

Review

Industrial Wastewater Treatment by Coagulation–Flocculation and Advanced Oxidation Processes: A Review

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Abstract

As human living standards have improved, the demand for industrial products—such as food, dyes, cosmetics, pharmaceuticals, and others—has significantly increased. This surge in production has, in turn, led to a rise in industrial wastewater (IW) generation, which is often marked by low biodegradability and a high concentration of toxic or refractory compounds. This review highlights the use of coagulation–flocculation–decantation (CFD) and advanced oxidation processes (AOPs) for treating such wastewater. A comprehensive analysis of CFD is provided, covering the underlying mechanisms, types of coagulants (including metal-based, animal-derived, mineral, and plant-based), and the optimal operational conditions required to maximize treatment efficiency. This review discusses the properties and performance of these coagulants in detail. In addition, this paper explores the methods used in AOPs to reduce organic carbon, focusing particularly on the roles of hydroxyl and sulfate radicals. Emphasis is placed on the enhancement of these processes using radiation, chelating agents, and heterogeneous catalysts, along with their effectiveness in IW treatment. Finally, the integration of CFD as a pre-treatment step to improve the efficiency of subsequent AOPs is provided.

Keywords: plant-based coagulants; recalcitrant compounds; solar radiation; chelating agents; raceway pond reactor; ozone; sulfate radical



Academic Editor: Alexandre T. Paulino

Received: 19 May 2025

Revised: 21 June 2025

Accepted: 24 June 2025

Published: 27 June 2025

Citation: Lucas, M.S.; Teixeira, A.R.; Jorge, N.; Peres, J.A. Industrial Wastewater Treatment by Coagulation–Flocculation and Advanced Oxidation Processes: A Review. *Water* **2025**, *17*, 1934. <https://doi.org/10.3390/w17131934>

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1. Introduction

In recent decades, developing countries have shown major changes connected with swift population growth, urbanization, and significant economic progress, reaching a notable increase in the consumption of natural water resources and causing deterioration of the water quality [1]. In contrast, most developed countries have been focusing on enhancing and increasing the efficiency of industries to respond to the growing demand by the population. In industry, water is mainly used for production, warming, cooling, raw material and waste carrying, and washing, and most of it becomes industrial wastewater (IW). Therefore, the mass production of industrial products results in the creation of massive wastewater volumes, with high concentrations of refractory compounds, causing deterioration of ecosystems and raising significant environmental and human health issues. Untreated wastewater can influence ecosystems through oxygen depletion, biodegradation of organic materials, and pathogens transported by water. Combined with the impacts of climate change, this condition has exacerbated the global scarcity of fresh water. Hence, the existing freshwater sources should be preserved, and the most effective way is through proper treatment of industrial wastewater. Suitable wastewater treatment is important for

recycling and the use of treated wastewater to meet human demand and reduce freshwater deficiencies, as well as to respect the limit values for wastewater discharge, minimizing the impact on surface water, groundwater, and soil [2].

Many agro-industries in Mediterranean countries are dedicated to the production of wine and olive oil. However, other industrial sectors such as dairy, pulp and paper [3,4], textiles [5,6], and pharmaceuticals [7,8] also contribute significantly to industrial wastewater generation. These wastewaters (Table 1) differ widely in their composition and are typically characterized by high organic content, an excess of turbidity, suspended solids, and polyphenols. In most cases, the treatment of wastewaters with high concentrations of organic carbon is performed in wastewater treatment plants (WWTPs), with biological processes. The biodegradability index, typically expressed as the BOD₅/COD ratio, is an important parameter for assessing the biological treatment potential of wastewater. Domestic wastewater usually presents a high biodegradability index (generally > 0.5), indicating that most of the organic content can be readily degraded by biological processes. In contrast, industrial wastewaters often exhibit lower biodegradability indices (<0.3) due to the presence of recalcitrant or non-biodegradable compounds. As a result, industrial wastewaters, such as those analyzed in this study, frequently pose significant challenges to conventional WWTPs, where their effective treatment may be difficult or even unfeasible. As shown in Table 1, wastewaters such as pulp and paper, winery, and olive mill carry high concentrations of polyphenols, and, above 8 g L⁻¹, the wastewaters become phytotoxic and result in highly toxic environments for microorganisms which are used in biologic processes [9], particularly bacteria in activated-sludge processes [10]. Considering the limitation of the biological treatments, it is essential to explore alternative approaches like physicochemical methods. Specifically, this review investigates the application of coagulation–flocculation–decantation (CFD) and advanced oxidation processes (AOPs).

Table 1. Physicochemical characteristics of various types of industrial wastewaters. COD—chemical oxygen demand; BOD₅—biochemical oxygen demand; and BOD₅/COD—biodegradability index.

Industrial Wastewater	COD (mg O ₂ /L)	BOD ₅ (mg O ₂ /L)	Total Polyphenols (mg Gallic Acid/L)	pH	BOD ₅ /COD	References
Landfill leachate	25,000–60,000	4000–15,000		>7.5	<0.1	[11–13]
Pharmaceutical	7893–32,500	1692–6000		4.0–9.2	0.09–0.59	[14,15]
Pulp and paper	1500–380	560–1200	190–220	8–10	<0.2	[16]
Textile	300–12,000	188–550		2–13.5	<0.39	[17]
Winery	1880–15,550	550–8860	10–700	4.0–5.3	<0.3	[18,19]
Olive mill	595–220,000	3400–100,000	12,600–21,700	4.4–5.2	0.19–0.49	[20,21]
Olive washing	990–4580	200–550	88–1027	4.1–7.5	0.16–0.43	[22,23]
Dairy	790–6000	410–4480		8.6–12	>0.5	[24,25]
Municipal	500–1000	250–500		7.2–8.4	>0.5	[1,26]

Coagulation–flocculation–decantation (CFD) has been exhaustively studied, with the goal of destabilizing colloidal particles and aggregate flocs toward sizeable particles that are more easily settleable and thus decreasing turbidity and soluble organic and inorganic pollutants in wastewater [27]. Most wastewater treatment plants employ metal-based coagulants, such as aluminum salts; however, several studies observed a relation between aluminum sulfate and the appearance of neurodegenerative diseases, namely Alzheimer’s disease [28]. To overcome the limitations of metal-based coagulants, the demand for green and eco-friendly products derived from plant roots, barks, stems, leaves, seedpods, and flowers, among others, from *Strychnos potatorium*, *Phyllanthus emblica*, *Luffa*

cylindrical, etc., has been studied [29]. Most researchers have shown that the application of *Moringa oleifera* lam seeds achieved a high turbidity and suspended-solids removal [30,31] and a waterborne-pathogen decrease [26]. Jorge et al. [32] showed that medicinal plants such as *Chelidonium majus* L. could be used to reduce the textile dye (methylene blue) from aqueous solution and [33] showed that food by-products could be applied to remove impurities from agro-industrial wastewaters.

As a means to improve organic carbon reduction, advanced oxidation processes (AOPs) can be used. AOPs operate at ambient and pressure water treatments, involving the generation of extraordinary reactive species, hydroxyl radicals ($\text{HO}^\bullet$), which attack organic molecules with rate constants around $10^6\text{--}10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [34]. AOPs are organized in relation to the oxidant used: hydroxyl-based AOPs and sulfate-based AOPs [35]. Hydroxyl-based AOPs are based on the reaction between ferrous iron (Fe^{2+}) and hydrogen peroxide (H_2O_2) (Fenton process) generating $\text{HO}^\bullet$ radicals with high oxidizing potential ($E^\circ = 2.80 \text{ V}$) [36,37]. However, the excess of reagent dosing leads to scavenging reactions for $\text{HO}^\bullet$ radicals, resulting in efficiency loss and cost increases [38]. In addition, the Fenton process is usually slow, due to the low Fe^{2+} regeneration and precipitation of iron as ferric hydroxide. Therefore, authors have applied radiation to regenerate the Fe^{2+} and at the same time increase the conversion of H_2O_2 [39]. Nowadays, more investigators have been testing the application of safer and cheaper radiation sources, such as sunlight. Compound parabolic collectors (CPCs) have been frequently used for microorganism inactivation and pollutant degradation, considering solar photons' successful exploration [40], but the cost for the installation of a large-scale CPC for solar photo-Fenton could be estimated as 400 EUR m^{-2} . To overcome the high costs, cost-effective reactors, like raceway pond reactors (RPRs) with low construction costs (10 EUR m^{-2}) have been explored as a more feasible option [41].

Although hydroxyl-based AOPs are effective in contaminant degradation, their practical application is restricted to a great extent by low pH (2 to 4) and the instability of H_2O_2 [42]. As an alternative, researchers have been developing new treatment processes based on sulfate radicals ($\text{SO}_4^{\bullet-}$) generation, which attack the organic molecules with rate constants of around $10^5\text{--}10^9 \text{ L mol}^{-1} \text{ s}^{-1}$ [43]. Peroxymonosulfate (HSO_5^- , PMS) and peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$, PS) are precursors of $\text{SO}_4^{\bullet-}$, which has great capacity to degrade recalcitrant compounds from wastewater [44]. $\text{SO}_4^{\bullet-}$ has a great many advantageous because it (1) is non-selective for oxidizing organic compounds, (2) has a high oxidizing potential ($E^\circ = 2.5\text{--}3.1 \text{ V}$), (3) has a higher half-life (30–40 μs) in comparison to $\text{HO}^\bullet$ radicals ($<1 \mu\text{s}$), (4) has better mass transfer performance, (5) has a higher contact chance with target pollutants, and (6) works within a high pH range (2 to 8) [45].

Ozone-based AOPs have been widely used for the degradation of micropollutants in wastewater treatment plants (WWTPs) and drinking water treatment plants (DWTPs). To accelerate the conversion of ozone (O_3) into $\text{HO}^\bullet$ radicals, several processes have been adapted, such as ozonation, UV/O_3 , $\text{O}_3/\text{H}_2\text{O}_2$, and catalytic ozonation [46].

Wastewaters with a high content of biodegradable organic carbon can be treated by biological processes; however, several wastewaters, such as pharmaceutical, carry high concentration in antibiotics, or winery and olive mill wastewaters carry high content in phenolic compounds, which represent high toxicity, and, therefore, these wastewaters present a low biodegradability index (BOD_5/COD) < 0.3 , which could cause serious environmental problems if released. Therefore, this paper aims to review and analyze a range of studies on the application of coagulation–flocculation–decantation, advanced oxidation processes, and their combined effects on organic carbon removal and water reuse. It also explores the underlying mechanisms of the CFD process, the various types of coagulants used, and the key variables influencing its efficiency. In addition, the paper

provides a comprehensive analysis of Fenton and photo-Fenton processes, evaluating their effectiveness in removing organic carbon and examining the contributions of hydroxyl radicals (generated from H_2O_2 and O_3) and sulfate radicals. The novelty of this review lies in its integrated analysis of CFD and AOPs for industrial wastewater treatment, while also addressing environmentally friendly alternatives, such as plant-based coagulants (PBCs) and cost-effective reactors, such as RPRs.

2. Coagulation–Flocculation–Decantation

Coagulation and flocculation is a water/wastewater treatment method involving the addition of coagulants/flocculants to induce the destabilization of colloidal particles and subsequent aggregation to achieve the purpose of settlement and separation via sedimentation, filtration, or air flotation [47].

2.1. Coagulation Mechanisms

In the 1940s, a new coagulation theory was suggested, distinguishing two mechanisms for the removal of colloidal impurities: (a) double layer compression, a process to allow particles to overcome repulsive forces to agglomerate and precipitate; and (b) precipitate enmeshment, a process in which small particles are physically enmeshed by metal precipitates when they are forming and settling [48]. Nowadays, the most widely accepted coagulation/flocculation mechanisms mainly include electrical double layer compression, charge neutralization, bridging, and sweeping [47], as described below and represented in Figure 1:

- (1) **Electrical double layer compression:** The electric double layer (EDL) is generated to retrain the particles negative surface charge, achieving electroneutrality. By enhancement of the ion concentration in the solution, or if the ions carry exceptional charge, the electroneutrality is achieved. In accordance with the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, the destabilization and flocculation of particles can be achieved by an enhancement in ionic strength, or ion valence compresses EDL thickness adequately, granting van der Waals forces prolongation beyond EDL. The ionic strength effect explains the particles' stability in freshwater (ionic strength $<$, $>$ EDL extension) and rapid flocculation in saltwater ($>$ ionic strength, $>$ EDL compression) [49];
- (2) **Charge neutralization:** The particles' destabilization is attained with adsorption of ions or polymers with opposite charge. A large number of particles (clays, humic acids, bacteria) in natural waters have a negative charge in neutral pH (pH 6 to 8). Using hydrolyzed metal salts with positive charge and cationic organic polymers, the destabilization of the particles is reached through neutralization of the charge on the particle surface. If the particle surface does not have a net charge, EDL will not subsist and van der Waals forces will make the particles stick together [50–52];
- (3) **Adsorption and interparticle bridging:** In an onwards polymer chain, particles are adsorbed in one or more locations due to (a) coulombic interactions (charge–charge), (b) dipole interaction, (c) hydrogen bonding, and (d) van der Waals forces of attraction. These polymers generate a “bridge” between particle surfaces, promoting the formation of larger aggregates that settle more effectively. When referring to polymer bridging, the best coagulant concentration is proportional to the concentration of the present particles. Adsorption and interparticle bridging materialize due to non-ionic polymers' high-molecular-weight (MW 10^5 to 10^7 g/mol) and low-surface-charge. High-molecular-weight cationic polymers have a great charge density, neutralizing surface charge [49,51];

- (4) Enmeshment in precipitate, or “sweep flocc”: With the application of coagulant in high concentrations, insoluble precipitates produced by iron and aluminum lead to particles becoming entangled in amorphous precipitates, which is known as precipitation and enmeshment or “sweep flocc”. At short coagulant concentrations, steps for iron and aluminum salts were described as (i) hydrolysis and polymerization of metal ions, (ii) hydrolysis products adsorption at the particle surface interface, and (iii) charge neutralization [51].

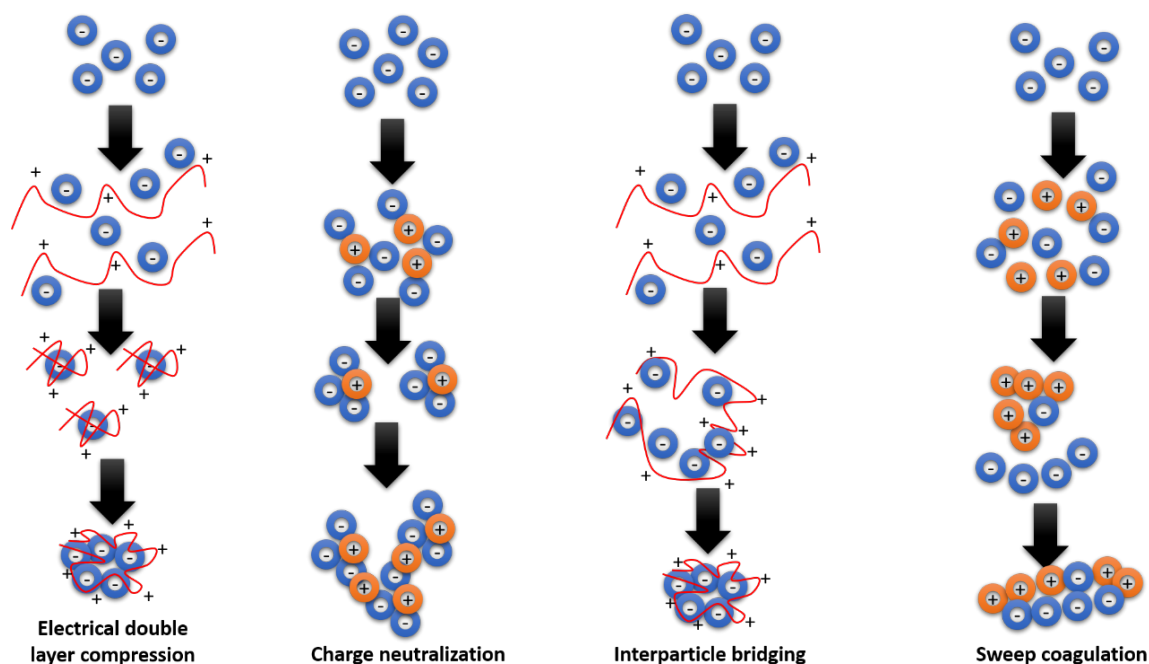


Figure 1. Coagulation–flocculation–decantation mechanism.

2.2. Types of Coagulants

To perform the coagulation mechanism, several types of coagulants can be used. These coagulants can be divided into metal-based coagulants or non-metal-based coagulants (Figure 2).

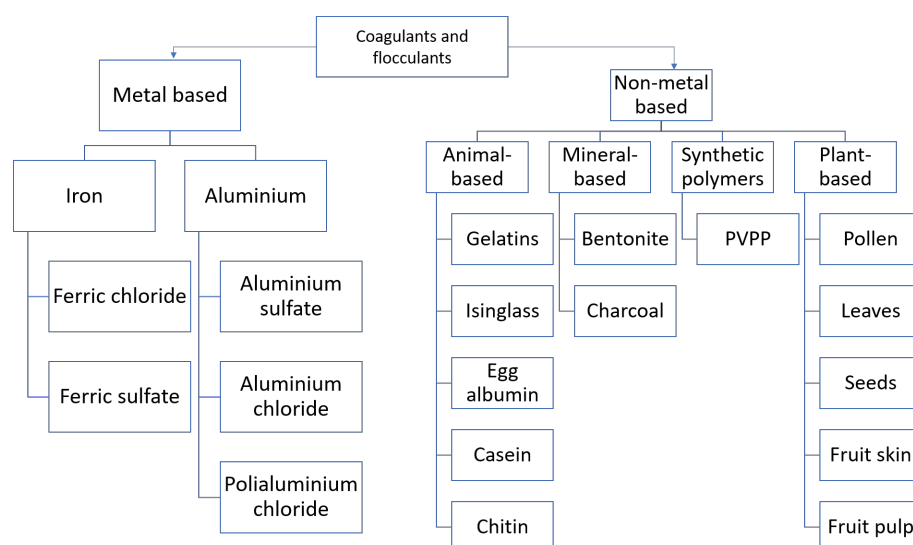


Figure 2. Metal and non-metal coagulants applied to wastewater treatment.

2.2.1. Metal-Based Coagulants

The treatment of IW by CFD processes commonly includes multivalent metal inorganic salts such as aluminum sulfate, ferric chloride, polyaluminum chloride, ferrous sulfate, calcium chloride, and magnesium chloride [53]. Table 2 reveals the main advantages and disadvantages of some inorganic coagulants applied to wastewater treatment.

Table 2. Advantages and disadvantages of metal-based coagulants applied in wastewater treatment.

Coagulant	Advantages	Disadvantages	References
Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$)	A 1% solution of aluminum sulfate corresponds to a pH of approximately 3.5. It is available at low cost and easy to apply.	In excess, it generates residual metal in treated water; the sludge produced by metal salts is often porous, non-compact, and hard to dewater as it has a high moisture content (99–99.7%).	[54]
Ferric chloride (FeCl_3)	The iron composites have floc characteristics and pH ranges similar to aluminum sulfate.	The iron compounds are corrosive, of difficult dissolution, and application leads to high soluble iron concentrations in wastewaters.	[55]
Calcium hydroxide ($\text{Ca}(\text{HO})_2$, lime)	It is a cheap coagulant, easy to apply. It can reduce wastewater components such as polyphenols, oil and grease, total solids, and COD.	Rapid increase in the pH to alkaline levels	[56]
Polyaluminum chloride	A higher efficiency in particle removal is observed, resulting in a smaller pH reduction in the treated water, which reduces the chemical consumption for pH adjustment.	Aluminum salts have been associated with potential health concerns, including a possible link to Alzheimer's disease and other neurological conditions such as presenile dementia.	[57]

2.2.2. Non-Metal-Based Coagulants

Animal-Based, Mineral-Based, and Synthetic Polymers

Considering the disadvantages associated with metal-based coagulants, it is important to find alternative products. A possible choice is the application of non-metal coagulants such as animal-based, mineral-based, and synthetic polymers, which are used in winemaking, posing no threat to human health. In winemaking operations, coagulation processes are commonly used for treating musts and wines. This operation, known as fining, consists of the incorporation of a compound capable of flocculation and/or sedimentation, removing the particles responsible for turbidity by adsorption [58,59]. This operation has the objectives of the clarification and stabilization of the wine, removing the compounds that cause instability, and improving the sensorial characteristics of the wine [59]. In Table 3 are shown some of the most-used coagulants in wine treatment, such as gelatins, c, albumin and egg white, milk and casein, polyvinylpyrrolidone, and activated sodium bentonite.

Table 3. List of non-metal coagulants and their characteristics.

Coagulant	Type	Characteristics	References
Gelatins	Animal-based	Manufacture of gelatins is achieved by near complete hydrolysis of collagen of pig skins and animal bones. The main elements are glycine, proline, hydroxyproline, and glutamic acid. Regarding the electric charge, gelatins are electropositive at acidic pH, and the isoelectric point varies between 7.5 and 9.5.	[58,60]
Isinglass	Animal-based	Isinglass is a raw product generated by the swim bladder of fish, such as sturgeon. The surface charge density ranges from 0.32 to 0.83 meq/g, and the isoelectric point oscillates between 4.20 and 6.48.	[61,62]
Egg albumin	Animal-based	Egg albumin involves many proteins and represents 12.5% of the weight of fresh egg white. It has an isoelectric point of 4.6, and surface charge density ranges from 0.22 to 0.96 meq/g.	[61]
Casein	Animal-based	Casein is heteroprotein holding phosphorus. The manufacture consists of coagulating skimmed milk. It has an isoelectric point of 4.6, and surface charge density estimated at pH 7 is near 0.5 meq/g.	[63]
Chitin	Animal-based	Chitin is a linear polymer composed of N-acetyl-D-glucosamine units linked by $\beta(1-4)$ -glycosidic bonds, synthesized by a large number of living organisms such as insects, algae, or fungi, among others. Chitosan is derived from chitin (the second most abundant polymeric material of biological origin aside from cellulose in the league of polysaccharides).	[64,65]
Sodium alginate	Plant-based	Sodium alginate is an alginic acid salt. The manufacture involves extraction from various Phaeophyceae algae, especially kelp, applying alkaline digestion and purification. Mixture of water with sodium alginate generates a viscous solution with pH between 6 and 8.	[58]
Polyvinylpyrrolidone (PVPP)	Synthetic polymer	Polymerization of vinylpyrrolidone generates water-soluble polyvinylpyrrolidone (PVP). However, in polymerization occurring in the presence of an alkali solution, the pyrrolidone cycle is broken, producing insoluble polyvinylpyrrolidone (PVPP), with high polyphenols affinity.	[58]
Bentonite	Mineral-based	Bentonites are hydrated aluminum silicates, with montmorillonites of simplified formulae, e.g., Al_2O_3 , SiO_2 . The main smectite minerals are sodium, calcium montmorillonite, saponite (magnesium montmorillonite), nontronite (iron montmorillonite), hectorite (lithium montmorillonite), and beidellite (aluminum montmorillonite). Smectite minerals composition encompasses two silica tetrahedral sheets with a central octahedral sheet, 2:1 layer (central octahedral sheet), with water molecules and cations occupying the space between the layers.	[66]
Charcoal	Mineral-based	Charcoal is prepared by pyrolysis, which involves heating the raw materials at high temperatures (600–900 °C), eliminating non-carbon constituents like hydrogen, nitrogen, oxygen, and sulfur as volatile gaseous products, and the residual carbon atoms are rearranged as condensed sheets of aromatic rings with a cross-linked structure in a random manner.	[67]

Plant-Based Coagulants

To achieve objectives related to economically sustainable, environmentally friendly, and viable production, scientific interest has been directed toward the evaluation of the application of unusual protein sources derived from plant products, such as seeds, leaves, and other agricultural by-products [68–71]. It was observed that several plants have the capacity to coagulate and flocculate colloidal particles, thereby reducing turbidity, COD, and color from wastewater. Furthermore, Figure 3 provides a schematic representation of the main mechanisms through which non-metallic coagulants operate in wastewater treatment processes. Several examples include *Moringa oleifera* Lam., *Dactylis glomerata* L., *Daucus carota* L., *Festuca ampla* H., *Vitis vinifera* L., *Platanus × acerifolia* (Aiton) W., *Quercus ilex* L., *Acacia dealbata* L., *Prunus dulcis* L., and *Tanacetum vulgare* L.

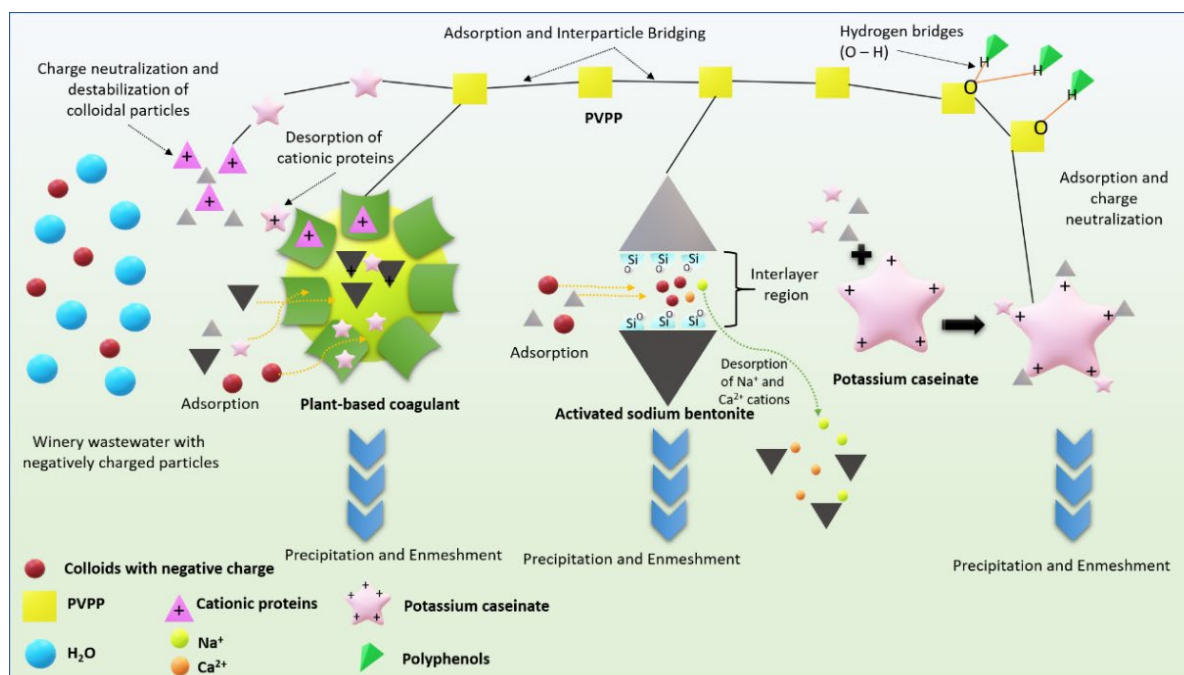


Figure 3. Representation of non-metal coagulants mechanism in wastewater treatment.

When evaluating the advantages of plant-based coagulants (PBCs), the literature offers a range of positive feedback regarding the use of PBCs. PBCs are produced from natural sources, therefore are safer for human health [72]. After CFD treatment, PBCs are easily degradable by bacteria, fungi, and other microorganisms, and the sludge produced is prosperous in nutrients and can be recycled as fertilizer [73]. In Jorge et al. [74], PBCs generated lower sludge volumes in comparison to metal-based coagulants; thus, one advantage of PBCs is the higher compaction of sludge. Finally, it is worth mentioning that several plants used to produce coagulants comes from invasive species, growing in abundance and easily collected (*Acacia dealbata* Link, *Daucus carota* L., *Festuca ampla* Hack., among others). In addition to invasive plants, it has also been used in agriculture sub-products which are produced in large quantities [73].

2.3. Variable Conditions Affecting CFD Process

The effectiveness of the coagulation–flocculation–decantation process depends on several factors, including the type and dose of coagulant, pH, temperature, and mixing conditions. Figure 4 illustrates key operational parameters that must be optimized to maximize the efficiency of the treatment process.

Optimizing the treatment process is crucial, as it allows for the validation of experimental results and contributes to reducing the industrial costs associated with wastewater treatment, leading to a more efficient and controlled process. In this context, several studies have employed Response Surface Methodology (RSM), a combination of statistical and mathematical techniques used to design experiments, develop predictive models, and evaluate the effects and interactions of multiple parameters, with the goal of identifying optimal conditions while minimizing the number of experimental runs [75–77].

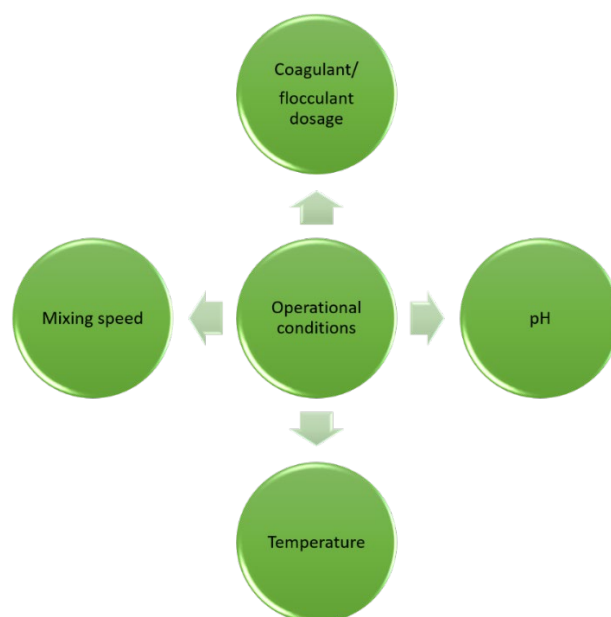


Figure 4. Main operational conditions influencing the CFD process.

2.3.1. Coagulant/Flocculant Concentration Effect

Coagulant and flocculant concentrations affect colloids and suspended-solids removal from wastewater. In Amuda et al. [78], it was observed that increasing FeCl_3 up to a certain concentration enhanced turbidity and suspended-solids removal. Above the optimum concentration, the efficiency decreased. This was related to a re-suspension of the solids, due to the presence of excessive coagulant (above optimum concentration), thus increasing the re-dispersion of the particles. In Jorge et al. [79], increasing PBC concentration resulted in lower total polyphenolic content and chemical oxygen demand (COD) removal from winery wastewater. The best way to determine optimum coagulant dosage is assessing the characteristics and nature of the IW and performance of several Jar-test assays.

2.3.2. pH Effect

The pH is considered an important factor for successful application of the CFD process. In fact, when applied to inorganic coagulants/flocculants, such as iron and aluminum (sulfate or chloride) metal salts, pH directly influences the hydrolysis and polymerization reaction of aluminum and iron ions and charge density [80,81]. In Dotto et al. [82], the PBCs' operational pH was in the acidic range, while aluminum sulfates worked at neutral pH. This was attributed to the presence of cationic protein, which can enhance the coagulant activity at low pH. When pH approaches equal to neutrality, aluminum hydroxide precipitates (main species) generate a sweeping mechanism. So, charge neutralization or sweeping can be reached when pH reaches below the isoelectric point, where the surface charge of the colloids is zero at this pH range [80].

2.3.3. Temperature Effect

Previous studies have shown that the best concentrations of coagulants/flocculants have a tendency to increase as the temperature decreases [83]. In Zhang et al. [84], it was shown that, by reducing the temperature of coagulation, the necessity for higher concentrations of coagulant increased. Two factors are attributed to this: (1) the viscosity of liquid increases with decreasing temperature, which blocks the Brownian movements of colloid particles and decreases the agglomeration as a consequence [84]; (2) at high temperature, the solubility and activity of polymeric coagulants can be upgraded, resulting in a high extended conformation of macromolecules, benefiting the flocculation [83].

2.3.4. Mixing Speed Effect

Proper mixing is required when coagulant is added to the wastewater and during the formation and growth of flocs. When the particle size increases, the stirring can collapse the existing flocs due to disruptive forces, and the collision efficiency of particles in a shear field decrease [85]. In fact, if the shear rate increases, the pre-formed flocs can collapse in a way that depends on floc size relatively to turbulence microscale [86]. In Jorge et al. [19], increasing the mixing speed led to the breakup of flocs formed by both PBCs and ferric chloride, resulting in lower removal efficiencies.

2.4. Application of CFD Process on Treatment of Industrial Wastewaters

Table 4 summarizes several studies employing different types of coagulants (such as metal-based, enological, and PBCs) in the treatment of different wastewater. It is worth mentioning that both enological and PBCs showed similar efficiency in comparison to metal-based coagulants.

In the work of Amuda et al. [78], a beverage wastewater was treated by a CFD process, in which ferric chloride was used as coagulant. The application of optimal operational conditions resulted in a 91% COD reduction. That study showed that polyelectrolyte application improved the efficacy of FeCl_3 and produced more compact sludges. In Amor et al. [87], concentrated-fruit-juice wastewater was treated with application of aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), and ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in a CFD process. The application of 0.4 g/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ at pH = 6.5 achieved 74.5, 75.9, 42.8, and 74.5% removal of COD, turbidity, total polyphenols (TPH), and total suspended solids (TSS). The $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, with 0.4 g/L, showed higher efficiency at lower pH (5.5), achieving 84.5, 95.8, 54.1, and 85.5% reduction of COD, turbidity, TPH, and TSS. Clearly metal-based coagulants show high efficiency; however, considering the disadvantages shown in Table 2, several authors tested the application of enological coagulants as feasible alternatives. In Suzuki et al. [88], casein in combination with FeCl_3 was applied to treat a municipal wastewater, with results showing 98 and 56.3% turbidity and TOC removal. In Jorge et al. [89], a mixture of [potassium caseinate] = 0.4 g L⁻¹, [bentonite] = [PVPP] = 0.1 g/L, pH = 3.0, showed high removal of turbidity, TSS, and organic carbon. Other authors showed that PBCs achieved high efficiency in IW treatment.

Beltrán-Heredia et al. [31] and Ndabigengesere et al. [90] used MO seeds to treat IW, in which MO seeds reduced the organic content and microorganisms, obtaining low sludge volumes. At the same time, MO seeds did not increase the organic content of the wastewater. In Jorge et al. [74], PBCs revealed empty spaces available in their structure; thus, a certain amount of organic carbon could be retrieved by adsorption and then removed along with the sedimentation of the PBCs by gravity. Considering these results, enological coagulants and PBCs appear as good alternatives for metal-based coagulants.

Table 4. Application of coagulation–flocculation process with metal and non-metal-coagulants in industrial wastewater treatment.

Wastewater	Coagulant	Operational Conditions	Results	References
Beverage industrial	FeCl_3	COD = 3470 mg O ₂ L ⁻¹ , [FeCl ₃] = 300 mg L ⁻¹ , Rapid mix = 200 rpm/ 2 min, Slow mix = 60 rpm/ 30 min, Sedimentation time = 1 h, pH = 9, [Polyacrilamine] = 25 mg/L	COD _{rem} = 91%, TSS _{rem} = 97%, TP _{rem} = 99%	[78]
Concentrated fruit juice	$\text{Al}_2(\text{SO}_4)_3$	COD = 21,040 mg O ₂ L ⁻¹ , Turbidity = 719 NTU, pH = 6.5, [Alum] = 0.4 g/L, Rapid mix = 150 rpm/ 3 min, Slow mix = 20 rpm/ 15 min, Sedimentation time = 60 min	COD _{rem} = 74.5%, Turbidity _{rem} = 42.8%	[87]

Table 4. Cont.

Wastewater	Coagulant	Operational Conditions	Results	References
Concentrated fruit juice	FeCl ₃	COD = 21,040 mg O ₂ L ⁻¹ , Turbidity = 719 NTU, pH = 5.5, [Ferric chloride] = 0.4 g L ⁻¹ , Rapid mix = 150 rpm/3 min, Slow mix = 20 rpm/15 min, Sedimentation time = 60 min	COD _{rem} = 84.5%, Turbidity _{rem} = 54.1%	[87]
Landfill leachate	FeCl ₃	COD = 5123 mg O ₂ L ⁻¹ , COD: [FeCl ₃] = 1:2.2, pH = 7.95, Rapid mix = 150 rpm/ 2 min, Slow mix = 50 rpm/30 min, Sedimentation time = 60 min	COD _{rem} = 75.3%	[91]
Olive mill	Lime	COD = 29.3 g L ⁻¹ , TSS = 52.7 g/L, TP = 2.5 mg/L, [Lime] = 30,000 mg L ⁻¹ , [K1] = 287 mg L ⁻¹ , pH = 5.1, rapid mix = 200 rpm/ 2 min, slow mix = 90 rpm/15 min, sedimentation time = 60 min	TSS _{rem} = 88.9%, TP _{rem} = 45.7%, COD _{rem} = 10.5%	[92]
Municipal	Casein	[Fe ³⁺] = 20 mg L ⁻¹ , [Casein] = 3 mg L ⁻¹ , pH = 5.5, Rapid mix = 150/3 (rpm/min), Slow mix = 40/15 (rpm/min), Sedimentation time = 15 min, V = 500 mL	Turbidity _{rem} = 98%, TSS _{rem} = 98%, TOC _{rem} = 56.3%	[88]
Winery	Bentonite PVPP Potassium caseinate	[potassium caseinate] = 0.4 g L ⁻¹ , [bentonite] = [PVPP] = 0.1 g L ⁻¹ , pH = 3.0, Rapid mix = 150/3 (rpm/min), Slow mix = 20/20 (rpm/min), Sedimentation time = 12 h	Turbidity _{rem} = 99.6%, TSS _{rem} = 95.5%, TOC _{rem} = 8.8%, COD _{rem} = 12.4%, Polyphenols _{rem} = 99.9%	[89]
Tofu industrial	PVP	[PAC] = 300 mg L ⁻¹ , V = 500 mL, Fast mix = 120/2 (rpm/min), Slow mix = 40/10 (rpm/min), Sedimentation time = 30 min, filtration by PVDF/PVP membrane	TSS _{rem} = 94.1%, Turbidity _{rem} = 93.0%, TDS _{rem} = 19.9%	[93]
Pulp and paper mills	Bentonite	[PAC] = 400 mg L ⁻¹ , [Bentonite] = 450 mg L ⁻¹ , T = 30 °C, Stirring speed = 300/30 (rpm/min), pH = 7.0	COD _{rem} = 60.87%, Color _{rem} = 41.38%	[94]
Textile dye	Bentonite	[Bentonite] = 0.9 g L ⁻¹ , [OFIP] = 0.4 g L ⁻¹ , Fast mix = 180/5 (rpm/min), Slow mix = 40/25 (rpm/min), Sedimentation time = 15 min	Dye _{rem} = 98.99%	[95]
Laboratory tap water	<i>Moringa oleifera</i> seeds (MO)	[MO] = 50 mg L ⁻¹ , pH = 6.4	Turbidity _{rem} = 90%, EC = 150 µmho cm ⁻¹ , V _{sludge} = 1.5 mL L ⁻¹	[30,90]
Acid red 88 (AR88)	<i>Moringa oleifera</i> seeds (MO)	[AR88] = 78 mg L ⁻¹ , [MO] = 17 mg L ⁻¹ , pH = 4–9, stirring = 30 rpm/ 1 h	TOC < 150 mg C/L	[30]
Methylene blue (MB)/malachite green (MG)	<i>Daucus carota</i> (DC)	[DC] = 2 g L ⁻¹ , pH = 7.0, temperature: 303 K, contact time: 30 min	MB _{rem} = 87%, MG _{rem} = 75%	[96]
Winery	<i>Acacia dealbata</i> Link (ADL)	pH = 3.0, [ADL] = 0.5 g L ⁻¹ , [Bentonite] = 50 mg L ⁻¹ , Fast mix = 150/3 (rpm/min), Slow mix = 20/20 (rpm/min), Sedimentation time = 12 h	TOC _{rem} = 8.4% Turbidity _{rem} = 97.2% TSS _{rem} = 94.8%	[97]

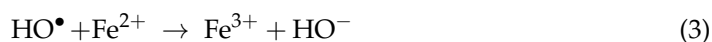
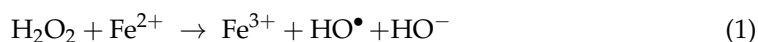
3. Hydroxyl Radical-Based AOPs

3.1. Homogeneous Fenton Process

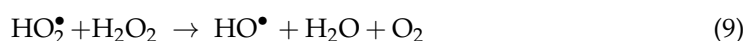
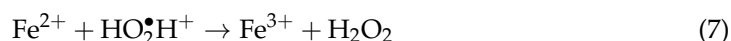
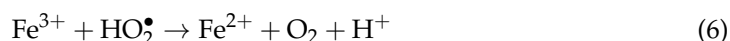
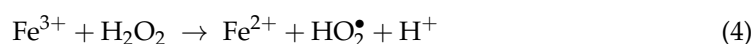
In the previous section, several studies demonstrated that the CFD process was efficient in removing colloidal particles and sediments. However, studies have also shown that the CFD process has limitations in removing dissolved organic carbon. Therefore, other treatment technologies should be investigated, particularly hydroxyl-radical-based advanced oxidation processes (AOPs), such as the Fenton process.

The Fenton process was described for the first time in 1894, in maleic acid oxidation. The Fenton process requires catalytic fragmentation of hydrogen peroxide (H₂O₂) by ferrous iron (Fe²⁺), generating hydroxyl radicals (HO•) according to Equation (1) [98]. The generated HO• radicals are responsible for oxidizing the target organic pollutant (Equation (2)).

The quick decomposition of H_2O_2 by Fe^{2+} (first stage) generates a considerable quantity of $\text{HO}^\bullet$ radicals and oxidizes Fe^{2+} to Fe^{3+} (Equation (3)). Despite the description of the Fenton process in these elementary steps, it is considerably more complex, involving a great deal of reactions. Normally, Fenton reactions can be assembled into Equations (1)–(3) [38,99].

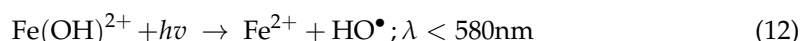


The structure advanced by [100,101] for H_2O_2 fragmenting in acidic solution, in the dark and in the absence of organic compounds, includes Equations (4)–(11). This sequence refers to the thermal Fenton reaction, meaning it is driven by thermal energy from the surroundings rather than photochemical energy. In this sequence, Fe^{2+} and Fe^{3+} are taken to represent all the species present in the solution in each respective oxidation state [102].



3.2. Homogeneous Photo-Fenton Process

The photo-Fenton process is the combination of H_2O_2 , Fe^{2+} , and UV–vis radiation ($\lambda < 600 \text{ nm}$), increasing auxiliary $\text{HO}^\bullet$ radicals by two extra reactions: (1) photoreduction of Fe^{3+} to Fe^{2+} ions, as seen in Equation (12) [103], and (2) briefer wavelengths for H_2O_2 photolysis (Equation (13)) [104]:



The abridged reaction sequence, directing to hydroxyl radical production from H_2O_2 in photo-Fenton processes, is identified by Equation (14) as follows [105]:



Depending on the dosage of reagents added in Fenton and photo-Fenton processes, the reactions can achieve a maximum effect or develop scavenging reactions, reducing the organic load (Figure 5).

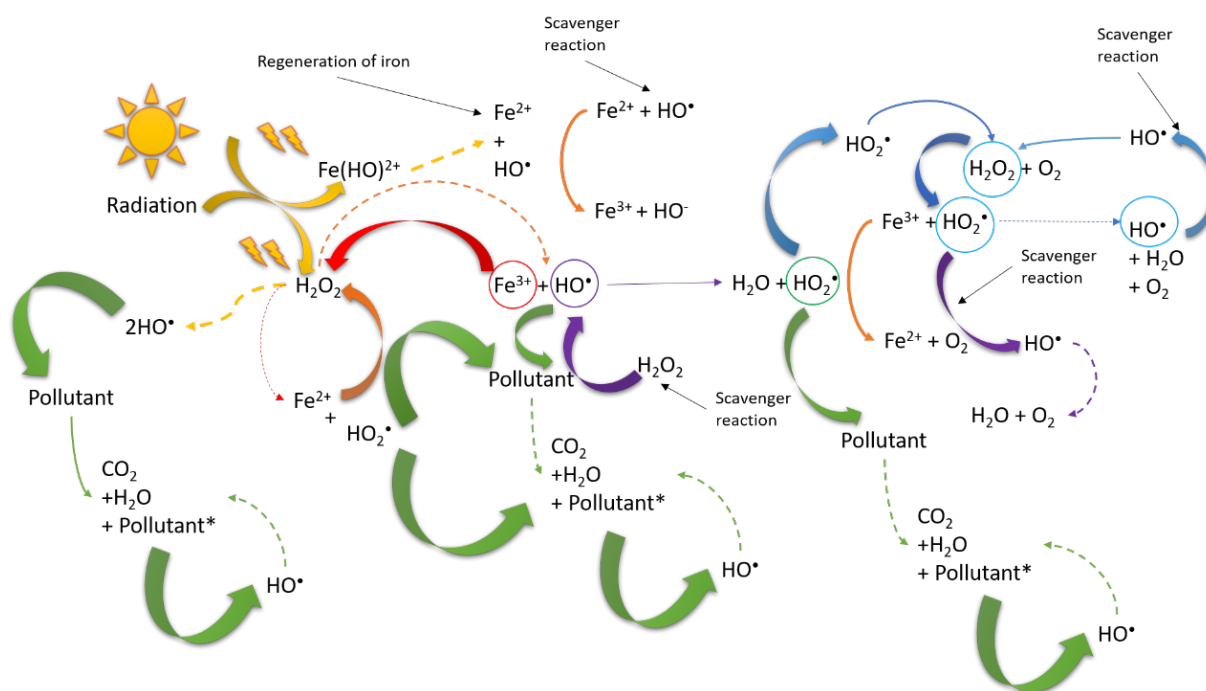


Figure 5. Basic scheme of Fenton-based process. Full arrows represent the attacks performed by the reagents; dashed arrows represent the formation of products; * represents the incomplete mineralization of the pollutant, resulting in the formation of degradation by-products.

The application of UV-C radiation in the photo-Fenton process is effective because its emission wavelength (254 nm) closely matches the absorption bands of ferric species and hydrogen peroxide, thereby enhancing the regeneration of Fe^{3+} to Fe^{2+} and promoting the conversion of H_2O_2 into hydroxyl radicals ($\bullet\text{OH}$) [106,107]. Considering the energy costs associated with UV-C lamps and the mercury hazards, researchers assessed the application of UV-A radiation (365 nm), with results showing a significant improvement of the Fenton reaction with low energy consumption and environmental risks [6,108,109]. Solar compound parabolic collectors (CPCs) have been widely used over the years as a means to collect solar energy to treat large volumes of wastewater at pilot scale. Several studies showed that these reactors were effective in pharmaceuticals mineralization [110,111] and organic carbon reduction of wastewater from beverage industry [112] and wine production [113]. Nowadays, raceway pond reactors (RPRs) have shown a significant growth in wastewater treatment. In an RPR, the liquid runs continually through open channels, pulled by a paddlewheel, in a raceway [114]. RPRs have shown to be efficient in waterborne pathogens inactivation [41,115] and contaminants of emerging concern (CECs) [116] and organic carbon removal from landfill leachate [117].

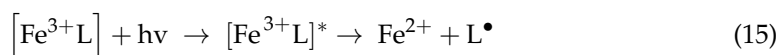
3.3. Iron Chelation in Fenton and Photo-Fenton Processes

The homogeneous Fenton and photo-Fenton process shows high effectiveness in organic contaminants degradation. However, several disadvantages are associated with these processes, such as the following [118,119]:

- (1) The Fe^{3+} regeneration is very slow, producing $\text{HO}_2^\bullet$ with low kinetic rates;
- (2) An acidic pH is required to avoid catalyst precipitation;
- (3) It is necessary to neutralize the treated water to recover the catalyst and to obtain a pH near neutral (6.0–8.0).

As a means to avoid these drawbacks, iron-chelating agents can be considered. These iron-chelating complexes keep their solubility at high pH, have high absorbance in the

UV-vis region, and are highly reactive photochemically via ligand-to-metal charge transfer (Equation (15)) [120].



Among the different chelating agents available, the application of ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-disuccinic acid (EDDS), diethylenetriaminepentaacetic acid (DTPA), L-Glutamic acid N,N'-diacetic acid (GLDA), hydroxyethyl ethylenediaminetriacetic acid (HEDTA), hydroxyethyliminodiacetic acid (HEIDA), citric acid (CA), oxalic acid (OA), and nitrilotriacetic acid (NTA) (Figure 6) has been reported. EDTA is an amino polycarboxylic acid (APC) that acts as a hexadentate agent when it reacts with metal ions. However, several studies showed that it has low degradability, is recalcitrant, and endures in the environment [121]. Hu et al. [122] showed that an EDTA-Fe(III) Fenton-like system could be applied in neutral conditions to remove textile dyes from wastewater; however, considering the disadvantages associated with EDTA, more sustainable approaches can be used. EDDS is an APC, with two chiral centers, existing as an enantiomeric isomer ((R,R')-EDDS and (S,S')-EDDS) and one meso isomer (R,S)-EDDS [123]. Ye et al. [124] observed that application of Fe^{2+} -EDDS or Fe^{3+} -EDDS enhanced the production of $\text{HO}^\bullet$ radicals, favoring the removal of fluoxetine from urban wastewaters by the photo-electro-Fenton process. DTPA is an octadentate chelating agent, with a high stability constant; however, it has low biodegradability and solubility in water and acidic solutions [125]. Li et al. [126] applied DTPA as a complexing agent with thallium (Tl). The results showed that DTPA was broken into smaller molecules that complexed with iron hydroxides under alkaline conditions, reducing the iron precipitation. GLDA is a chelating agent with high solubility in water. In the work of Guo et al. [127], it was shown that GLDA had higher capacity than EDTA to remove cadmium, zinc, lead, and copper from wastewater. HEDTA (APC) has a structure of a quinque-dentate chelating agent, structural like EDTA, with a hydroxyethyl group in place of one acetate group, which improves its solubility regarding EDTA [128]. HEIDA has a structure of a tridentate chelating agent, closer to NTA; however, it has only two acetate groups and a hydroxyethyl group, with high solubility and biodegradability [129]. CA is a natural compound of citrine fruits. The Fe^{3+} -citrate molecules can undergo a ligand-to-metal charge transfer process and then an oxygen-related radical cycling, producing Fe^{2+} and radicals such as $\text{HO}^\bullet$, $\text{HO}_2^\bullet/\text{O}_2^{\bullet-}$, and H_2O_2 [130]. Serna-Galvis et al. [131] observed that citric acid enhanced the removal of antibiotics such as ciprofloxacin, norfloxacin, and levofloxacin by solar photo-Fenton. OA is a strong organic acid with a pKa of 1.3–4.3. Its conjugated base, oxalate ($\text{C}_2\text{O}_4^{2-}$), acts as a chelating agent of metal ions. It is a bidentate ligand with four atoms with one pair of electrons. This photosensitive complex can expand the range of the solar spectrum up to 450 nm, thus improving radical generation and consequently oxidation efficiency [132]. In the work of Giménez et al. [133], using an Fe^{2+} /oxalate 1:10 molar ratio, a considerable development of paracetamol removal by the photo-Fenton process was shown. NTA (APC) is a tripodal tetradentate trianionic ligand, capable of forming water-soluble compounds with divalent or trivalent metal ions [132]. NTA has shown considerable advantages in the treatment of real wastewaters, such as shown by Teixeira et al. [134], in which NTA improved DOC removal from winery and olive mill wastewaters under the photo-Fenton process.

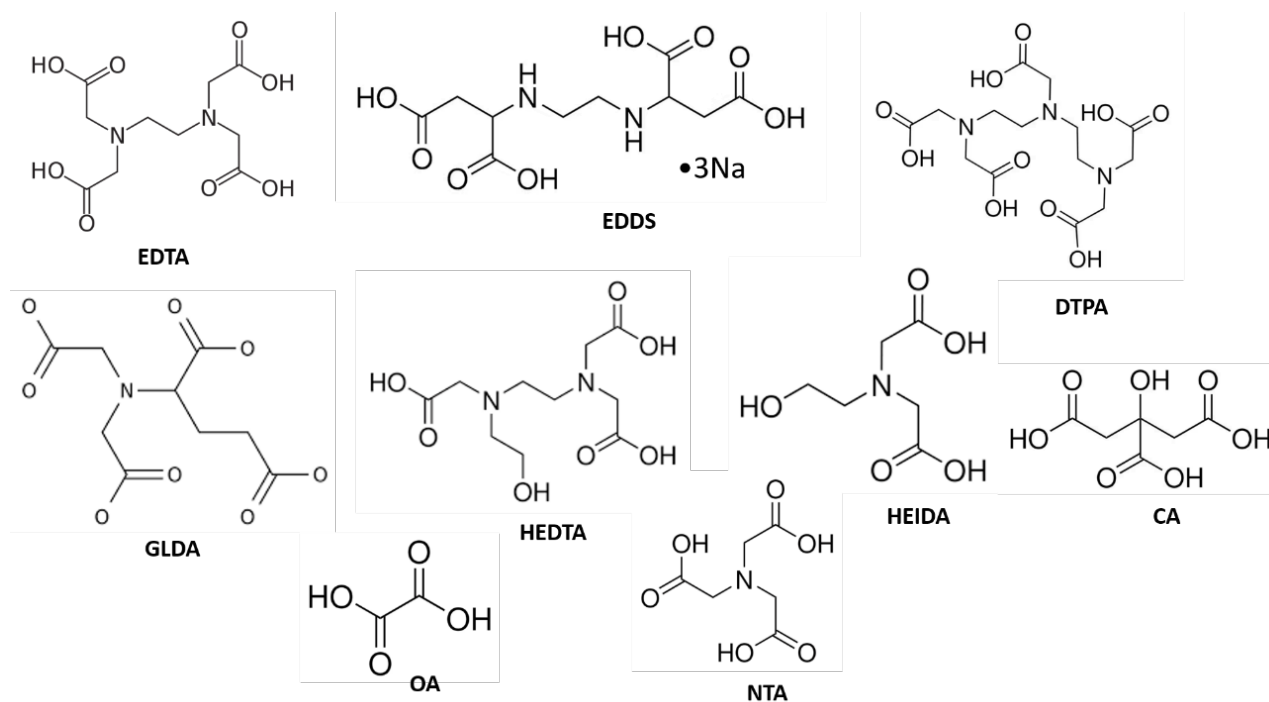


Figure 6. Chemical structure of chelating agents used in industrial wastewater treatment.

3.4. Heterogeneous Fenton and Heterogeneous Photo-Fenton Processes

Another way to reduce the impact of homogeneous catalysis is by employing heterogeneous catalysts. Recalcitrant pollutants have been degraded with success using heterogeneous Fenton oxidation. Two evident advantages of heterogeneous Fenton oxidation are (1) sludge cutting and (2) the wider range of pH operating potential [38]. Similarly to the homogeneous Fenton and photo-Fenton processes, in heterogeneous catalysis, iron existing in the surface of the catalyst reacts with H_2O_2 , producing $\text{HO}^\bullet$ radicals and resulting in mineralization of organic matter from the wastewater. However, considering the porous nature of the catalysts, adsorption of contaminants occurs simultaneously [135]. Figure 7 shows the mechanism proposed for the heterogeneous photo-Fenton process.

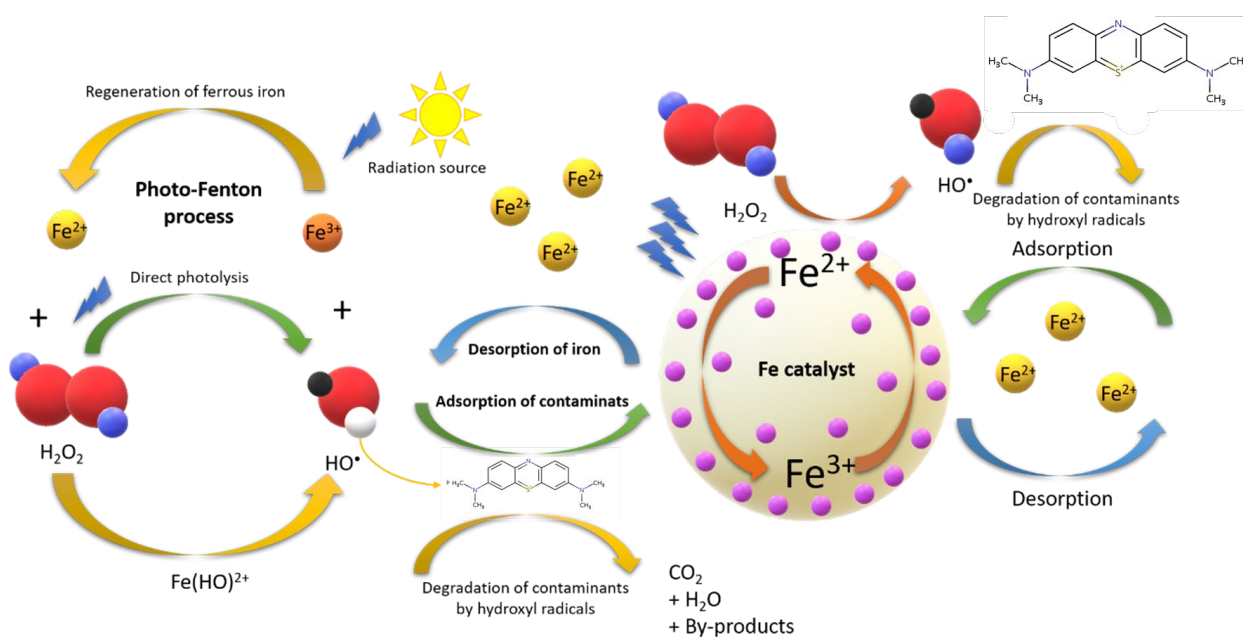


Figure 7. Heterogeneous photo-Fenton mechanism.

There are several materials that can be used as physical support for the iron. Table 5 shows the characteristics of some of these materials.

Table 5. Materials used for heterogeneous catalysts.

Materials	Characteristics	References
Alginate	Alginate is a biopolymer acquired by brown algae and bacteria. It is composed of mannuronic and guluronic acid residues and blocks of these ranged alternately.	[136]
Chitosan	Chitosan is a biopolymer generated by living organisms. Chitosan is biodegradable, non-toxic, and easily available.	[137]
Silica	Silica exists both crystalline and amorphous forms. The advantages of using silica to produce iron-based catalysts lie in the properties of the material, like pore volume and diameter, structural stability, and large surface area.	[138]
Zeolite and perlite	Zeolites are crystalline hydrated aluminosilicates, built upon cations, alkali pieces, or alkali earth metals. They have well-defined porous structure with micropores distributed in molecular dimensions. Perlite is amorphous, glassy volcanic rock that can expand to beyond original volume (20 times) in the presence of high temperatures (700–1100 °C).	[139,140]
Activated carbon	Activated carbon is a material that can be produced from raw agriculture by-products, like coconut shells, sugarcane bagasse, or rice husk, among others. It is characterized by high surface area, porosity, and stability.	[141]
Biochar	Biochar is characterized by a high porosity and surface area. It is an excellent material for iron-based catalysts because (1) it can be used raw agro-waste to produce biochar, and (2) the porosity, surface area, and functional groups can be enhanced.	[142]
Clay minerals	Clay minerals are a group of hydrous aluminum phyllosilicates. Their small dimensions and sizable proportion of surface area to volume gives them a set of significant properties, namely, high cation-exchange capacity (CEC), catalytic properties, and plastic behavior when wet. Furthermore, clay minerals are cheap, abundant, and environmentally friendly.	[119,143]

3.5. Employment of Fenton-Based Processes to Wastewater Treatment

The Fenton-based processes have proven to be effective in producing hydroxyl radicals ($\text{HO}^\bullet$); however, it is essential to understand their performance in the treatment of IW. Table 6 shows examples of treatments carried out with homogeneous Fenton, homogeneous photo-Fenton, and heterogeneous photo-Fenton processes. In Lucas et al. [144], winery wastewater with a COD of $20 \text{ g O}_2 \text{ L}^{-1}$ was treated by a combined biological–Fenton process. Although the biological process showed effectiveness, $1560 \text{ mg O}_2 \text{ L}^{-1}$ COD remained undegraded due to its recalcitrant nature. By application of the Fenton process, it was observed that a mass ratio of $2.5 \text{ H}_2\text{O}_2/\text{COD}$ achieved 93.2% COD degradation. Although the Fenton process shows effectiveness, there is a high consumption of oxidant. To reduce this consumption, in the work of Ormad et al. [145], a Xenon light emitting at 290–400 nm was used to treat a WW. The use of UV radiation enhances the Fenton process's efficiency and improves the degradation of organic carbon.

In Primo et al. [146], the following order was considered: photo-Fenton > Fenton-like > Fenton > UV/ H_2O_2 > UV. In Jorge et al. [19], DOC removal results were fitted to a pseudo-first-order kinetic rate ($\ln[\text{DOC}] = -kt + \ln[\text{DOC}]_0$), which showed a significantly increased kinetic rate with the application of the photo-Fenton. By application of electric energy per g/DOC (Equation (16)) it was seen that the CFD with photo-Fenton process combination had no real change in energy consumption; however, operational costs were observed to decrease from 2.05 EUR/gDOC to 1.79 EUR/gDOC.

$$E_{\text{EM}} = \frac{P \times t}{(\text{DOC}_i - \text{DOC}_f) \times V} \times 1000 \quad (16)$$

where E_{EM} is the electric energy per mass (kWh g/DOC); P is the nominal power (kW); t is time (h); and V is the volume (dm^3). Although the photo-Fenton process showed an efficiency increase, there is still the problem of the iron leaching associated with these types

of treatments. To solve this issue, in Guimarães et al. [147], an iron-based catalyst was built, using smectite as base material. Increased organic carbon removal was shown with heterogeneous photo-Fenton application. The results were fitted into Fermi's kinetic model (Equation (17)), with results showing a $k = 0.0294 \text{ min}^{-1}$. Finally, the catalyst showed good regeneration, able to remove high content of organic carbon for three consecutive cycles.

$$\frac{\text{DOC}}{\text{DOC}_0} = \frac{1 - x_{\text{DOC}}}{1 + \exp[k_{\text{DOC}}(t - t_{\text{DOC}}^*)]} + x_{\text{DOC}} \quad (17)$$

where k_{DOC} corresponds to the apparent reaction rate constant; t_{DOC} represents the transition time related to the DOC content curve's inflection point; and x_{DOC} corresponds to the fraction of non-oxidizable compounds that are formed during the reaction.

A real WW was treated by a combined adsorption/heterogeneous photo-Fenton process. The adsorption process was performed employing montmorillonite clay, which revealed effectiveness in adsorption of organic matter from wastewater, with 52.5% TOC removal. Then, the impregnation of Fe^{2+} was performed toward montmorillonite clay—Fe-Mt. The Fe-Mt catalyst was used in a heterogeneous photo-Fenton (H-PF) process, achieving a TOC removal of 88.3%. The results were fitted with success to Fermi's kinetic model, achieving a high kinetic rate ($k_{\text{TOC}} = 2.95 \times 10^{-2} \text{ min}^{-1}$).

Although batch systems showed high efficiency in IW treatment, it is necessary to study pilot systems in order to adapt treatments to a larger scale. In the work of Campos et al. [148], seven contaminants of emerging concern (CECs) were degraded by solar photo-electro-Fenton (SPEF), employing a solar electrochemical raceway pond reactor (SEC-RPR). Based on the results, the reactor's geometry provided a high contact area between the wastewater and natural UV radiation, along with continuous and uniform electrogeneration of H_2O_2 within the system. This combination enhanced the efficiency of pollutant removal through the SPEF process. In the work of Salazar et al. [149], a SEC-RPR was used to degrade industrial wastewater polluted by a textile dye, methyl orange (MeO). The results showed that the application of electric current allowed the electrogeneration of H_2O_2 , in which its conversion was accelerated by the solar radiation, thus reaching MeO-contaminant near complete removal. It is also important to consider the economic efficiency of these types of reactors so that they can be applied in industrial wastewater treatment at pilot scale. In Belachqer-El Attar et al. [150], an RPR was used to degrade an antibiotic sulfamethoxazole (SMX) contaminant by a solar-Fenton process. On application of the optimal operational conditions, the results showed low treatment costs (141 mg SMX/EUR·h); thus, RPRs could be feasible for industrial wastewater treatment at large scale.

Although the successful application of Fenton and photo-Fenton-based processes has been reported, in many cases, wastewater has high content in turbidity, TSS, and polyphenols, which blocks the penetration of radiation and scavenges the $\text{HO}^\bullet$ radicals. In Jorge et al. [151], a WW presented high values of COD ($2148 \text{ mg O}_2 \text{ L}^{-1}$), turbidity (295 NTU), and TSS (752 mg L^{-1}). With the performance of solar-Fenton, the results showed 81.6% COD removal. With the employment of CFD with *Acacia dealbata* pollen, turbidity and TSS were reduced by 97.6 and 94.7%. Solar-Fenton as a post-treatment reached 90.4% COD removal. In a different case, a landfill leachate wastewater was analyzed, revealing $4950 \text{ mg O}_2 \text{ L}^{-1}$ (COD) and 5040 mg L^{-1} (TSS) [152]. Considering the high organic carbon content, a high demand in reagents would be required for Fenton-based processes to remove organic carbon. Thus, electrocoagulation was initially performed, using the best conditions ($\text{pH} = 6.87$, current density 120 A m^{-2} , time = 17.3 min), reaching 72.5 and 82.5 COD and TSS removal, respectively. Then, a photo-Fenton process was employed ($\text{pH} = 3$, $\text{HP}/\text{COD} = 2$; $\text{Fe}^{2+}/\text{HP} = 0.3$, radiation UV-C, time = 20 min), reaching 93.1% COD

removal. Thus, based on these results, for highly contaminated wastewater, a pre-treatment with CFD is recommended before HR-AOPs.

Table 6. Appliance of Fenton-based processes to industrial wastewater treatment.

Wastewater	Catalyst	Operational Conditions	Results	References
Winery	Fe ²⁺	pH = 3.5, BOD ₅ /COD = 0.55, [H ₂ O ₂]:[Fe ²⁺] = 15	COD _{rem} = 93.2%	[144]
Reactive Black 5 (RB5)	Fe ²⁺	pH = 5.0, [H ₂ O ₂] = 7.3×10^{-4} mol L ⁻¹ , [Fe ²⁺] = 1.5×10^{-4}	[RB5] _{rem} = 95%	[153]
Olive mill	Fe ²⁺	pH = 3.5, [H ₂ O ₂]:[Fe ²⁺] = 15	COD _{rem} = 17.6%, TPh _{rem} = 82.5%	[154]
Municipal	Fe ²⁺	pH = 6.0–7.0, [H ₂ O ₂] = 30 mg L ⁻¹ , [Fe ²⁺] = 4 mg L ⁻¹ , radiation = UV-C	Pollutant _{rem} = 95%	[155]
Landfill leachate	Fe ²⁺	pH = 3.0, [H ₂ O ₂] = 10,000 mg L ⁻¹ , [Fe ²⁺] = 2000 mg L ⁻¹ , radiation = UV-C	COD _{rem} = 86%	[146]
Winery	Fe ²⁺	pH = 3.0, [H ₂ O ₂] = 0.5 M, [Fe ³⁺] = 5 mg L ⁻¹ , radiation: Xenon emitting at 290 and 400 nm spectral range.	TOC _{rem} = 95%	[145]
Winery	Fe ²⁺	[DOC] ₀ = 400 mg C/L, [Fe ²⁺] = 2.5 mM, [KPS] = 1.0 mM, [PMS] = 1.0 mM, pH = 3.0, radiation UV-C, mercury lamp (254 nm), agitation 350 rpm, temperature 298 K, reaction time 240 min	TOC _{rem} = 84.9%	[19]
Sulfamethazine (SMT), carbamazepine (CBZ), diclofenac (DFC), ibuprofen (IBF), β-estradiol (E2), progesterone (P4) and estrone (E1)	Fe ²⁺	[CEC] = 100 µg L ⁻¹ , V = 20 L, [Na ₂ SO ₄] = 0.05 M, [Fe ²⁺] = 0.05 mM, pH 3, current density 20 mA cm ⁻² , conductivity 1.62 mS cm ⁻¹ , RPR with solar light	CEC _{rem} = 90–96%	[148]
Caffeic acid (CA)	Fe ²⁺	[CA] = 5.5×10^{-4} mol L ⁻¹ , [Fe ²⁺] = 1.1×10^{-4} mol L ⁻¹ , pH = 3.0, radiation UV-A, I _{UV} = 32.7 W m ⁻² , F = 4 mL min ⁻¹ , agitation 150 rpm, temperature = 298 K, HRT = 15 min	Ca _{rem} = 99.2% DOC _{rem} = 35.9%	[156]
<i>E. coli</i> contaminated wastewater Trimethoprim (TMP) contaminated wastewater	Fe ³⁺ -NTA	5-cm deep RPRs with solar light, [Fe ³⁺ -NTA] = 0.2 mM Fe, [H ₂ O ₂] = 4.41 mM, pH = 7, time = 60 min— <i>E. coli</i> inactivation 5-cm deep RPRs, [TMP] = 50 µg/L, [Fe ³⁺ -NTA] = 0.2 mM, [H ₂ O ₂] = 4.41 mM, pH = 7—TMP removal	<i>E. coli</i> _{rem} < detection limit TMP _{rem} = 95%	[115]
Urban wastewater contaminated with Diclofenac (DCF)	Fe ³⁺ -EDDS	[DCF] = 100 µg/L, [Fe ³⁺] = 0.1 mM, [EDDS] = 0.1 mM, [H ₂ O ₂] = 50 mg/L, pH = 7, RPR with solar light	DCF _{rem} > 99%	[116]
Winery	Fe ²⁺ -EDDS	pH = 6.0, [H ₂ O ₂] = 175 mM, [Fe ²⁺] = 5 mM, [EDDS] = 1 mM, T = 298 K, solar radiation, time = 240 min	COD _{rem} = 81.6%	[151]
Landfill leachate	Fe ²⁺	pH = 3, H ₂ O ₂ /COD = 2, Fe ²⁺ /H ₂ O ₂ = 0.4, time = 20 min (Fenton) pH = 3, H ₂ O ₂ /COD = 2; Fe ²⁺ /H ₂ O ₂ = 0.3, radiation UV-C, time = 20 min (Photo-Fenton)	COD _{rem} = 71.9% (Fenton) COD _{rem} = 75.1% (photo-Fenton)	[152]
Acid Black 194 (AB194) dye	Fe ²⁺	pH = 2.31, [Fe ²⁺] = 1977 mg L ⁻¹ , [H ₂ O ₂] = 3679 mg L ⁻¹ , agitation = 190 rpm, T = 20 °C, time = 180 min	COD _{rem} = 89% TOC _{rem} = 87%	[157]
Cheese wastewater	Fe ³⁺	COD = 12,511 mg O ₂ L ⁻¹ , pH = 3, [Fe ³⁺] = 5.0×10^{-4} mol L ⁻¹ , [H ₂ O ₂] = 0.2 mol L ⁻¹ , radiation = UV-A, t = 24 h	COD _{rem} = 91.2% TOC _{rem} = 97.5%	[158]
Industrial wastewater with methyl orange (MeO)	Fe ²⁺	Solar electrochemical-raceway pond reactor (SEC-RPR), [MeO] = 20 mg L ⁻¹ , pH = 3, [Fe ²⁺] = 0.05 mM, A = 40 mA cm ⁻² , solar UV radiation = 38 W m ⁻²	[MeO] _{rem} > 99% TOC _{rem} > 80%	[149]
Sulfamethoxazole (SMX)	Fe ³⁺ -NTA	5-cm deep raceway pond reactors (RPR), [H ₂ O ₂] = 1.47 mM, [NaOCl] = 0.134 mM, [Fe ³⁺ -NTA] = 0.1 mM	[SMX] > 50%	[150]
Winery wastewater	Fe-Sm	[H ₂ O ₂] = 98 mM, [Catalyst] = 3.0 g L ⁻¹ , pH = 4.0, UV-C (254 nm)	TOC _{rem} = 65.1%	[147]
Winery wastewater	Fe-Mt	[Fe-Mt] = 3.0 g L ⁻¹ —single addition, [H ₂ O ₂] = 136 mM, pH 3.0, agitation 350 rpm, reaction time 270 min, radiation UV-C mercury lamp (254 nm)	TOC _{rem} = 52.5% (Ads) TOC _{rem} = 88.3% (H-PF)	[159]
Acid black 1 (AB1)	Pillared laponite clay-based Fe nanocomposites (Fe-Lap-RD)	[H ₂ O ₂] = 6.4 mM, [Catalyst] = 1.0 g L ⁻¹ , pH = 3.0, UV-C (254 nm)	TOC _{rem} = 100%	[160]
Winery wastewater	LaCoO ₃ –TiO ₂ composite	[MPS] = 0.01 M, [Catalyst] = 0.5 g L ⁻¹ , pH = 7.0, UV-A light	Polyphenols _{rem} = 95%, COD _{rem} = 60%	[161]

4. Sulfate Radical-Based AOPs

Concerns about persulfate began around 2000–2002, with persulfate work showing often in conference proceedings and presentations at leading remediation meetings [162]. Since then, sulfate radical-based AOPs (SR-AOPs) have been constantly attracting attention, complementing HR-AOPs oxidation processes. Peroxymonosulfate (HSO_5^- ; PMS), a solid white powder, is a triple potassium salt ($2\text{KHSO}_5 \bullet \text{KHSO}_4 \bullet \text{K}_2\text{SO}_4$) active agent. It is stable at $\text{pH} < 6$ or $\text{pH} > 12$. At $\text{pH} 9$, PMS presents low stability, and half of HSO_5^- breaks down to SO_5^{2-} [163]. PMS is quickly dissolved in water, with solubility $> 250 \text{ g L}^{-1}$; it shows an asymmetrical structure, its water solution is acidic, its O–O bond distance is $1.453 \text{ \AA}$, and its bond energy is estimated in the range $140\text{--}213.3 \text{ kJ/mol}$ [163–166]. Its advantages when compared to H_2O_2 are recognized, such as its HSO_5^- oxidation potential ($E^\circ = 1.82 \text{ V}$) being higher than H_2O_2 ($E^\circ = 1.78 \text{ V}$), although lower than hydroxyl radicals ($E^\circ = 2.80 \text{ V}$) [167].

Persulfate (PS) is a crystal without color, of high stability, comfortably dissolved in water (solubility $\approx 730 \text{ g L}^{-1}$) [168], with a symmetrical structure; its water solution is acidic, its distance of O–O bond is $1.497 \text{ \AA}$, and its bond energy is 140 kJ/mol [163,164]. Peroxydisulfate (PDS, $\text{S}_2\text{O}_8^{2-}$) is often found in the form of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), and ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) [169]. The persulfate sodium anion ($\text{S}_2\text{O}_8^{2-}$) is a strong oxidant ($E^\circ = 2.01 \text{ V}$), activated by heat, light, ultrasound, or catalyst, generating sulfate radicals ($\text{SO}_4^{\bullet-}$) [170].

When compared to Fenton-based processes, the application of SR-AOPs has several advantages [171]:

1. The concentration of oxidant agent necessary for $\text{SO}_4^{\bullet-}$ radicals generation is solid at room temperature, facilitating delivery and holding;
2. $\text{SO}_4^{\bullet-}$ radicals have considerable steadiness and a longer life span than $\text{HO}^\bullet$ radicals;
3. Fenton-based processes require acidic pH (around 3); however, SR-AOPs operate in a wider pH range (3–9);
4. In aqueous solution, $\text{SO}_4^{\bullet-}$ radicals have greater solubility than $\text{HO}^\bullet$ radicals;
5. The efficiency of $\text{HO}^\bullet$ radicals are limited, considering that they act throughout unselective multi-step pathways.

However, there are several drawbacks associated with sulfate radical generation:

1. In heat activation, which involves increasing temperatures, the rate of reaction is accelerated; however, it can result in very aggressive oxidizing conditions and high energy consumption [162];
2. Ultraviolet penetration into water is constrained and unfeasible in the subsurface, affecting UV-activated PS and PMS reactions enforcement;
3. Dissolved metal ions reacts with PS and PMS; however, metal ions recovery is hard in homogeneous systems [163,172].

4.1. Activation Methods of Persulfate

Several approaches are adapted for PS and PMS activation, such as, heat, UV, alkaline, metal ions, and activated carbon (Figure 8) [173]. The redox potential of sulfate radicals produced through activation of PDS and PMS depends on the activation methods [163].

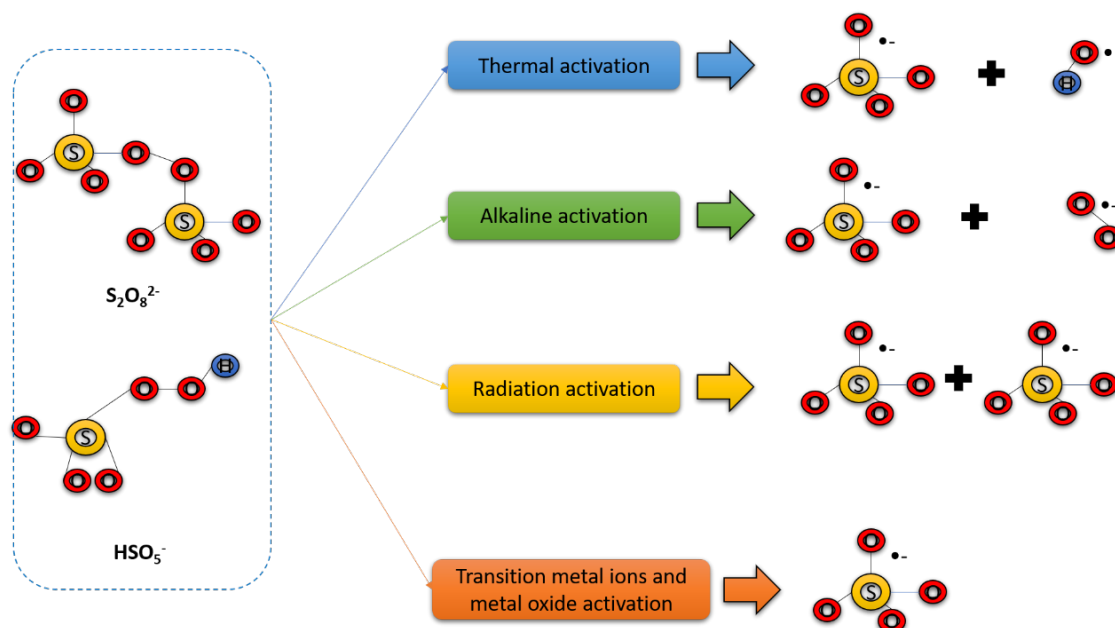


Figure 8. Activation methods of peroxymonosulfate and persulfate.

4.1.1. Thermal Activation

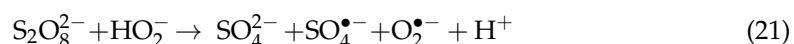
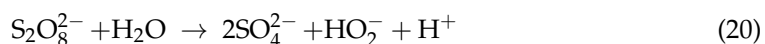
Rising the temperature is an effective way to accelerate the decomposition of PMS and PS and generate $\text{SO}_4^{\bullet-}$ radicals [173]. To acquire O–O bond fission of the PS and PMS structure, a high amount of energy is required to be applied ($140\text{--}213.3\text{ kJ mol}^{-1}$) during the treatment process. For this reason, high temperatures application can activate PS and PMS ($>50\text{ }^\circ\text{C}$), causing O–O bonds fission, generating $\text{SO}_4^{\bullet-}$ radicals with PS (Equation (18)) and $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ radicals with PMS (Equation (19)) [163]:



4.1.2. Alkaline Activation

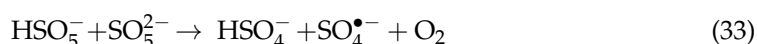
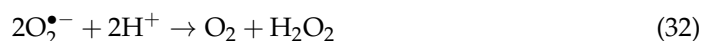
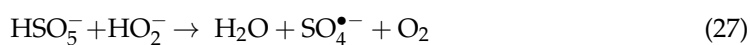
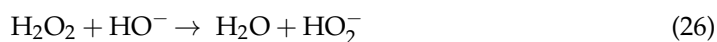
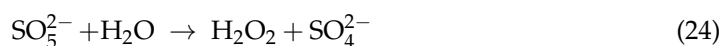
Most IWs have alkaline pH, which makes FBPs employment difficult and requires acid consumption to reduce the pH, increasing the operational costs. However, PS and PMS can be activated in alkaline conditions, avoiding higher costs. Liang and Su [174] and Yang et al. [175] observed inter-conversions between $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$, as follows: (1) at pH < 7 , $\text{SO}_4^{\bullet-}$ is the prevailing radical; (2) at pH = 9, $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ are both present; (3) at pH > 9 , $\text{HO}^\bullet$ is prevailing radical.

For PDS alkaline activation, O–O bond nucleophilic attack is the contemplated main mechanism, as shown in Equations (21) and (22) [176]:



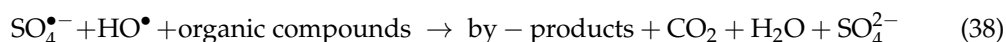
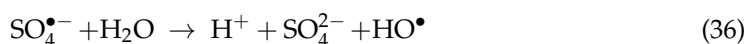
For alkaline activation of PMS, a similar mechanism is observed but with different pathways, as observed in Equations (22)–(33) [177], as follows:





4.1.3. Radiation Activation

Ultraviolet, gamma ray, and ultrasonic radiation activates PS and PMS. Quantum yields of sulfate radicals decrease with UV wavelength increments in the 248–351 nm range, with 0.12 (248 nm) and 1.4 (253.7 nm); thus, 254 nm is best wavelength for persulfate [178]. The UV/PS and UV/PMS process removes organic pollutants directly by photolysis or indirectly by $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ radicals, as shown in Equations (34)–(38) [179]:

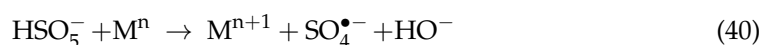


An efficient mechanism that has been applied to achieve thermal activation of PS and PMS is ultrasound radiation. With ultrasound (US) activation, two mechanisms are implied simultaneously: (1) the increase in the wastewater temperature, caused by cavitation of bubbles, which activates PS and PMS; and (2) cavitation bubbles break down water molecules into $\text{HO}^\bullet$ radicals and H_2O_2 , enhancing PS and PMS activation [163]. In Daware et al. [180], 4-Methylpyridine (4-MP) degradation was shown by application of PS and PMS in combination with an ultrasound. It was observed that, by increasing power from 15 W to 120 W, the 4-MP degradation increased from 20.76 to 43.76%, respectively. When applied in combination with the electrochemical activation of PS and PMS, it promoted reactive oxygen species (ROS) generation, and the mechanical oscillation effect of US accelerates mass transfer, enhancing pollutants degradation [181].

4.1.4. Transition Metal Ions and Metal Oxide Activation

PS and PMS can be activated with efficiency by transition metals application, such as silver, copper, iron, zinc, cobalt, and manganese, for sulfate radical production, through one-electron transfer [169,182]. A great deal of studies concerning iron and its oxide were performed because they are mostly non-toxic, environmentally friendly, and cost-effective compared to other transition metals [183]. Ferrous iron is shown to be effective in PS and PMS activation, while ferric iron shows worse activation performance [184,185]. Dissolved metal ions can react with PS and PMS freely in homogeneous systems; thus, mass transfer

has a low effect on PS and PMS activation. For the activation of PS and PMS by metal ions and metal oxide, the mechanism is reduction, observed in Equations (39) and (40) [163]:



4.2. Application of Sulfate Radicals in Wastewater Treatment

Table 7 presents studies of the treatment of IW employing sulfate radicals. It shows the operational conditions and the attained efficiencies. In Rodríguez-Chueca et al. [186], KPS was activated by ferrous iron in a solar reactor for the treatment of WW. The photolytic and catalytic solar-driven sulphate radical generations were concluded to be a feasible technology, with a COD removal = 67%. In Li et al. [187], a copper-spent activated carbon (Cu-AC) was employed for peroxydisulfate (PDS) activation and for Acid Orange 7 (AO7) decolorization, and electrical current was introduced to enhance the process. The results showed that by increasing current density, $\text{HO}^\bullet$ and $\text{SO}_4^{\bullet-}$ radicals generation was increased, thus increasing the degradation of AO7. Tannic acid (TA) is a major pollutant present in the wastewater generated from the vegetable tanneries process and food processing. In the work of Dbira et al. [188], two AOPs (UV irradiation at 254 nm + hydrogen peroxide (H_2O_2) and ferrous iron (photo-Fenton) in the presence of potassium persulfate) were added for TA removal. The results showed a similar removal of TA by UV/PS in comparison to the photo-Fenton process (96.38 and 99.32%, respectively). When compared with studies involving application of HR-AOPs for IWW treatment [11,189], the results show high consumption of H_2O_2 , increasing treatment costs in comparison with PMS and PDS consumption.

Although batch systems have demonstrated high efficiency in degrading organic contaminants using sulfate radicals, further studies are needed to explore the potential for scaling up these processes. In Rodríguez-Chueca et al. [190], several micropollutants (MPs) were degraded by UV-C/sulfate radicals at a pilot scale. The treatment plant employed a UV-C reactor emitting 254 nm (maximum emission), with 140 L volume capacity. Photolysis of PMS and H_2O_2 reached similar average MPs removal in all the range of oxidant dosages, obtaining the highest efficiency with 0.5 mM and 18 s of contact time (48 and 55%, respectively). In the work of Sbardella et al. [191], several pharmaceutically active compounds (PhACs) were degraded by UV/PDS and UV/PMS technologies employment at pilot scale. The reactor was fitted with a UV-C lamp, with 45 W power, emitting at 254 nm. Under the best operational conditions, both UV/PDS and UV/PMS revealed high efficiency in the removal of these contaminants. The economic feasibility of this process was also evaluated. By application of electric energy per order (Equation (40)), a consumption of 0.7 and 0.5 $\text{kWh m}^{-3} \text{ order}^{-1}$, respectively, was calculated. However, to determine the costs of this operation, it is necessary to consider (1) the energy demand of UV device, (2) the replacement frequency of critical, high-cost components, such as lamps, and (3) the PDS and PMS demand. Considering these factors, a total cost of 0.088 and 0.280 EUR m^{-3} , respectively, was determined; thus, UV/PDS could be considered a feasible option for large-scale treatments.

$$E_{\text{EO}} = \frac{\text{Pt1000}}{\text{Vlog}(C_i/C_f)} \quad (41)$$

where E_{EO} is electric energy per order.

Previous examples showed that sulfate radicals can be very effective for organic carbon removal; however, in several wastewaters, due to the presence of high values of organic carbon, turbidity, TSS, and polyphenols, the application of SR-AOPs is not viable. In the work of Jorge et al. [192], a WW showed 9870 $\text{mg O}_2 \text{ L}^{-1}$ COD, 1205 NTU turbidity, 3910

mg L⁻¹ TSS, and 87 mg gallic acid L⁻¹ polyphenols. Application of SR-AOPs under the conditions showed in Table 7 achieved 53.0% TOC removal. Application of adsorption with bentonite as a pre-treatment, followed by SR-AOPs, enhanced TOC removal, achieving 76.7%. Clearly this type of wastewater poses a serious problem due to scavenging of radicals and reduced penetration of radiation, as well as increasing the cost in reagent consumption. A similar case is shown in the work of Kashani et al. [193], in which a landfill leachate with high organic carbon (COD = 4040 mg O₂ L⁻¹) was treated by SR-AOPs. Due to the wastewater composition, electrocoagulation (EC)/aeration was initially performed. The results showed 61.3% COD removal after 40 min, with 310 mL L⁻¹ sludge formation. This pre-treatment allowed the clearance of the wastewater, which was submitted next to a PMS/ZVI/UV system and electro-Fenton, achieving 98% COD removal and enhancing biodegradability from 0.19 to 0.56. However, in the work of Nidheesh et al. [194], it was observed that application of a combined system SR-EAOP + EC achieved higher COD removal (88.7%) than EC + SR-EAOP (74.5%) in the treatment of municipal landfill leachate. In sum, all these works demonstrated that combined systems are necessary to reduce reagent consumption, reaction time, and energy requirements.

Table 7. Industrial wastewater treatment using sulfate-based advanced oxidation processes.

Wastewater	Operational Conditions	Results	References
Winery	COD = 5000 mg O ₂ L ⁻¹ , TOC = 1700 mg C L ⁻¹ , [KPS] = 25 mM, [KPS]:[Fe ²⁺] = 1:1, pH = 7.0, Solar radiation	COD _{rem} = 67%	[186]
Winery	[HSO ₅ ⁻] = 2.5 mM, [M ₂ (SO ₄) _n] = 1.0 mM, pH = 6.5, Temperature = 323 K	COD _{rem} (Fe ²⁺) = 51%, COD _{rem} (Co ²⁺) = 42%, COD _{rem} (Cu ²⁺) = 35%	[167]
Winery	S ₂ O ₈ ²⁻ / H ₂ O ₂ ratio = 1 : 0.25, S ₂ O ₈ ²⁻ / H ₂ O ₂ dosage = 0.1:0.025 (g/g), pH = 7.0, T = 343 K, agitation 350 rpm, t = 2 h	TOC _{rem} = 76.7%, COD _{rem} = 81.4%, Polyphenols _{rem} > 99%	[192]
Winery	[PMS] = 5.88 mM, [Co ²⁺] = 5 mM, pH = 6, radiation UV-A 32.7 W m ⁻² , UV-C 15 W, US 500 W, T = 343 K, reaction time = 240 min	COD _{rem} (UV-A) = 82.3%, COD _{rem} (UV-C) = 76.0%, COD _{rem} (US) = 52.2%	[74]
Micropollutants (MP)	[PMS] = 0.5 mM, pH = 7.17, Contact time (4–18 s), UV-C radiation	MP _{rem} (%) = 48%	[190]
Acid Orange 7 (AO7)	[PDS] = 10 mM, [Cu-AC] = 0.5 g L ⁻¹ , current density = 16 mA/cm ² , pH = 5.0	AO7 _{rem} = 95.7%	[187]
Ciprofloxacin (CIP)	PDS = 1 mM, Cu _{0.84} Bi _{2.08} O ₄ = 1 g L ⁻¹ , Visible light	[CIP] _{rem} = 90%	[195]
Aniline	PDS = 0.08 mol L ⁻¹ , pH = 5, UV = 30 W, Aniline = 20 mg L ⁻¹ , Time = 60 min	[Aniline] _{rem} = 96%	[196]
Tannic Acid (TA)	[TA] = 0.1 mM, [S ₂ O ₈ ²⁻] = 53.10 mM, pH = 9.0, UV-C (254 nm)	Aromatic _{rem} = 96.32%, TOC _{rem} = 54.41%	[188]
Levofloxacin (LFX)	LFX/S ₂ O ₈ ²⁻ /Fe ²⁺ (mM) = 1/30/3, pH = 3.0	[LFX] _{rem} = 56%, k ₁ = 5.74 × 10 ⁻² min ⁻¹	[197]
Penicillin G (PEN G)	[PEN G] = 0.02 mM, [persulfate] = 0.5 mM, pH = 5.0, [temperature] = 353 K	[PEN G] _{rem} = 98%	[198]
Pharmaceutical active compounds (PhACs)	pilot-scale UV-C photoreactor (254 nm), 45 W, pH = 8.2, flow rate = 0.36 m ³ /h, [PDS] = [PMS] = 0.4 mmol; [PhACs] = 10 mg L ⁻¹	PhAC _{rem} (UV/PDS) = 84%, PhAC _{rem} (UV/PMS) = 85%	[191]
Acid orange II (AO II)	AO II: 100 mg L ⁻¹ , ribbon Cu ₄₆ Zr _{44.5} Al _{7.5} Y ₂ = 0.6 g, [PS] = 0.25 mM, temperature: 313 K, pH = 2, t = 70 min	AO II _{rem} = 98%	[199]
Imidazolium-based ionic liquids (ILs)	[ILs] ₀ = 100 μM, [PDS] ₀ = [PMS] ₀ = 500 μM, pH unadjusted	[Emim][Cl] _{rem} = 99%, [Omim][Cl] _{rem} = 99%, [Emim][Br] _{rem} = 97%	[200]
Congo red (CR)	[CR] = 20 mg/L, current density = 5.71 mA/cm ² , [PMS] = 30 μM, [Cu(II)] = 15 μM	AR _{rem} = 95.4%	[201]
2-chlorobiphenyl (2-PCB)	[2-PCB] ₀ = 8 mg L ⁻¹ , [PS] ₀ = 0.2 mM, [pH] ₀ = 6.5.	2-PCB _{rem} = 83%	[202]
Sulfamethazine (SMZ)	[SMZ] = 30 mg L ⁻¹ , [Na ₂ SO ₄] = 0.2 M, pH = 7, t = 30 min	SMZ _{rem} = 100%	[203]
Ammonia nitrogen	Electrochemical (EC) system—Ti/RuO ₂ anode, Ti cathode, and Fe inductive electrode (EC/PDS system) [NH ₄ ⁺] = 100 mg L ⁻¹ , [PO ₄ ³⁻] = 10 mg L ⁻¹ , [Cl ⁻] = 100 mM, cell voltage = 2.5 V, t = 60 min, pH = 3.0	NH ₄ ⁺ _{rem} = 100%	[204]

Table 7. Cont.

Wastewater	Operational Conditions	Results	References
Table Olive Manufacturing	COD = 28.6 g L ⁻¹ , turbidity = 170 NTU, [Al ₂ (SO ₄) ₃] = 8.0 g L ⁻¹ , pH = 7.0, T = 20 °C, [PMS] = 0.2 M, [Fe ³⁺] = 0.03 M, pH = 7.0, T = 20 °C, time = 200 min	COD _{rem} = 70.0%	[205]
Industrial	TOC = 100 mg C L ⁻¹ , UV radiation, [PS] = 4 g L ⁻¹ , time = 180 min	TOC _{rem} = 90.0%	[206]
Landfill leachate	[PMS] = 30 mM, [ZVI] = 0.6 g L ⁻¹ , pH = 4.0, UV radiation, time = 40 min	TOC _{rem} = 98.0%	[193]
Municipal landfill leachate	COD = 5650 mg O ₂ L ⁻¹ , applied voltage = 3 V, pH = 6.0, [PS] = 500 mg L ⁻¹ , [Fe ²⁺] = 100 mg L ⁻¹	COD _{rem} = 88.7%	[193]

5. Ozone-Based AOPs

Schönbein first discovered ozone in 1840; later, in 1872, the chemical structure of ozone was confirmed as a triatomic oxygen molecule (O₃) [207]. De Meritens showed in 1886 that the properties of ozone (O₃) included sterilization of contaminated water, and, years later, pilot tests were conducted in a WWTP in Paris. O₃ was initially enforced in water treatment (and used continuously) in Nice, France, in 1906, in the disinfection of drinking water [208,209]. The O₃ has high oxidation potential ($E^{\circ} = 2.07$ V) and the capacity to selectively oxidize unsaturated double bonds and aromatic structures. In addition, O₃ can react in water and generate HO• radicals [210]. Among the AOPs, ozonation in combination with UV-C radiation and/or peroxidation showed very capable wastewater remediation for a large concentration of polyphenols, found in the cork, olive oil, and winery industries [211].

5.1. Types of Ozone Treatments

Although the ozonation process can achieve organic pollutant removal and mineralization up to 100%, in water, molecular O₃ is not economic when balanced against other AOPs. Therefore, to achieve good mineralization, it has been developed by researchers' application of O₃ in different conditions. Among these conditions are the employment of ozone with alkaline conditions, O₃ + H₂O₂, radiation, and metallic catalysts (Figure 9) [212].

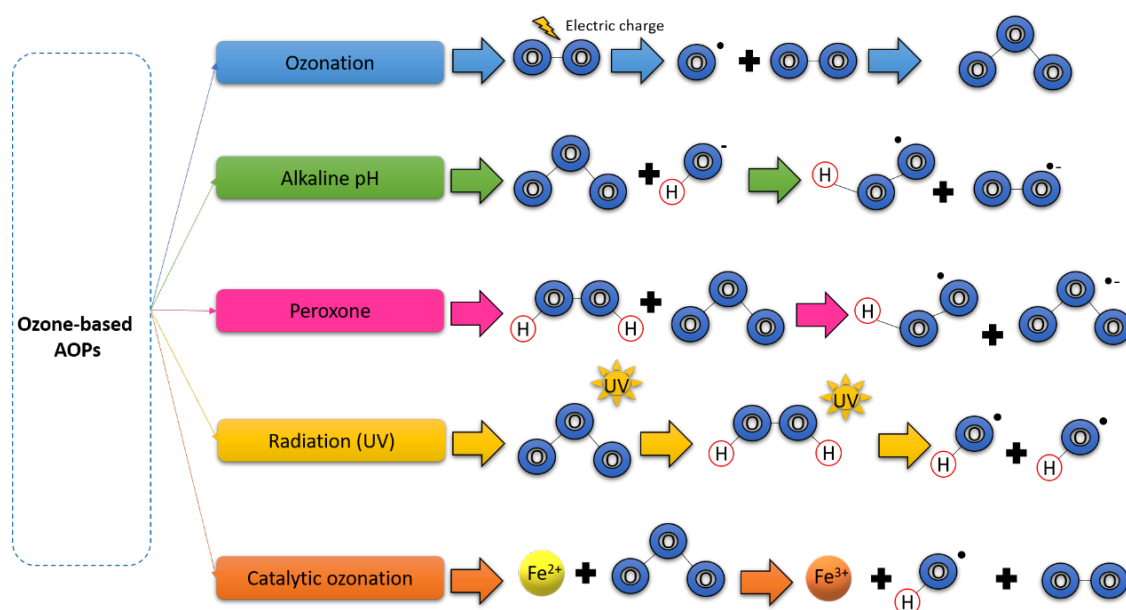


Figure 9. Different ozone-based AOPs.

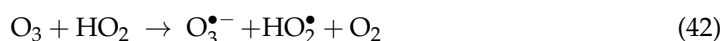
5.1.1. Ozonation

Ozone (O₃) is a colorless or pale blue gas, characterized by low melting point (−251 °C), instability, harsh odor, and high redox potential (2.07 V) at alkaline pH, capable of oxidizing a large range of organic and inorganic substances. The ozonation can take place via direct (oxidation–reduction, cycloaddition, electrophilic substitution, and nucleophilic reaction) or indirect pathways [213].

Direct Ozonation

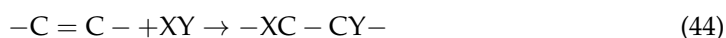
(a) Oxidation–reduction

Considering the high redox potential of O₃, several pollutants are able to be removed by oxidation–reduction reactions through O₃ and HO₂[−] or O₂^{•−}, as shown in Equations (42) and (43) [214]:



(b) Cycloaddition

In these types of reactions, the interaction occurs between an electrophilic compound and an unsaturated compound (double bond connection or p-electrons), generating additional compounds (Equation (44)). In accordance with the Criegee cycloaddition reaction scheme, the reaction between O₃ and olefinic compounds takes place in three steps: (1) generating required ozonide (five-part ring); (2) age of zwitterions; (3) reaction pathways of zwitterions and generation of products like aldehydes, ketones, or acids [215,216].



(c) Electrophilic substitution

Several reactions point to the attack of the nucleophilic position of organic compounds, substituting a section of the molecule when O₃ is the electrophilic agent. It must also be considered the effect of Cl, HO[−], and NO₂[−] on the reactivity of aromatic rings with O₃. This leads to the production of reaction substitutions, due to the properties of the substitution groups. Deactivation occurs with relief of H from the meta-position, and activation occurs with substitution in the ortho- and para-positions [209].

(d) Nucleophilic reaction

Considering the O₃ resonance structure, it exhibits a negative charge, thus contains nucleophilic properties, and can react with molecules in its electrophilic positions, particularly when it contains carbonyl, double, and triple N₂ and C bounds. However, this reaction type has only been established in non-aqueous solutions [215].

Indirect Ozonation

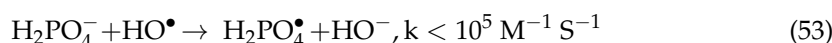
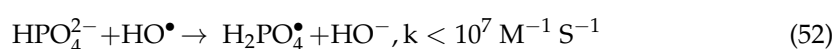
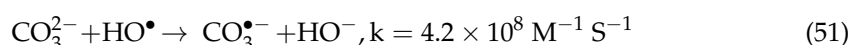
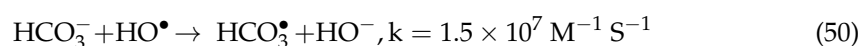
In aqueous solutions, O₃ can be converted, leading to the generation of radical species (Equations (45) and (46)) [217]:



In a lack of O_3 , generated $O_2^{\bullet-}$ and $HO_2^{\bullet}$ can be converted to O_2 and HO_2^- ($k = 9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and protonate to H_2O_2 . The existence of O_3 in the mean allows the generation of $HO^{\bullet}$ radicals (Equations (47)–(49)) [218]:



In addition, there must be considered $HO^{\bullet}$ scavenging reactions with HCO_3^- , CO_3^{2-} , HPO_4^{2-} and $H_2PO_4^-$, as shown in Equations (50)–(53) [219]:



(a) Alkaline pH

Wastewater pH enhancement has advantages regarding direct ozonation process. In alkaline conditions, the HO^- increase can improve $HO^{\bullet}$ radical generation, as shown in Equations (54)–(58). However, several drawbacks should be considered, such as calcium carbonate precipitation and pH changes-associated costs [209,217].



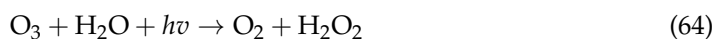
5.1.2. Peroxone (O_3/H_2O_2)

The addition of H_2O_2 to the ozonation process increases the generation of $HO^{\bullet}$ radicals, promoting the efficiency of the degradation process. In accordance with Fischbacher et al. [220], the addition of H_2O_2 allows the reactions, as follows throughout Equations (56) and (59)–(63):



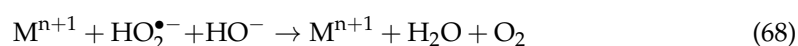
5.1.3. Ozone and UV Radiation (O_3/UV)

UV radiation, when applied in combination with O_3 , can be considered as a catalytic ozone-based AOP, accelerating the O_3 decomposition and enhancing the generation of $HO^{\bullet}$ radicals, as shown in Equations (64) and (65). Furthermore, in Section 5.1.2, the H_2O_2 generated by this process can considerably enhance ozonation process efficiency [221].



5.1.4. Catalytic Ozonation

Catalytic ozonation is performed involving the addition of a homogeneous or heterogeneous catalyst. When homogeneous catalysts are involved, the degradation of organic contaminants follows mainly two ways: (1) metallic-ions addition improves the O_3 perishing and $\text{HO}^\bullet$ radical production, and (2) the complexes produced due to the combination of metallic ions and organic molecules are oxidized by the ozone or the $\text{HO}^\bullet$ radicals [216]. The metallic catalysts react with O_3 to generate $\text{HO}^\bullet$ radicals (Equation (66)), and, afterwards, the metal ions are regenerated by ozonation of $\text{HO}^\bullet$ radicals, as shown in Equations (67)–(69) [221,222].



Several studies point out the use of metal oxides and carbon-based heterogeneous catalysts [223–227] (Figure 10). When considering heterogeneous catalysis, it is important to take note that (1) O_3 can be adsorbed and decomposed onto the catalyst, producing radicals, and (2) organic compounds adsorbed on the catalyst will react with ozone or generate radicals [209].

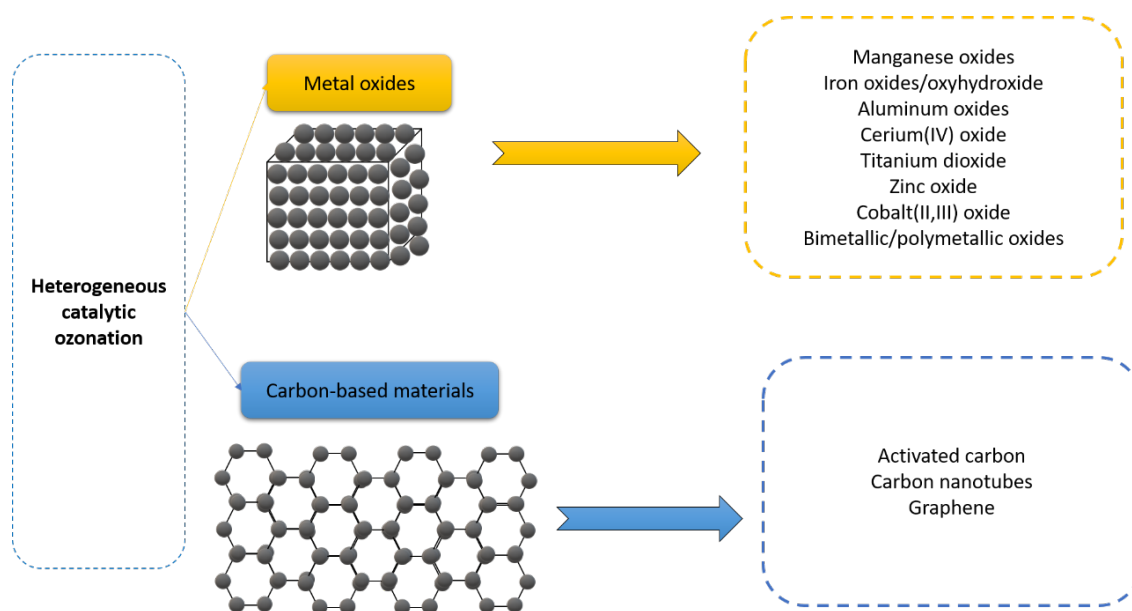


Figure 10. Catalysts used in heterogeneous catalytic ozonation.

5.2. Application of Ozonation Process to Wastewater Treatment

It was shown in the preceding sections that several mechanisms could be used to decompose O_3 and generate $\text{HO}^\bullet$ radicals. In Table 8 are shown some examples of ozonation process enforcement for IW remediation. In Lucas et al. [211], a real winery WW with a COD of $4650 \text{ mg O}_2 \text{ L}^{-1}$ and a polyphenol content of $103 \text{ mg gallic acid L}^{-1}$ was treated by

an ozonation process (O_3/UV and $O_3/UV/H_2O_2$), conducted in a bubble-column, semi-batch reactor. The results showed that O_3/UV and $O_3/UV/H_2O_2$ achieved the highest COD removal at pH 4.0. When the pH increased to 10, the COD removal was further increased; thus, UV, H_2O_2 , and alkaline medium all acted as catalysts for the ozonation process. In addition, to study the removal efficiency, it is also necessary to study the cost of treatments, to decide treatment feasibility.

The ozonation process is also able to be enhanced by combining it with biologic processes. In the work of Chávez et al. [228], an industrial wastewater received a primary treatment in a sequential batch reactor (SBR), followed by ozone-based AOPs. The biologically treated wastewater (BW) was additionally administered to several ozone-based AOPs such as single ozonation (O_3), solar photo-ozonation (O_3 -solar), and photocatalytic ozonation (O_3 -solar-cat). A semi-batch mode was employed for the experiments, using a cylindrical glass-made reactor equipped with a magnetic stirring system, a gas diffuser, and gas inlet, gas outlet, and liquid sampling ports. For the photocatalysis, a solar box with 1500 W Xe lamp and cut-off filters ($\lambda = 300\text{--}800\text{ nm}$, irradiation intensity 550 W m^{-2}) was used. The results showed that O_3 /Solar radiation/ TiO_2 -based catalyst employment achieved the highest efficiency, decreasing the COD $< 125\text{ mg L}^{-1}$ and BOD₅ $< 25\text{ mg L}^{-1}$.

In Ling et al. [229], an Fe-based catalyst ($g\text{-C}_3\text{N}_4/\text{Fe-MCM-48}$) employment in combination with an ozonation process was applied for azithromycin (AZY) degradation. Photocatalytic ozonation experiments were controlled in a 1 L glass tubular photoreactor ($h = 400\text{ mm}$, $\Phi_{in} = 85\text{ mm}$) equipped with a cylindrical high-pressure xenon long-arc lamp. The results showed that, by combining the three factors, the UV + O_3 generated H_2O_2 and the catalyst enhanced $HO^\bullet$ radical production, which degraded the AZY contaminant. Considering the cost associated with the application of H_2O_2 , the generation of H_2O_2 by O_3/UV reduces the cost of treatments. Similarly, to Ling et al., Wang et al. [230] performed mineralization of contaminant aniline with heterogeneous catalytic ozonation, using catalyst $CaMn_2O_4$. It was shown that both catalysts enhanced the conversion of O_3 into H_2O_2 , and reactions inside the catalysts and with the iron or magnesium in the sheets enhanced the conversion of H_2O_2 into $HO^\bullet$ radicals. Figure 11 shows the different interactions between ozone, the catalyst, and contaminant under UV radiation.

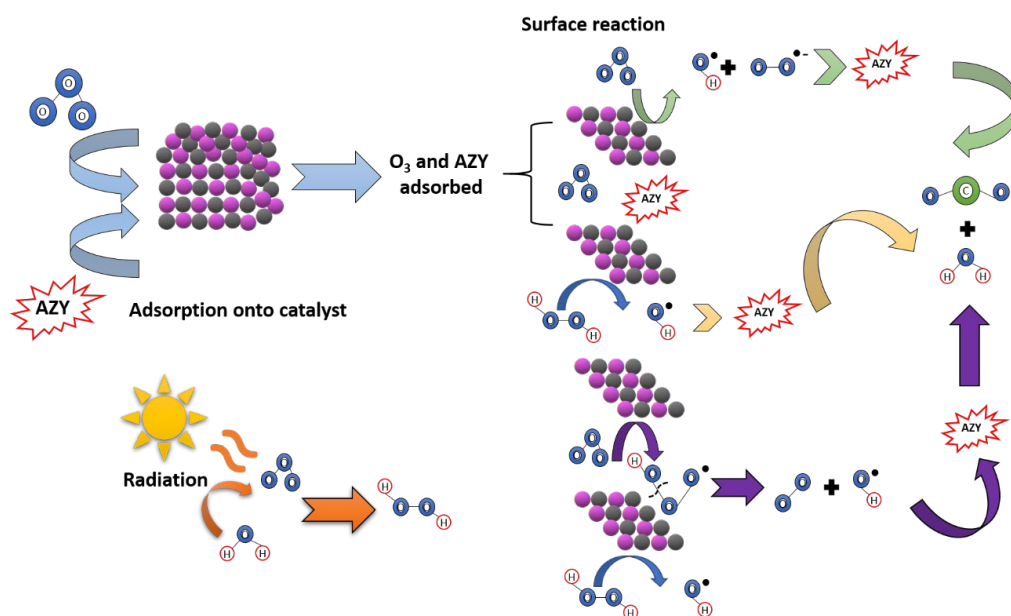


Figure 11. Proposed heterogeneous photocatalytic ozonation of contaminants onto catalyst surface and inside catalyst.

Despite the efficiency of ozonation, several wastewaters present serious challenges for organic carbon reduction, due to the excessive elements present. For this purpose, authors have performed combined CFD + O₃ systems, as a means to overcome wastewater impurities. In Jorge et al. [231] a winery wastewater presenting high values of COD (2430 mg O₂ L⁻¹), turbidity (1040 NTU), and TSS (2430 mg L⁻¹) was treated by ozonation (Table 8), achieving 53.1% COD removal. Considering the high content of turbidity and TSS, a great number of radicals were scavenged by the impurities present in the WW. By performing CFD as a pre-treatment, using a mixture of potassium caseinate + bentonite, turbidity and TSS removals achieved 98.3 and 97.6%, respectively. The application of a CFD + O₃ system achieved a COD removal of 60.7%. A similar study performed by Asaithambi et al. [232] on the treatment of industrial wastewater, revealed high content of COD (90 g O₂ L⁻¹) and TSS (15.44 g L⁻¹). The results showed 100% COD and color removal with O₃/AC-EC, with low energy consumption (4.90 kWh m⁻³). In this context, for several types of wastewater, it is necessary to apply a CFD process as a pre-treatment in order to reduce the energy requirement for organic carbon reduction.

Table 8. Some ozonation processes applied to industrial wastewater.

Wastewater	Operational Conditions	Results	References
Winery	O ₃ /UV-C/H ₂ O ₂ , COD/H ₂ O ₂ = 2, pH = 4.0, Time = 300 min	TOC _{rem} = 49%	[211]
Winery	[TiO ₂] ₀ = 1.5 g L ⁻¹ , [O ₃] _{inlet} = 50 mg L ⁻¹ , pH = 7.0	COD _{rem} = 80%	[233]
Winery	COD = 9432 mg O ₂ L ⁻¹ , TOC = 1962 mg C L ⁻¹ , pH = 4.0, [Fe ²⁺] = 1.0 mM, ozone flow rate 5 mg min ⁻¹ , air flow 1.0 L min ⁻¹ , agitation 350 rpm, time 600 min and a UV-C mercury lamp (254 nm).	TOC _{rem} = 63.2% E _{EO} = 1843 kWh m ⁻³ order ⁻¹	[231]
Industrial	O ₃ /Solar radiation/TiFeAC, Time = 5–8 h, pH = 7.0	TOC _{rem} = 40% COD _{rem} = 50%	[228]
Landfill leachates	O ₃ , O ₃ production rate = 3.98 g, O ₃ h ⁻¹ , pH = 6.9	Color _{rem} = 99%, Turbidity _{rem} = 98%, BOD _{5rem} = 97%, COD _{rem} = 19%	[234]
Landfill leachates	O ₃ /TiO ₂ , [TiO ₂] = 0.5 g/L, O ₃ production rate = 3.98 g, O ₃ h ⁻¹ , pH = 6.9	Color _{rem} = 95%, Turbidity _{rem} = 94%, BOD _{5rem} = 98%, COD _{rem} = 24%	
2,4-dichlorophenoxyacetic acid (2,4-D)	TiO ₂ /UVA/O ₃ , [2,4-D] ₀ = 2 × 10 ⁻³ mol dm ⁻³ , pH = 2.6, Time = 120 min, [TiO ₂] = 2 g dm ⁻³ , O ₃ flow rate = 1.4 ± 0.1 g h ⁻¹ , Radiation = UVA (350 nm)	(2,4-D) _{rem} = >99%	[235]
Simazine, [2-chloro, 4,6-bis(ethylamino)-1,3,5-s-triazine]	T = 293 K, pH = 7, C _{Simz} = 2.5 × 10 ⁻⁵ M, C _{O₃} in = 9.5 mg L ⁻¹ , Gas flow-rate = 30 L h ⁻¹ , [Mn ²⁺] = 0.5 mg L ⁻¹	Simazine _{rem} = 90%	[236]
<i>p</i> -chlorobenzoic acid	[PMS] = 0.103 mmol L ⁻¹ , [pCBA] = 1 mmol L ⁻¹ , [O ₃] ₀ = 0.103 mmol L ⁻¹ , pH = 7.9	pCBA _{rem} = 88.2%	[237]
Phenol	[O ₃] = 15.3 g m ⁻³ , [Fe ³⁺] = 1 mM, UV radiation, Time = 2 h	TOC _{rem} = 97%	[238]
Azithromycin (AZY)	O ₃ dose = 50 mg h ⁻¹ , catalyst dose = 0.2 g L ⁻¹ , [AZY] = 50 ppm, temperature = 298 K	AZY _{rem} = 99%	[229]
Leather wastewater (LW)	[O ₃] = 10 mg L ⁻¹ , DOC = 46.02 mg C L ⁻¹ , SCOD = 138 mg O ₂ L ⁻¹	DOC _f = 17.99 mg C L ⁻¹ SCOD _f = 66 mg O ₂ L ⁻¹	[239]
Bisphenol A (BPA)	[BPA] = 50 ppm, [δ-MnO ₂] = 0.1 g L ⁻¹ , [O ₃] = 4 mg L ⁻¹ , O ₃ flow rate: 0.2 L min ⁻¹ , t = 20 min	BPA _{rem} = 68.2%	[240]
4-nitrophenol (4-NP)	[4-NP] = 25 mg L ⁻¹ , [O ₃] = 2 mg min ⁻¹ , [a-MnO ₂ -50] = 0.1 g L ⁻¹ , pH = 7, time = 90 min	4-NP _{rem} = 100% (t = 45 min) TOC _{rem} = 91.1% (t = 90 min)	[241]
Ibuprofen (IBP)	[IBP] = 13.1 mg L ⁻¹ , ozone dosage = 5 mg L ⁻¹ , gas flow rate = 100 mL min ⁻¹ , volume = 200 mL, catalyst particles packed rate = 10%—catalysts (CuMn ₂ O ₄ -LR; MnO ₂ -Co ₃ O ₄ -LR)	IBP _{rem} = 91% (CuMn ₂ O ₄ -LR) IBP _{rem} = 88% (MnO ₂ -Co ₃ O ₄ -LR)	[242]
Aniline	[Aniline] = 500 mg L ⁻¹ , [CaMn ₂ O ₄] = 600 mg, 35 mg L ⁻¹ O ₃ gas flow, 0.6 L min ⁻¹ gas flow rate, pH = 10.3, T = 298 K, time = 120 min	[Aniline] _{rem} = 100% COD _{rem} = 78.2%	[230]

Table 8. Cont.

Wastewater	Operational Conditions	Results	References
Petroleum refinery wastewater (PRW)	COD = 1146 mg O ₂ L ⁻¹ , [catalyst] = 0.25 g L ⁻¹ , ozone flow = 0.063 m h ⁻¹ , pH = 5.5, T = 25 °C, time = 5 h	COD _{rem} = 90% (Mn ₂ O ₃) COD _{rem} = 89% (FeOOH) COD _{rem} = 89% (CeO ₂)	[243]
Benzene	[benzene] = 90 mg L ⁻¹ , [CeO ₂ /Y-Al ₂ O ₃] = 5.0 w/t, [O ₃] = 560 mg L ⁻¹ , 300 mL min ⁻¹ gas fed, T = 30 °C, time = 360 min	[benzene] _{rem} = 92.5%	[244]
Humic acids (HA)	[HA] = 0.50 g L ⁻¹ , [ACN ₂ O ₂ N ₂] = 0.50 g L ⁻¹ , pH = 5.0, V = 1 L, T = 20 °C, t = 30 min, O ₂ flow rate = 200 NmL min ⁻¹	COD _{rem} = 96%	[245]
Ibuprofen (IBP)	[IBP] = 0.5 mM, [GO/Fe ₃ O ₄] = 30 mg L ⁻¹ , [O ₃] = 4 mg L ⁻¹ , [BuOH] = 0.05 mg L ⁻¹ , pH = 7.0, t = 5 min	TOC _{rem} = 51%	[246]
Industrial	COD = 3000 mg O ₂ L ⁻¹ , DBE = 1 cm, [O ₃] = 4 g L ⁻¹ , CD = 5 Adm ⁻² , EP = Fe/Fe, PDC = 0.6, t = 200 min	COD _{rem} = 100% Color _{rem} = 100% UEE = 4.90 kWh m ⁻³	[232]
Dairy	COD = 9430 mg O ₂ L ⁻¹ , fast speed = 200 rpm/ 2 min, slow speed = 45 rpm/ 15 min, sedimentation time = 30 min [O ₃] = 1 g h ⁻¹ , air flow rate = 10 L min ⁻¹ , V = 2 L, t = 240 min	COD _{rem} = 37.2% (O ₃) COD _{rem} = 65.0% (CFD/O ₃)	[247]
Paper pulping	Aeration time = 10 µm, [O ₃] = 0.18 g h ⁻¹ , [H ₂ O ₂] = 100 mg L ⁻¹ , pH = 9, t = 80 min	COD _{rem} = 73.6%	[248]

6. Conclusions

In industry, water is a crucial resource, and its availability, quality, and reliability can affect process performance and, consequently, business profitability. The development and expansion of the industrial sector all over the world has brought a new challenge: ensuring adequate treatment and discharge of generated wastewaters. Furthermore, responsible water management is essential for industries to promote sustainability and ensure the long-term viability of their operations. This work highlights the environmental challenges posed by industrial wastewater pollution, particularly due to their low biodegradability and the presence of toxic and refractory compounds that can persist in the environment for extended periods. These contaminants pose significant risks to ecosystems, with potentially harmful effects on plants, animals, and human health. This review explored key aspects of industrial wastewater (IW) treatment, with a central focus on the coagulation–flocculation–decantation (CFD) and advanced oxidation processes (AOPs).

The coagulation–flocculation–decantation process is effective in removing turbidity and total suspended solids (TSS) from industrial wastewater. However, this process presents two significant limitations: it is inefficient in removing dissolved organic carbon, and, instead of degrading pollutants, it only separates them from wastewater, leading to the generation of sludge. The use of plant-based coagulants is a sustainable alternative that reduces risks to human health and the environment and allows the resulting sludge to be reused as fertilizer thereby. This review presented the role of CFD in the treatment of IW, highlighting the advantages and disadvantages of different types of coagulants and flocculants, as well as the key parameters influencing the effectiveness of the process.

Advanced oxidation processes offer significant advantages in the treatment of toxic and refractory industrial wastewater. In recent years, substantial progress has been made in improving degradation efficiency and reducing operational costs. However, major barriers remain before AOPs can practically become large-scale applications in the treatment of industrial wastewater. Considering the main limitation of the Fenton process, namely the requirement to operate at an acidic pH (around 3), the use of chelating agents has proven to be a promising solution. The use of radiation was of great interest, and numerous studies have investigated its application in industrial wastewater treatment, but it is important to consider that the high turbidity and intense color of some IW significantly limit light penetration into deeper layers of the wastewater, thereby reducing the efficiency of photochemical processes. Sulfate radicals have demonstrated high efficiency in removing organic carbon from industrial wastewater, showing similar performance to hydroxyl

radicals. Ozone-AOPs were also shown to be effective in radical generation, with emphasis on the application of O_3 /UV as means to produce H_2O_2 and $HO^\bullet$.

Combining CFD and AOPs processes can provide a more comprehensive and effective approach for treating industrial wastewater. The application of CFD as a pre-treatment followed by AOPs allows the reduction of radical scavenging and reagent consumption and increases radiation penetration into the water.

7. Future Perspectives

The integration of CFD as a pre-treatment step followed by AOPs presents a promising approach for the treatment of industrial wastewater. However, several aspects require further investigation to enhance the applicability, efficiency, and sustainability of these combined treatment methods:

1. Pilot-scale and full-scale validation: scaling up from laboratory studies to pilot and full-scale applications is essential to assess the performance, reliability, and operational challenges of CFD-AOPs systems under real industrial wastewater conditions;
2. Sustainability and economic assessments: comprehensive life cycle assessments and cost-benefit analyses are needed to evaluate the environmental impacts and economic viability of integrated CFD-AOPs processes compared to conventional treatment methods.

By addressing these aspects, future research can help overcome current limitations and facilitate the broader adoption of CFD-AOP combined systems for sustainable industrial wastewater management.

Author Contributions: Conceptualization, M.S.L., A.R.T. and N.J.; information collection, A.R.T. and N.J.; information curation, M.S.L., A.R.T. and N.J.; investigation, A.R.T. and N.J.; resources, M.S.L. and J.A.P.; writing—original draft preparation, A.R.T. and N.J.; writing—review and editing, M.S.L. and J.A.P.; supervision, M.S.L. and J.A.P.; project administration, M.S.L. and J.A.P.; funding acquisition, M.S.L. and J.A.P. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for the financial support of Fundação para a Ciência e a Tecnologia (FCT) to CQVR (UIDB/00616/2025). This work was also financially supported by project “Vine and Wine Portugal—Driving Sustainable Growth Through Smart Innovation”, with reference number C644866286-011, and co-financed by the Recovery and Resilience Plan (RRP) and NextGeneration EU Funds. Ana R. Teixeira also thanks for the financial support provided through the scholarship BI/UTAD/3/2025.

Data Availability Statement: The data is contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

AZY—Azithromycin; AOPs—advanced oxidation process; ADL—*Acacia dealbata* Link; CA—citric acid; CFD—coagulation–flocculation–decantation; Cu-AC—copper-spent activated carbon; CECs—contaminants of emerging concern; DC—*Daucus carota*; DTPA—diethylenetriaminepentaacetic acid; DWTPs—drinking water treatment plants; EDL—electric double layer; EDDS—ethylenediamine- N,N' -disuccinic acid; EDTA—ethylenediaminetetraacetic acid; E_{EM} —electric energy per mass; FBP—Fenton-based processes; GLDA—L-Glutamic acid N,N -diacetic acid; HEDTA—hydroxyethyl ethylenediaminetriacetic acid; HEIDA—hydroxyethyliminodiacetic acid; HR-AOP—hydroxyl-based AOPs; IW—industrial wastewater; MO—*Moringa oleifera*; MeO—methyl orange; NTA—nitrilotriacetic acid; OA—oxalic acid; O_3 —single ozonation; O_3 -solar—solar photo-ozonation; O_3 -solar-cat—photocatalytic ozonation; PBCs—plant-based coagulants; PVP—polyvinylpyrrolidone; PVPP—polyvinylpolypyrrolidone; PhACs—pharmaceutical active compounds; ROS—reactive oxy-

gen species; SR-AOP—sulfate radical AOP; SPEF—solar photo-electro-Fenton; SEC-RPR—solar electrochemical raceway pond reactor; TA—Tannic acid; WWTP—wastewater treatment plant; 4-MP—4-Methylpyridine.

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