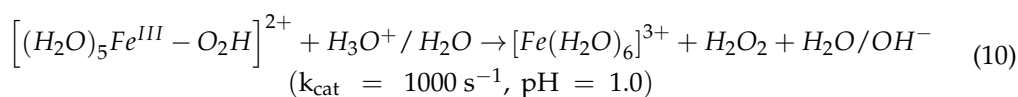
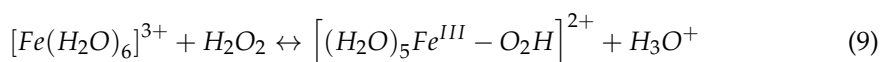
A thermodynamic analysis of Fenton and Fenton-like reactions, based on Marcus theory, suggests that an intermediate complex is formed [50,51], as shown below:



Assuming that $M^n L_{m-1} (O_2H^-)$ is the transient complex. It has been described that this species decomposes through reactions involving external ligands or organic species, as described below:



Considering the above, in the original Fenton reaction, when there is an excess of H_2O_2 in the system, the following reactions are carried out [52]:



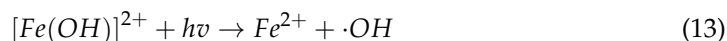
The above reactions show a clear dependence on pH. In addition, the product $[(H_2O)_5Fe^{IV} = O]^{2+}$ was later shown to form under catalytic conditions [52]. Subsequently, Bataneh et al. [53] demonstrated that the $\cdot OH$ radical predominates in acid solution, while the $[(H_2O)_5Fe^{IV} = O]^{2+}$ radical predominates in neutral solutions. However, Novikov et al. [54] found that $\cdot OH$ radicals are formed even when H_2O_2 reacts with redox-inactive metal ions such as $Al(III)$.

On the other hand, Patra et al. [55] found that, in many biological and environmental systems, with the presence of HCO_3^- (pH above 7.4), the mechanism of the Fenton reaction changes drastically. Therefore, under these conditions there is no formation of $[(H_2O)_5Fe^{IV} = O]^{2+}$, and instead, the active oxidant is the carbonate radical anion radical $CO_3^{\cdot -}$. Trials with citrate reached the same conclusion.

In general, the mechanism of the Fenton (and Fenton-like) reaction depends on many factors, such as the nature of the central cation, its ligands, the peroxide used, the pH , and the substrates present; therefore, it is not possible to generalize that all cases behave identically and that in all cases the $\cdot OH$ radical is the oxidizing species [25].

4. Photo-Fenton Process

The photo-Fenton process has aroused great interest in the removal of refractory organic contaminants (synthetic dyes [56,57], petrochemicals [58,59], and pharmaceuticals [60–63], among others) due to the low production of iron sludge. The photo-Fenton $Fe^{3+}/H_2O_2/UV$ -Vis process is an improvement to the Fenton reaction (40 times faster than the conventional process) [64,65] that uses the near-visible UV region, up to the wavelength of 600 nm [66], to improve the generation of reactive species with high oxidizing power and reduce Fe^{3+} to Fe^{2+} (Equations (13) and (14)). This implies that a lower amount of iron is used compared to the traditional process, since the iron is constantly reduced [67]. Furthermore, the reduction of Fe^{3+} to Fe^{2+} is accompanied by the formation of another hydroxyl radical, which results in H_2O_2 being completely converted into two radicals [67,68]. Both UV and visible light can be used, but a wavelength less than 310 nm will photolyze H_2O_2 (Equation (15)). In addition to the aforementioned advantages, as suggested by O'Dowd and Pillai [68], the photo-Fenton process shows better efficiencies in the removal of emerging contaminants compared to systems similar to Fenton, such as H_2O_2/UV and UV/TiO_2 .



Light has a significant influence on the degradation of organic pollutants and the light source is the main component of the photo-Fenton process [69]. Although UV light has been successfully used in Fenton-UV systems for the degradation of refractory compounds [70,71], its application on a real scale implies high costs given the short useful life of UV lamps, high risks of environmental contamination, and high energy consumption [72]. To overcome these limitations, sunlight has been used to drive the photo-Fenton process. Recent studies have shown the efficacy of using sunlight for the degradation of refractory organic compounds [73,74], reaching higher total organic carbon removal efficiencies compared to the traditional Fenton process. Table 2 presents an overview of the experimental conditions tested for the degradation of emerging contaminants using the photo-Fenton or Fenton-like process.

Table 2. Relevant studies of the degradation of emerging pollutants (emphasizing pharmaceuticals) using a photo-Fenton (or Fenton-like) process.

Pollutant	AOP	Reactor Volume	Aqueous Matrix	Reaction Conditions	Significant Findings	Reference
Tetracycline	Photo-Fenton	500 mL	Sewage treatment plant effluent	[TC] = 24 mg/L; 5 min; [Fe(NO ₃) ₃] = 0.20 mM; [H ₂ O ₂] = 3.0 mM. Solar and black light irradiation (15 W, 365 nm).	Total mineralization of total carbon.	[75]
Amoxicillin (AMX), bezafibrate (BZF) and paracetamol (PCT)	Photo-Fenton	800 mL	Sewage treatment plant effluent	[AMX] = 42 mg/L; [PCT] = 15 mg/L; [BZF] = 20 mg/L; [FeOx] = 0.2 mM; [H ₂ O ₂] = 5.0 mM; Solar and black light irradiation (15 W, 365 nm).	Up to 98% removal of BZF and PCT and 84% removal of AMX using FeOx.	[76]

Table 2. Cont.

Pollutant	AOP	Reactor Volume	Aqueous Matrix	Reaction Conditions	Significant Findings	Reference
5-fluorouracil (5-FU)	Photo-Fenton	100 mL	Ultrapure water	[5-FU] = 30 mg/L; pH = 2.8; $[Fe^{3+}]$ = 0.08 mM; $[C_2K_2O_4 \cdot H_2O]$ = 0.24 mM; $[H_2O_2]$ = 2.9 mM or $[S_2O_8^{2-}]$ = 0.42 mM; simulated solar light (SSL) 500 W/m ² ; 30 min	Of the three processes tested (SSL/ Fe^{3+} / H_2O_2 , SSL/ Fe^{3+} / $S_2O_8^{2-}$, SSL/ $[Fe(C_2O_4)_3]^{3-}$ / H_2O_2) the SSL/ $[Fe(C_2O_4)_3]^{3-}$ / H_2O_2 process was the most efficient.	[77]
Ibuprofen (IBU), Carbamazepine and ciprofloxacin (CIP)	Photo-Fenton	700 mL	Real urban wastewater	$[Fe^{3+}]$ = 0.71 mM; $[H_2O_2]$ = 0.73, 1.47 or 2.94 mM; [IBU] = 59.83 µg/L; [CIP] = 54.60 µg/L; [carbamazepine] = 17.17 µg/L; 150 W (190 nm).	Complete degradation of all drugs after 20 min of reaction.	[78]
Cloxacillin	Photo-Fenton	100 mL	Synthetic pharmaceutical wastewater	$[Fe^{3+}]$ = 90 µM; $[H_2O_2]$ = 10 mM; 30 W	Total degradation for antibiotic after 240 min	[79]
Antipyrine	Photo-Fenton (UV-A LED photocatalytic reactor)	150 mL	Aqueous solution	$[H_2O_2]$ = 2.9 mM; $[Fe^{2+}]$ = 0.35 mM; $[C_2H_2O_4]$ = 1.1 mM; 24–26 °C; pH = 2.8.	Complete degradation of antipyrine and 93% mineralization was reached in 2.5 and 60 min.	[80]
Diatrizoate	Photo-Fenton	100 mL	Aqueous solution	[Diatrizoate] = 25 mg/L; $[Fe^{3+}]$ = 0.09 mM; $[H_2O_2]$ = 0.74 mM; pH 2.8, 90 min and Solar radiation (the best condition).	Total degradation of diatrizoate	[81]
Paracetamol	Photo-Fenton	500 mL	Aqueous solution	[Paracetamol] = 100 mg/L; $[H_2O_2]$ = 6.5 mM; $[Fe^{2+}]$ = 0.36 mM; pH = 3.0; 15W (300–570 nm) room temperature; 60 min.	100% removal	[82]
Salicylic acid, ketoprofen, diclofenac, paracetamol and caffeine	Photo-Fenton	200 mL	Aqueous solution	[Drug] = 10 mg/L; LEDs power: 1.768 W; $[Fe^{3+}]$ = 0.27 mM; $[H_2O_2]$ = 0.82 mM; [oxalate] = 0.81 mM; pH = 6.5; 25 min.	>80% removal of all drugs and 30–40% mineralization	[83]
Ibuprofen	Electro-Fenton	400 mL	Synthetic wastewater (SW)	[Ibuprofen] = 400 mg/L; pH = 2.43; 28 min; current density of 23.08 mA/cm; H_2O_2/Fe^{2+} molar ratio of 2.69, volume ratio of H_2O_2/SW of 1.84 mL/L.	98.29% COD removal	[84]
Norfloxacin	Electro-Fenton	175 mL	Aqueous solution	[Norfloxacin] = 0.25 mM; 25 °C; pH = 3.0; 5 h; Fe^{3+} = 0.1 mM; I = 60 mA	97.7% mineralization after 5 h	[85]
Enoxacin	Electro-Fenton	250 mL	Aqueous solution	[Enoxacin] = 50 mg/L; pH = 3.0, 60 min, Fe^{2+} = 0.2 mM; $[Na_2SO_4]$ = 50 mM; I = 300 mA; room temperature.	97% drug removal and 43% mineralization (measured as TOC removal).	[86]
Amoxicillin	Electro-Fenton	500 mL	Aqueous solution	[AMX] = 0.082 mM; 25 °C, pH = 3; I = 600 mA, $[Fe^{2+}]$ = 1 mM; graphite electrode.	95% degradation and 74% mineralization	[87]

Table 2. Cont.

Pollutant	AOP	Reactor Volume	Aqueous Matrix	Reaction Conditions	Significant Findings	Reference
Sulfamethoxazole (SMX)	Fenton or Fenton-like	30 mL	Aqueous solution	[SMX] = 158 µM; 25 °C, pH = 3.0, 50 min, [Fe ²⁺] = 179 µM, [H ₂ O ₂] = 100 µM; UV (254 nm) or sun light	97% and 100% removal of SMX for the process with sunlight and UV, respectively.	[88]
Trimethoprim (TMP)	Fenton or Fenton-like	30 mL	Aqueous solution	[TMP] = 138 µM; 25 °C, pH = 3.0, 50 min, [Fe ²⁺] = 179 µM, [H ₂ O ₂] = 100 µM; UV (254 nm) or sun light	52% and 79% removal of SMX for the process with sunlight and UV, respectively.	[88]
Ciprofloxacin (CIP)	Fenton	100 mL	Synthetic wastewater	[CIP] = 100 mg/L; [H ₂ O ₂]:[Fe ²⁺] = 10; stoichiometric H ₂ O ₂ concentration = 14.2 mM; pH = 3.0; 60 min	70% and 55% removal of CIP and TOC, respectively	[89]
Carbamazepine	Fenton-like	50 mL	Aqueous solution	[carbamazepine] = 10 mg/L; [H ₂ O ₂] = 1.47 mM; [Fe ³⁺] = 0.035 mM; 50 °C, pH = 3.0, 60 min.	100% removal and 73% mineralization of the drug	[90]
Amphetamine	Fenton-like	300 mL	Wastewater	[amphetamine] = 14–233 mg/L; 20 °C; pH 3.0; 60 min; [Fe ²⁺] = 1 mM; [H ₂ O ₂] = 1.75 mM	>80% amphetamine removal	[91]
Methylparaben (MeP)	Fenton	300 mL	Ultrapure water	[MeP] = 100 mg/L; [Fe ²⁺] = 0.29 mM; [H ₂ O ₂] = 1.82 mM; pH 3; 30 °C.	33.3% TOC removal	[92]
Methylparaben (MeP)	Photo-Fenton	300 mL	Ultrapure water	[MeP] = 100 mg/L; [Fe ²⁺] = 0.07 mM; [H ₂ O ₂] = 1.53 mM; pH 3; 30 °C; UVC lamp 4 W	34.9% TOC removal	[92]
Methylparaben (MeP)	Fenton	300 mL	Tap water	[MeP] = 10 mg/L; [Fe ²⁺] = 0.29 mM; [H ₂ O ₂] = 1.82 mM; pH 3; 30 °C.	20.6% TOC removal	[92]
Methylparaben (MeP)	Photo-Fenton	300 mL	Tap water	[MeP] = 10 mg/L; [Fe ²⁺] = 0.07 mM; [H ₂ O ₂] = 1.53 mM; pH 3; 30 °C; UVC lamp 4 W	23.8% TOC removal	[92]
Methylparaben (MeP)	Fenton	Not specified	Ultrapure water	[MeP] = 10 mg/L; [H ₂ O ₂]: 1.5 mM; [Fe ²⁺]: 0.18 mM; 60 min; pH: 3.6; room temperature.	82% COD removal	[93]
Methylparaben (MeP)	Photo-Fenton	200 mL	Ultrapure water	[MeP] = 10 mg/L; [H ₂ O ₂]: 4.57 mM; [Fe ²⁺]: 0.38 mM; 300 min; pH: 3.0; 35 °C; Xenon lamp 350 W/m ² .	>60% TOC removal	[94]
Sulfamethoxazole (SMX)	Photo-Fenton	2.0 L	Aqueous solution	[SMX] = 0.079 mM; [H ₂ O ₂]: 0.294 mM; [Fe ³⁺ -EDTA]: 0.089 mM; 75 min; pH: 7.0; 25 °C; UV lamp (8 W, 350–400 nm).	77.3% of SMX degradation	[95]

Table 2. Cont.

Pollutant	AOP	Reactor Volume	Aqueous Matrix	Reaction Conditions	Significant Findings	Reference
Bisphenol A (BPA)	Photo-Fenton	500 mL	Synthetic water	[BPA] = 50 mg/L; [H ₂ O ₂]: 1.5 mM; [Fe ³⁺]: 4 mM; 90 min; pH: 5; UV-A lamp (8W, 350 nm).	Complete removal of BPA and COD	[96]
Phenol	Photo-Fenton	Not specified	Aqueous solution	[Phenol] = 200 mg/L; [H ₂ O ₂]: 31.8 mM; [Fe ³⁺]: 0.09 mM; 120 min; pH: 3; UV lamp (3 × 15 W, 365 nm).	Removal of 98% of the COD	[97]
2-Nitrophenol, 4-Nitrophenol, 2,4-Dinitrophenol, 2,4,6-Trinitrophenol	Photo-Fenton	500 mL	Aqueous solution	[Pollutants] = 200 mg/L; [H ₂ O ₂]: 10.4–17.6 mM; [Fe ³⁺]: 0.36–0.45 mM; 120 min; pH: 3; UV lamp (150 W, 254 nm) or sunlight.	mineralization of more than 92% of the nitrophenols, using sunlight or UV light.	[98]

5. Factors Affecting the Homogeneous Photo-Fenton Process

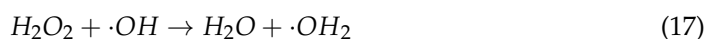
5.1. Catalyst Concentration

The initial concentration of the catalyst affects the efficiency of the photo-Fenton process, in general, the degradation efficiency of a pollutant increases as the iron concentration increases (keeping the H₂O₂ concentration constant), since there is a greater conversion of H₂O₂ into ·OH [96,99,100]. The typical ratio of iron to H₂O₂ used in the literature is 1:2 [101]. However, various works have come to use ratios greater than 1:50 [70]. However, iron cannot be added without limitations, since this would increase operating costs and the generation of iron sludge, and iron at high concentrations has a scavenging effect on hydroxyl radicals (Equation (16)) [70,102,103]. On the other hand, the level of iron in the effluents is a widely regulated parameter, due to the environmental effects that it has on the ecosystem [104]. In this sense, from an economic and environmental perspective, the catalyst concentration is a parameter to be optimized.



5.2. H₂O₂ Concentration

Similar to what happens with iron, the rate of degradation of organic contaminants increases with increasing H₂O₂ levels (keeping the iron concentration constant) up to a threshold value [105,106]. The amount of H₂O₂ needed is dependent on the chemical oxygen demand (COD) of the water, recent studies suggest that a H₂O₂ to COD ratio of 1:2 is the most appropriate [107]. However, a H₂O₂ concentration higher than the optimal concentration not only increases operating costs; but, in addition, it does not improve the efficiency of the process. This is due to (i) the scavenger effect, consuming hydroxyl radicals (Equation (17)); (ii) recombination of hydroxyl and perhydroxyl radicals (Equations (18)–(20)); and (iii) self-decomposition of H₂O₂ (Equation (21)), which decreases the oxidizing power of the system [70,103,108].



In addition to the above, it is necessary to manage low levels of H_2O_2 since its biocidal capacity (even at low concentrations) represents a risk to organisms [109], especially if the effluents are subsequently discharged into a body of water.

5.3. Initial Contaminant Concentration

The initial concentration of contaminants present in the wastewater will determine the amount of photo-Fenton Reagents to be used, even though this process has proven to be efficient in treating highly charged petrochemical wastewater [110,111], the degradation efficiency of these contaminants is inversely proportional to the initial concentration of the contaminants, keeping the concentration of the Fenton reagent constant [106].

5.4. pH

The efficiency of EC degradation is strongly influenced by the pH of the wastewater. Various studies have been carried out to optimize this parameter [96,106], finding optimum efficiency at a pH close to 3. At lower pH values, the activity of the Fenton reagent drastically reduces, which may be due to the generation of stable oxonium ions ($H_3O_2^+$) by the solvation of a proton by H_2O_2 [106,112]; as well as the scavenging effect of the $\cdot OH$ by protons (Equation (22)) [113]. On the other hand, at $pH > 4$ there is formation of $Fe(OH)_2$ (Equation (23)), which precipitates, reducing the availability of iron ions. Furthermore, the redox potential of the $\cdot OH$ decreases as the pH increases. This implies that the pH range to carry out the photo-Fenton process efficiently is very limited and that it must be carried out under acidic conditions. However, the ferriccarboxylate complexes (formed by iron ions with carboxylic acids) allow the working pH range of the photo-Fenton process to be extended, keeping the iron in the solution [96,114].



The pH affects the distribution of iron species in solution [115], at a pH close to 3 the most abundant species is $Fe^{3+}(OH)^{2+}$, which is suggested to be the most photoactive species. However, when the pH increases, iron species with less photoactive capacity prevail ($Fe^{3+}(OH)_2^+$, $Fe_2^{3+}(OH)_2^{4+}$, and $Fe_3^{3+}(OH)_4^{5+}$), as suggested by Simunovic et al. [116] and Rubio et al. [115]. In contrast, when the pH decreases, the species $[Fe(H_2O)_6]^{3+}$ abounds, which reacts more slowly with H_2O_2 [114,117,118]. On the other hand, when ferriccarboxylate complexes (specifically ferrioxalate) are used, an increase in pH leads to the formation of species ($Fe^{3+}(C_2O_4)^{2-}$, $Fe^{3+}(C_2O_4)_3^{3-}$ and $Fe^{2+}(C_2O_4)$) with greater photoactivity than the $Fe^{3+}(OH)^{2+}$ species [64].

The ferriccarboxylate complexes not only allow the iron to be kept soluble in a greater pH range but also extend the useful range of the UV-visible spectrum to regenerate ferrous ions, favoring the use of solar radiation more efficiently [45].

5.5. Effect of Radiation: Type and Intensity

As discussed above, the application of radiation to the conventional Fenton process improves the removal efficiency of organic contaminants in these systems [96,98,119]. In the conventional Fenton process, applied to the degradation of organic contaminants, byproducts are formed that are refractory to the non-photoassisted Fenton reaction; such as acetic acid and oxalic acid [67,120]. However, these reaction byproducts can form ferriccarboxylate complexes with photolytic activity [115,119,120]. These complexes generate reactive species that lead to the mineralization of contaminants. Although radiation significantly improves the efficiency of the Fenton process, the type and time of radiation applied affects operating costs. Various studies have concluded that UV radiation achieves better contaminant removal efficiencies compared to the use of sunlight [67,96]; however, ferriccarboxylate complexes are photoactive at wavelengths up to 600 nm, which allows the application of the photo-Fenton process in the visible region of the spectrum, which

makes this process more attractive for application on an industrial scale compared to other similar processes, such as electro-Fenton [121]. On the other hand, the intensity affects the efficiency of the process proportionally [122,123], which implies that the location of the photo-Fenton processes must be chosen strategically in places with high solar radiation.

5.6. Temperature Effect

Temperature directly affects the rate of degradation of chemical reactions and the Fenton (or photo-Fenton) reaction is no exception, to the extent that Villota et al. [124] have suggested that this parameter has a greater impact on the efficiency of the Fenton process than the iron concentration. Various studies have shown that the efficiency of contaminant removal is directly proportional to the temperature applied to the Fenton process [106,124,125], which is due to the more efficient conversion of H_2O_2 to $\cdot OH$. However, an increase in temperature (beyond the optimum) could promote the self-decomposition of H_2O_2 into molecular oxygen and water [126,127]. Despite the above, various works have been carried out to evaluate the effect of temperature on the efficiency of the photo-Fenton process (and conventional Fenton) in temperature ranges that go from 20 °C to 90 °C without reaching a threshold value after which the efficiency of the process is compromised [126–128]. This implies that in a large-scale application of the photo-Fenton process, using sunlight, it would be practically impossible to reach temperatures where this process is negatively affected.

5.7. Background Matrix Effect

In addition to the concentration and type of catalyst and H_2O_2 , other species present in the aqueous matrix (such as inorganic salts) can influence the efficiency of the photo-Fenton process. Phosphate ions ($H_2PO_4^-$ and HPO_4^{2-}) show a scavenging effect of $\cdot OH$ [129,130], and they can form iron precipitates, decreasing the availability of the catalyst [129], inhibiting the photo-Fenton process. Meanwhile, chloride ions, carbonates, and sulfates interact with iron forming less reactive species (CO_3^{2-} , Cl^- , SO_4^{2-}) that limit the efficiency of the process [96,129]. However, recent studies have shown that chloride interference is strongly influenced by pH, they inhibit the process at pH 2.8; however, they improve it at pH 5 [131]. In addition, some of these inorganic salts, such as HCO_3^- , can undergo photolysis, which makes it difficult for light to penetrate the solution [115]. On the other hand, it has been shown that perchlorate and nitrate ions do not scavenge $\cdot OH$ nor do they form complexes with iron (both ferrous and ferric) [129,130]. Even nitrate ions improve the efficiency of the process since their photolysis generates $\cdot OH$, in the range of 250–325 nm, a range in which H_2O_2 absorbs weakly [132,133].

In addition to inorganic salts, wastewater contains organic compounds and macromolecules that play an important role in the efficiency of the photo-Fenton process, such as humic-type substances [134]. Although the negative effect of dissolved organic matter (DOM) on the efficiency of the photo-Fenton process has been reported, other studies affirm that DOM does not reduce the efficiency of the process [135]. Even Fukushima and Tatsumi [136] reported that the presence of humic substances improved the degradation of pentachlorophenol in a photo-Fenton system. Furthermore, Rubio et al. [115] confirmed the results. It is suggested that the DOM present in wastewater can form stable complexes with iron, which also have catalytic activity [115,137].

6. Parameter Optimization

6.1. Design of Experiments

As previously described, the performance of the Fenton process depends, among other factors, on the concentration of the oxidizing and catalytic agent, temperature, pH, reaction time, type of radiation, and the reactor used [68,70,108]. Likewise, the efficiency of the process is related to the nature of the contaminant to be degraded and the aqueous matrix [61,138]. The excessive consumption of chemicals (hydrogen peroxide, iron salts, acids, and bases) and the high reaction times make the application of this process on a

real scale unfeasible [139]. In this sense, it is necessary to implement a design of experiments (DOE) that allows the optimization of parameters. Optimization techniques are mainly classified into two groups: univariate and multivariate approach approaches. The univariate approach, known as one factor at a time, involves the evaluation of a single parameter in each experimental run [140,141]. In the 20th century, most of the studies carried out on the optimization of the Fenton process were based on the univariate approach. However, starting in the 21st century, there was a transcendental change in the conceptualization of DOE and statistical analysis, introducing the study of two or more independent variables (simultaneously) on one or more response variables [28,29,142–144]. This last approach (multivariate) has several advantages over the univariate approach: (i) it provides global knowledge throughout its experimental domain; (ii) study the joint influence of variables and their relationship with the response variables; (iii) allows the investigation of more realistic problems; (iv) the number of experiments needed to optimize the process is considerably lower than those required in a univariate approach [140,145,146].

The DOE is defined as a set of statistical techniques applied to the planning, conducting, analysis, and interpretation of controlled tests to find and define factors that influence the values of a parameter or a set of parameters. Its basic principle allows varying all levels of all variables (discrete or continuous), in a programmed and rational way, reducing the number of experiments, resources, time, and physical efforts without limiting the number of factors to be analyzed [140,145]. The main DOE used to evaluate the influence of multiple factors that affect the performance of the photo-Fenton process are factorial designs, the central composite design (CCD), the Box-Behnken design (BBD), and, in some cases, artificial neural networks (ANN) have been used (Table 3).

Table 3. Relevant studies in the optimization of the Fenton process (and Fenton-like) using experiment designs applied to the degradation of emerging contaminants.

Organic Contaminant	Applied Process	DOE Used	Evaluated Factors	Reference
Amoxicillin and cephalexin	Fenton	Factorial design (2 ²)	[Fe ²⁺]: 1.79–8.95 mM [H ₂ O ₂]: 2.94–44.12 mM	[147]
Amoxicillin and cephalexin	Photo-Fenton	Factorial design (2 ²)	[Fe ²⁺]: 1.79–8.95 mM [H ₂ O ₂]: 2.94–44.12 mM	[147]
Amoxicillin	Photo-Fenton	Factorial design (2 ⁴)	Amoxicillin: 20–60 mg/L [Fe ²⁺]: 0.09–0.27 mM [H ₂ O ₂]: 1.47–4.41 mM UV light intensity: 0–96 W	[148]
Crystal violet dye	Heterogeneous Fenton-like	Full factorial design	pH: 5–9 [H ₂ O ₂]: 0.65–3.26 Type of catalysts (PET–NH ₂ –Fe, PET–Si–NH ₂ –Fe, and PET–SH–Fe)	[129]
Alprazolam and diazepam	Photo-Fenton	CCD	[Fe ²⁺]: 9×10^{-3} – 7.2×10^{-2} mM [H ₂ O ₂]: 8.8×10^{-2} –0.88 mM	[149]
Sulfamethazine	Photo-Fenton	CCD	[Fe ²⁺]: 0.25–1.22 mM [H ₂ O ₂]: 5.18–30.12 mM	[150]
Acid Blue 193	Photo-Fenton-like	CCD	Reaction time: 15–60 min [COD]: 0.10–0.30 g/L [H ₂ O ₂]: 25–65 mM [Fe ³⁺]: 0.5–4.5 mM	[151]
Oilfield produced water	Electro-Fenton	CCD	[Fe ³⁺]: 0.1–0.5 mM Reaction time: 22–81 min Current intensity (100–500 mA)	[152]

Table 3. Cont.

Organic Contaminant	Applied Process	DOE Used	Evaluated Factors	Reference
Distillery effluent	Photo-Fenton	CCD	[COD]: 3–39 g/L pH: 2.5–8.5 [H ₂ O ₂]: 0.09–0.21 mM [Fe ²⁺]: 13.17–65.83 mM	[153]
Carbofuran	Photo-Fenton	CCD	[Carbofuran]: 1–100 mg/L H ₂ O ₂ dosage rate: 7×10^{-3} –0.1746 mM/min [Fe ³⁺]: 0.02–0.90 mM	[154]
2,4-Dichlorophenoxyacetic acid (2,4-D)	Photo-Fenton	CCD	Temperature: 25–50 H ₂ O ₂ to 2,4-D ratio: 7–50	[143]
Rhodamine B	Photo-Fenton	CCD	Reaction time: 3–39 min [Fe ²⁺]: 0.36–1.07 mM H ₂ O ₂ : 2.2–11.0 mM [Dye]: 50–250 mg/L	[144]
Acid Blue 113	Fenton	CCD	[Dye]: 100–300 mg/L H ₂ O ₂ : Fe ²⁺ : 5–25 (w/w) Dye: Fe ²⁺ : 10–50 (w/w) pH: 2–9	[27]
Black liquor effluent from the pulp and paper industry	Fenton	CCD	Temperature: 28–60 °C [H ₂ O ₂]: 29.4–58.8 mM [Fe ²⁺]: 0.36–8.95 mM	[28]
Methylene blue dye	Photo-Fenton	BBD	[Fe ³⁺]: 0.36–1.07 mM [H ₂ O ₂]: 5.9–17.6 mM pH: 2.5–3.5	[29]
Simulated industrial wastewater	Photo-Fenton	BBD	pH: 1.9–7.0 [Fe ²⁺]: 1.0–12 mM [H ₂ O ₂]: 30–400 mM	[120]
Amoxicillin	Photo-Fenton	BBD	[Amoxicillin]: 10–200 mg/L [H ₂ O ₂]: 0.3–14.7 mM [Fe ²⁺]: 0–0.9 mM	[155]
Carmoisine edible dye	Fenton	Taguchi method	pH: 2–6 [Fe ²⁺]: 0.1–0.3 mM [H ₂ O ₂]: 2–6 mM [Dye]: 10–30 mg/L	[32]
Carmoisine edible dye	Photo-Fenton	Taguchi method	pH: 2–6 [Fe ²⁺]: 0.1–0.3 mM [H ₂ O ₂]: 2–6 mM [Dye]: 10–30 mg/L	[32]
Ciprofloxacin	Fenton	Taguchi method	pH: 2–5 [Fe ²⁺]: 5–50 mM [H ₂ O ₂]: 10–100 mM [Ciprofloxacin]: 10–200 mg/L Reaction time: 10–30 min	[101]
Phenol	Electro-Fenton	Taguchi method	Current density: 0–16 mA/cm ² pH: 2–8 [H ₂ O ₂]: 0–8.8 mM Reaction time: 20–100 min Salinity: 0–4% [Phenol]: 0.25–2.0 g/L	[33]

Table 3. Cont.

Organic Contaminant	Applied Process	DOE Used	Evaluated Factors	Reference
Acid Blue 113	Fenton	Taguchi method	[Dye]: 100–300 mg/L $H_2O_2:Fe^{2+}$: 5–25 (w/w) Dye: Fe^{2+} : 10–50 (w/w) pH: 2–9	[27]
Dairy wastewater	Fenton	Taguchi method	pH: 3–4.5 Reaction time: 50–70 min [H_2O_2]: 20.6–32.4 mM	[156]
Polyester resin effluent	Heterogeneous photocatalysis	Taguchi method	UV: 0–21 W pH: 3–7 [H_2O_2]: 3.53–5.35 mM [TiO_2]: 1.04–2.28 mM	[157]

6.1.1. 2^k Factorial Design

Factorial designs allow studying the effect of two or more factors (and their interaction between them) on the response variables. The most important factorial design is the 2^k , which is used to evaluate the effect of “ k ” factors with two levels. The levels range from a “low” level (−1) to a “high” level (+1) (Figure 4). The results of a 2^k factorial design can be expressed as a first-order regression model:

$$y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum \sum_{i < j} \beta_{ij} x_i x_j \quad (24)$$

where y corresponds to the response variable, $x_j(x_i)$ represents the coded factors, β_0 is the mean value of the response variable, β_j represents the linear coefficients, and β_{ij} represents the interaction between the coefficients.

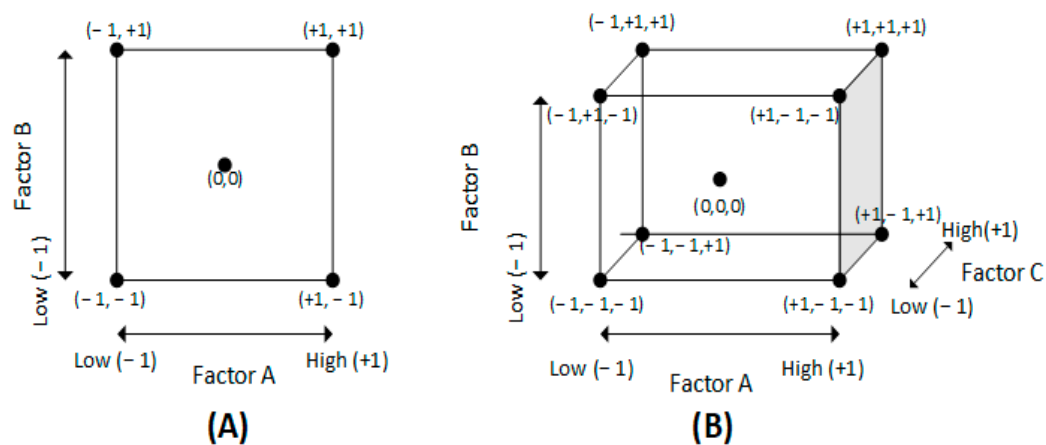


Figure 4. The geometry of a factorial design with 2 (A) and 3 (B) factors.

Several studies have applied the 2^k design to study the photo-Fenton process, most of them have focused on studying the effect of the concentration of pollutants, catalyst, and oxidant used [147,148], and few have studied the effect of 4 factors at the same time; Vargas da Silva [148] studied amoxicillin degradation by varying the concentration of Fe, H_2O_2 , amoxicillin, and radiation intensity. This tool is very useful for the initial stages of an investigation; however, other methodologies have a greater scope when the optimization of a process is required.

6.1.2. Central Composite Design (CCD)

The difference between a response surface equation (Equation (25)) and a factorial design equation (Equation (24)) is the addition of quadratic terms that allow the curve to be modeled in the response.

$$y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum \sum_{i < j} \beta_{ij} x_i x_j + \sum_{j=1}^k \beta_{jj} x_{jj}^2 \quad (25)$$

where β_{ij} represents the coefficients of the quadratic terms.

The CCD is the most widely used response surface-designed experiment. It is often used when the design plan calls for a sequential experiment, because these designs may include information from a correctly planned factorial experiment. In this sense, CCD is a fractional factorial design with central points, extended with a range of axial points (also called star points) that allow the curvature of the response surface to be estimated. The addition of more coefficients to the model implies the need for a greater number of runs to allow a more reliable estimation of the coefficients. This increase is usually carried out by adding axial points to the factorial design so that the study space is larger compared to the factorial design (Figure 5).

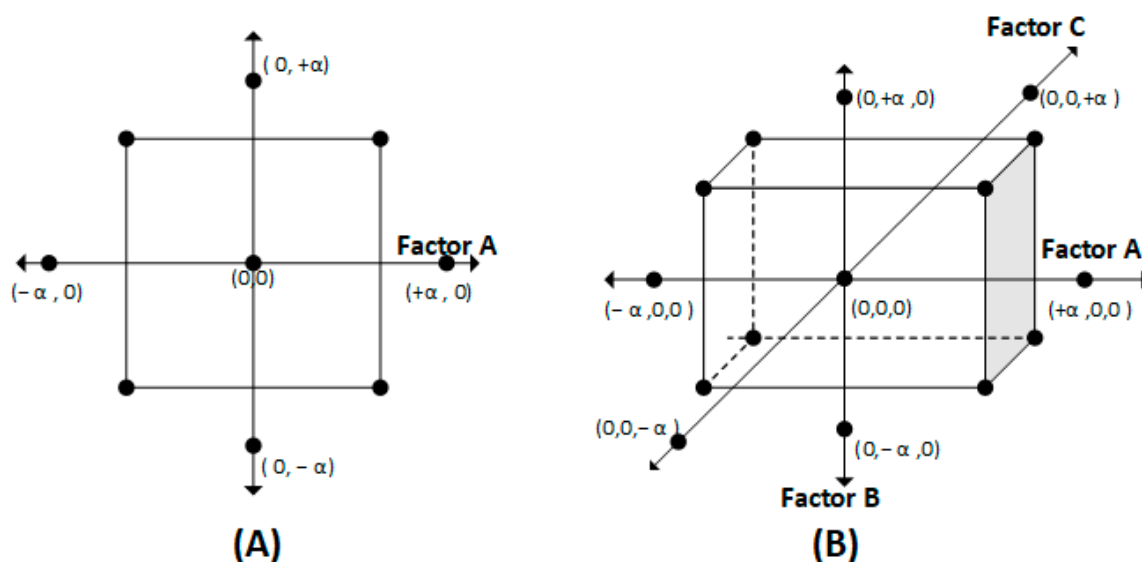


Figure 5. Graphical representation of a CCD with 2 (A) and 3 (B) factors.

Several studies using this DEO have been applied to maximize COD removal in Fenton processes [28,153,158] and, homogeneous [143,144,150,153,154,159–161] and heterogeneous Fenton-like [152,162]. Except for the studies carried out by Schenone et al. [143] and Al-Khafaji and Mohammed [152], most of the works carried out the Fenton process (or Fenton-like) in acid conditions (pH 3); however, this limitation can be overcome using ferri-carboxylate complexes, which are useful to carry out the Fenton process at circumneutral pH. Some reports have included within their variables to optimize energy consumption, in addition to COD removal [152]. The factors that take on greater significance in the optimization model are generally the pH (in the case of the Fenton process), the initial concentration of the contaminant, and the concentration of the oxidizing agent and catalyst.

6.1.3. Box-Behnken Design (BBD)

The Box-Behnken design is a spherical response surface, including a center point and midpoints between the corners, circumscribed on a sphere. This design must have three levels per factor, unlike CCD, which can have up to five levels; furthermore, they do not have an embedded factorial design, so they are not suitable for sequential experiments. Another difference concerning CCD is that Box-Behnken designs never include runs where the factors are at their extreme value, this ensures that all design points are within their

safe operating zone (Figure 6). In general, these designs tend to have fewer design points than a CCD, which is less expensive to execute with the same number of factors [140,163].

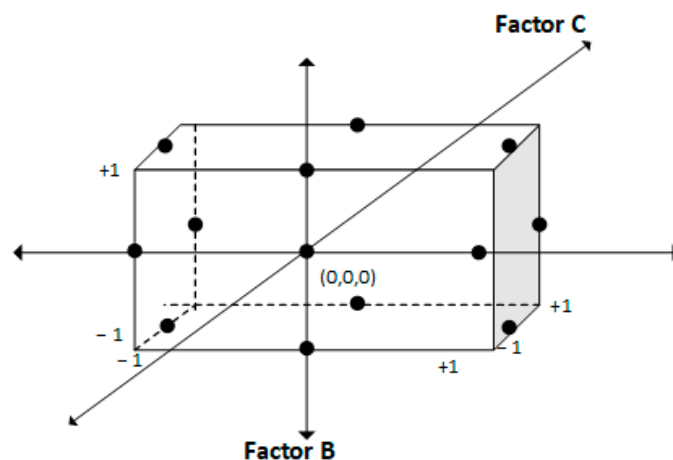


Figure 6. Graphic representation of a Box-Behnken design.

A few studies have been published using this approach [29,120,155,164]. Ay and Kargi [164] applied this approach to maximize amoxicillin degradation and mineralization, studying the combined effect of drug concentration, oxidizing agent, and catalyst; finding that the effect of the oxidizing agent and the initial concentration of amoxicillin on the efficiency of the photo-Fenton process is more significant. For their part, Dopar et al. [120], studied the influence of pH and concentration of oxidant and catalyst on the removal of total organic carbon, using a simulated industrial water. They concluded that pH has the most important role in the efficiency of the photo-Fenton process. On the other hand, Tayeb et al. [29], evaluated the influence of the same factors studied by Dopar et al. [120] on color removal from synthetic water with methylene blue (as a model dye); however, neither COD nor TOC removal was monitored, so it is difficult to define the mineralization percentage of the dye.

These methods (based on a response surface) have the limitation that increasing the number of factors substantially increases the number of experiments. For example, a trial that involves evaluating 6 experimental factors leads to 90 and 54 experimental runs for a CCD and a Box-Behnken design, respectively. Therefore, with multiple factors to analyze, these techniques are not appropriate, since they increase the cost associated with the use of chemicals, time, and physical effort. Therefore, other strategies must be implemented that can overcome these limitations.

6.1.4. Taguchi Method

Genichi Taguchi between 1950 and 1960 developed the foundations of a robust statistical technique and multiparametric optimization, which can be applied to any discipline, including environmental engineering. It is based on many ideas drawn from the standard statistical design of experiments, since the optimization of a conventional design may not always satisfy the desired goals. In addition, it provides advantages such as economic reduction and the variability of the response variable. Therefore, it is an important tool to improve the productivity of a process; reduces the number of tests and can be used to optimize processes [30].

Taguchi's method uses orthogonal arrays for experimental design and the Signal-to-Noise (S/N) ratio rather than the responses themselves to determine the optimal set of control factors, thus ignoring variations caused by uncontrollable factors. The orthogonal matrices are the minimum set of experiments that represent the various combinations of factors. With this method, the experimental results can be analyzed through the S/N ratio and ANOVA, simultaneously evaluating the importance of the factors in terms of their contribution to the response values.

In Taguchi's method, the S/N ratio is a measure of the deviation of the response from the desired value. Here, the "signal" refers to the average value, while the "noise" is associated with the standard deviation. This means that by maximizing the S/N ratio there is less variability in the process. However, depending on the type of signal desired, Taguchi classified the S/N ratio into three categories [30,157]:

Smaller is better:

$$S/N = -10 \log \left(\frac{1}{n} \sum_{k=1}^n y_i^2 \right) \quad (26)$$

Larger is better:

$$S/N = -10 \log \left(\frac{1}{n} \sum_{k=1}^n \frac{1}{y_i^2} \right) \quad (27)$$

Nominal is better:

$$S/N = -10 \log \left(\frac{1}{n} \sum_{k=1}^n \frac{\mu^2}{\sigma^2} \right) \quad (28)$$

where $\mu = \frac{1}{n} \sum_{k=1}^n y_i$; $\sigma^2 = \frac{1}{n-1} \sum_{k=1}^n (y_i - \mu)^2$ and y_i represents the response variable and "n" denotes the number of experiments.

One of the distinctive features of the Taguchi method is that it determines the optimal value in the form of an S/N ratio. The predicted S/N ratio at optimal conditions can be calculated from the following mathematical equation:

$$S/N_{\text{predicted}} = \bar{S}/N + \sum (S/N_j - \bar{S}/N) \quad (29)$$

where $\bar{S}/N$ shows the average of all S/N ratios, S/N_j is the S/N ratio at the optimal level for each parameter.

Several studies have successfully applied this method to optimize parameters of a Fenton process [27,32,101,156] and heterogeneous photo-Fenton [157] and other Fenton-like processes [33]; most of them tending as a response variable to optimize the removal of COD, TOC and the pollutant in question. In most of the works cited above, it is confirmed that the parameters that have the most influence on the efficiency of the Fenton process (or Fenton-like) are pH, UV radiation, and the concentration of the oxidizing agent and catalyst.

Asghar et al. [27], carried out the treatment of synthetic wastewater based on Acid Blue 113 dye (a diazo dye widely used in the textile industry) using a Fenton process. They studied the influence of dye concentration, pH, and dye/iron and H_2O_2 /iron ratios on COD removal, using 3 levels for each factor. For this purpose, they compared two optimization methods, the Taguchi method and a CCD. They found that both methods were good at modeling COD removal; however, the Taguchi method had advantages over CCD: (i) it required only 9 experimental runs vs. 30 runs for the CCD case (and 81 runs for a full factorial design) and; (ii) it is possible to know the contribution percentage of each variable to the response value, information that the CCD cannot provide. Taguchi's method is very useful for single-objective optimization, but it is difficult to apply to solve multi-objective optimization problems.

7. Grey-Taguchi Method

The Taguchi method has proven to be an effective approach to producing high-quality products at low cost [30]. However, Taguchi's method was originally designed to optimize a single performance characteristic. Taguchi recommends the use of the S/N ratio to measure how much the performance characteristic deviates from the desired value. Regardless of the category of the performance characteristic (lower-the-better, higher-the-better, or nominal-the-better), the larger S/N ratio corresponds to a better performance characteristic. Therefore, the optimal level of a process parameter is the level with the highest S/N ratio, which is true when it comes to optimizing a single performance characteristic. Therefore, a higher S/N ratio for one performance characteristic may correspond to a lower S/N ratio for another. Thus, a global evaluation of the S/N relationship is required to optimize

multiple performance characteristics, which is achieved by adopting a Gray relational analysis [34,165].

Grey relational analysis was developed by Deng [34] in 1989, it is a progressive form of Taguchi's method, which transforms a multi-objective optimization problem into a single-objective one. This analysis assumes that for a real system, the information is always limited, imperfect, or ambiguous. The stages of the Grey–Taguchi method approach are 3:

Step 1. The central idea of the analysis is based on assigning a certain Grey degree to each factor. For this, it is necessary to normalize the S/N ratios of the response factors in a range of 0–1.

Larger is better

$$X_i^*(k) = \frac{X_i^0(k) - \min X_i^0(k)}{\max X_i^0(k) - \min X_i^0(k)} \quad (30)$$

Smaller the better

$$X_i^*(k) = \frac{\max X_i^0(k) - X_i^0(k)}{\max X_i^0(k) - \min X_i^0(k)} \quad (31)$$

where X_i^* is the generated Grey relational value, $\min X_i^0(k)$ and $\max X_i^0(k)$ are the maximum and minimum values of $X_i^0(k)$, respectively, for the k th response.

Step 2. The Grey relational coefficient ($\xi_i(k)$) is calculated to express the relationship between the optimal (best = 1) and actual normalized results [166].

$$\xi_i(k) = \frac{\Delta_{\min} + \zeta \Delta_{\max}}{\Delta_{0i}(k) + \zeta \Delta_{\max}} \quad (32)$$

where $\Delta_{0i}(k) = \|X_0^*(k) - X_i^*(k)\|$, is the absolute value of the difference between the reference sequence $X_0^*(k)$ and the comparability sequence $X_i^*(k)$; ζ , is the identification coefficient ($0 \leq \zeta \leq 1$), which is typically set to a value of 0.5; $\Delta_{\min}$ and $\Delta_{\max}$ are the minimum and maximum values of Δ_{0i} . A higher Grey relational coefficient implies that the corresponding experimental result is closer to the optimal normalized value for a single response.

Step 3. Finally, the Grey relational grade (GRG) is calculated

$$\gamma_i = \frac{1}{n} \sum_{k=1}^n \xi_i(k) \quad (33)$$

where γ_i represents the estimated GRG for each i th experiment, the larger its value, the better.

Various studies support the application of the Grey–Taguchi method in the (multi-objective) optimization of processes and products, in the area of materials and manufacturing [36–38]. However, its application in environmental engineering is limited, even more so in AOP optimization; being that most of the works use the traditional Taguchi method to optimize the photo-Fenton process in a single response variable. To date, there is only one report on the application of this method in the optimization of the traditional Fenton process for the degradation of ciprofloxacin [101]. The factors to be evaluated were pH, reaction time, initial concentration of the drug, iron, and hydrogen peroxide (considering four levels for each factor). On the other hand, the performance characteristics to be optimized were antibiotic and COD removal and lower sludge production. The analysis also allowed us to know the influence of each factor on each performance characteristic evaluated.

8. Challenges and Perspectives

The optimization of the photo-Fenton process is a key factor for the implementation of this technology. In this sense, different strategies have been applied to carry out this purpose, the most used experimental designs to optimize this process have been those based on the response surface (CCD and BBD) and the Taguchi method. The latter has shown advantages over CCD and BBD, since it obtains similar results with a smaller number of

experiments, which implies lower costs. However, the traditional Taguchi method can only be applied to optimize a single performance characteristic, with most studies focused on pollutant or COD removal. However, there are other parameters to consider in the optimization of the process, such as the generation of sludge or the costs associated with its implementation, which suggests that it is necessary to resort to other statistical tools that allow optimization of the photo-process. Fenton on more than a single performance characteristic (or response variable), to overcome these limitations imposed by traditional methods of design of experiments, the Grey–Taguchi method is an attractive option.

Gray relational analysis was described for the first time in 1989 and from then to date, the application of this statistical tool has been increasing almost exponentially, due to the great scope it has and that it can be coupled with the traditional Taguchi method. The fields where this method has been successfully applied are not only limited to the field of engineering but also in other areas such as economics, meteorology, sports (sports and financial performance analysis), military affairs, management, and judicial system, among others [34]; being mostly applied to optimize processes related to the synthesis of materials, an area in which the potential of this statistical tool for multi-objective optimization has been demonstrated [39,167,168]. On the other hand, the area of environmental sciences is where it has been applied to a lesser extent. Initially, this method was adapted to effectively study air pollution [169] and the impact of socioeconomic activities on air quality in China [170]. However, its application to AOP information is very limited.

Despite the great scope of the Grey–Taguchi method, to the best of our knowledge, to date, all preceding studies applied the traditional Taguchi method for optimization of the Fenton (or Fenton-like) process on a single response variable, but there are no reports on the application of the Grey–Taguchi method in the multi-objective optimization of the photo-Fenton process. In a recent study, the application of the Grey–Taguchi method to optimize the degradation of ciprofloxacin using a Fenton process was reported [101]. It is the first report on the successful application of this method to optimize the traditional Fenton process, in more than one performance characteristic. However, given the benefits and scope of the Grey–Taguchi method, it is suggested that its application to carry out the multi-objective optimization of the photo-Fenton process is a promising option.

9. Conclusions

The photo-Fenton process is efficient in the degradation of emerging contaminants. However, its performance is influenced by various factors (independent variables), such as the concentration of oxidizing agent and catalyst, reaction time, pH, and irradiation, among others. In addition to this, the efficiency of the photo-Fenton process (or Fenton-like), not only implies the removal of the contaminant, but also the low generation of sludge due to the addition of iron and lower costs. This makes it necessary to implement strategies that make it possible to optimize the photo-Fenton process in more than one response variable or performance characteristic (multi-objective optimization). In this sense, the Grey–Taguchi method is suggested as an attractive option to achieve multi-objective optimization of the photo-Fenton process, with the least number of experimental runs, minimizing the time and costs associated with its execution.

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