Advanced Oxidation Process as a Green Technology for Dyes Removal from Wastewater: A Review

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ABSTRACT: The combination of green chemistry and green engineering is needed for the production of minimum waste, renewable sources, increasing utilization of raw materials, the use of simpler and safer products, and novel technologies. The use of novel cleaner technologies leads to effective production in chemical industries. The dyes involve a complex structure, recalcitrant nature, and more intermediates. The generation of oxidative species with higher yields is obtained by advanced oxidation processes as a green and powerful treatment technology. These processes are effective, inexpensive, and eco-friendly methods for decaying toxic pollutants. The AOPs are classified as non-photochemical and photochemical processes. There are included various technologies such as ozonation, Fenton oxidation, wet air oxidation, electrochemical oxidation, and photocatalytic oxidation. The production of highly reactive free radicals is the main purpose of the AOPs process. The generation of free radical increases by the combination of two or more AOPs processes that leads to higher oxidation rates. This study was aimed to present the various attempts for degradation dyes in textile wastewater using the diverse advanced oxidation processes.

KEYWORDS: Advanced Oxidation Processes, Degradation, Dyes, Green Technologies

INTRODUCTION

The precious materials in high-tech matters, agrochemicals, biomolecules, food products, dyes, cosmetics, medicines, polymers, nanoparticles, and liquid crystals have been provided by chemistry and chemical processes. Chemists' knowledge and skill have been applied to make a great number of new materials that are far efficient and more appropriate than natural products. These materials are produced in the laboratory and on an industrial scale. The industrial processes include many chemical reactions using vast quantities and wider collections of smaller molecules, solvents, acids, alkali, reagents, and catalysts. These chemical procedures generate the required products. Furthermore, large quantities of the harmful materials produced, in the form of solids, liquids, and gases, are the biggest challenge in chemistry. Hence, minimizing chemical pollution is an urgent need for synthetic chemists [1].

The use of environmentally acceptable processes is needed in the chemical industry. This concept was shown in green chemistry, clean chemistry, environmental

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chemistry or sustainable technology. In this way, chemical yield, the economic value of removing waste, and avoiding the use of toxic and hazardous materials are mainly focused [2-7]. The term "Green Chemistry" is the most favorable among other common methods.

Green Chemistry

At the beginning of 1990, the concept and definition of green chemistry were first introduced. It is defined as the "design of chemical products and procedures to remove or decrease utilization and production of hazardous materials" [2,5].

Designing is the most important characteristic of green chemistry, involving novelty, planning, and systematic conception. Chemists have achieved the purposeful goal of sustainability using the twelve principles of green chemistry as the "design rules" through the exact and safer planning of chemical synthesis and chemical transformations. In this way, an increasing emphasis on waste reduction in the required source is seen [8]. Therefore, a decrease in waste is the essential purpose of green chemistry. It is shown as a series of reductions (Fig. 1) [9]. These reductions lead to benefit the economic, environmental, and social enhancements through the saving of costs, materials, and energy. Moreover, the use of renewable resources will give sustainable industries. Careful design based on the twelve principles will remove or decrease intrinsic hazards within chemical processes [9].

The Twelve Principles of Green Chemistry

Paul Anastas and John Warner presented the twelve principles of green chemistry in 1998 (Table 1). They are the guiding principles for the design of novel chemical products from raw materials through chemical transformation [2].

A significant first step in pollution prevention is to redesign chemical transformations, which decrease the production of hazardous waste. It can produce many shapes and may affect the environment differently depending on nature, toxicity, quantity, or released source. The conversion of all raw materials into the final compound is one of the most beneficial ways that can prevent the production of wastes. The concept of the atom economy was determined as the second principle of green chemistry. The other principles have been dedicated to subjects such as energy, toxicity, solvent, and utilization of raw matters from renewable sources [10].

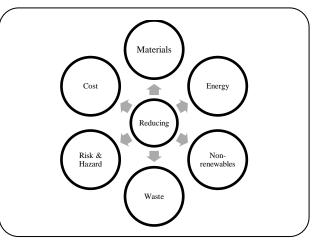


Fig. 1: Reducing: The main of green chemistry.

A synthesis of the organic compounds often generates by-products that may require removal. In this view, the degradation of chemical products to nontoxic, simple, and environmentally-friendly substances has been considered [10].

One important area of research in green chemistry is solvents [11,12], because they often generate the huge majority of waste in chemical syntheses [13]. Additionally, many conventional solvents are flammable, toxic, and corrosive. Their solubility and volatility are related to water, air, and land pollution. Solvents often consume high energy in the recovery and reuse process. Generally, large amounts of organic solvents are used in the pharmaceutical and fine chemicals industries for the chemical reactions and separation processes. These solvents often add to the environment. The cost of processing and recovery operations is due to their volatile and water-solubility to pollute air emissions and aqueous discharge streams [14]. Therefore, chemists studied for safer green solutions. Some examples included solventless systems [15,16], water [17,15], Super Critical Fluids (SCF) [15,18], and, more recently, ionic liquids [19-29].

Raw materials are extracted from the limited sources of the earth that cannot be replaced. Thus, renewable raw materials should be utilized. The major renewable material from living organisms is biomass that includes wood, crops, agricultural residues, food, etc. Cellulose, lignin, suberin and other wood compounds, poly hydroxyl alkanoates, lactic acid, glycerol, starch, chitin, and oil are examples of renewable materials. The efficiency of the chemical processes can be increased by using the catalyst.

1- Prevention of Waste. It is better to prevent waste than to treat or clean up waste after it is formed.
2- Atom Economy. Synthetic methods should be designed to maximize the incorporation of all materials used into the final product as expressed by "atom economy".
3- Less Hazardous Chemical Syntheses. Wherever synthetic, practicable methodologies should be designed to apply and generate matters that possess little or no toxicity to human health and the environment.
4- Designing Safer Chemicals. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5- Safer Solvents and Auxilliaries. The use of auxiliary substances (e.g. solvents, separation agents) should be made unnecessary wherever possible and, innocuous when used.
6- Design for Energy efficiency. Energy requirements should be identified for their economic and environmental impacts and should be minimized. Synthetic procedures should be conducted at ambient temperature and pressure.
7- Use of Renewable Feedstocks. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8- Reduces Derivatives. Unnecessary derivatization (temporary modification of chemical/physical processes, blocking group, protection/deprotection) should be avoided whenever possible.
9- Catalysis. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10- Design products for degradation. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11- Analytical methodologies for pollution prevention. Analytical procedures need to be developed to allow for real-time, in-process monitoring and control prior to the generation of hazardous substances.
12- Inherently safer processes. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

Table 1: The twelve principles of green chemistry.

Lowering the input required energy, avoiding the use of the stoichiometric amount of reagents and the selectivity product will result. Consequently, the energy and waste will reduce. The production of minimum wastes is important through using the new computerized systems in "real-time" control of chemical processes. Thus, careful knowledge of the concentrations of materials used in the chemical process of green chemistry is needed [30].

Today, designing the chemical process in the context of green chemistry with new effective approaches and reduced toxicity is considered.

Dyes

Dyes include an organic compound or complex molecular constructions. They use extensively in different types of industries such as textiles, pharmaceuticals, cosmetics, waxes, greases, leather plastics, paper, food, and paint. The important groups of dyes are phthalocyanine, anthraquinone, triarylmethane, and azo dyes [31-33]. In this way, azo dyes are the most extensively applied commercial reactive dyes whose color is due to the nitrogen to nitrogen double bond [34,35].

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In addition, azo dyes are the largest class of dye pollutants [36].

The effluents of the textile industry mainly contain large amounts of synthetic dyes, natural dyes, and organic dyes. They can affect the chemical and physical characteristics of water. The strong color is one of the chief properties of textile effluent that can cause serious problems in the environment. The synthetic dyes contain organic compounds with fused aromatic rings or connected by covalent bonds. These compounds were improved by several hydrophilic functional groups like carbonyl, amine, hydroxyl, and carboxylic acid groups. Synthetic organic dyes are often resistant to biodegradation in engineered treatment methods. Moreover, some types of dyes such as azo dyes and their derivatives can be mutagenic and carcinogenic. Therefore, the removal of dyes from wastewater is very important. Today, designing the chemical process in the context of green chemistry with new effective approaches and reduced toxicity is considered. A successful approach is the use of green technologies for dyes removal in the textile industry and wastewater treatment [31-36].

Green Technology

Dye wastewater from industries is one of the serious environmental problems due to the characteristics of wastewater such as strong color, low biodegradability, high pH, and high Chemical Oxygen Demand (COD) [37]. Dye-containing effluents are usually treated by Physico-chemical (coagulation, activated carbon adsorption, membrane filtration) and biological (bacterial, algal, fungal) conventional technologies [31,38,39]. The dye effluents often included stable, toxic, and non-biodegradable organic compounds. In fact, they are not treated suitably by conventional treatment methods. Physico-chemical treatments lead to the transfer of pollutants from one phase to other. Furthermore, the dye effluents can eliminate using anaerobic/aerobic and bacterial degradation in biological methods. In this method, the unsuitable removal of dyes leads to environmental or health problems and defective degradation, and insufficient decolorization. Therefore, it is essential to discover an effective treatment technology for complete degradation and effective decolorization. The emerging field for dye effluent treatment is the use of Advanced Oxidation Processes (AOPs) that are efficient, cheap, and eco-friendly methods for decaying toxic pollutants. In these methods, highly reactive radicals are produced that oxidize most of the complex chemical compounds in the dye effluents. In this regard, highly reactive free radicals can be generated by using ultraviolet irradiation, hydrogen peroxide (H₂O₂), ultrasound, ozone (O₃), and catalysts (homogeneous or heterogeneous) [37,40-45].

Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs) are a class of chemical treatment techniques to eliminate organic compounds in water and wastewater. These methods have firstly suggested in 1987 for the purification of water by the generation of hydroxyl radicals. Today, these processes include techniques such as ozonation, photocatalytic degradation, Fenton's reagent (H_2O_2/Fe^{2+}), photo-Fenton, and Electro-Fenton, wet air oxidation, and UV/chlorine processes which are effective for the of the organic pollutants at ambient degradation temperature and pressures [46-54]. Moreover, combinations of advanced oxidation processes are used for the effective removal of the dyes from water and wastewater. The formation of strong oxidants (generally hydroxyl radicals) and the reaction of these radicals with organic pollutants in water are two main stages of AOPs. The advanced oxidation processes can be categorized into two general groups based on using the ultraviolet irradiation source. The classification of AOPs is shown in Table 2 [55].

Nonphotochemical Advanced Oxidation Processes

These methods include four desirable nonphotochemical processes such as ozonation, Fenton's reagent oxidation, wet air oxidation, and electrochemical oxidation. The nonphotochemical processes of recent research will be given in the following sections.

Ozonation

Ozone and ozone-based advanced oxidation systems are well-known, powerful, and environmentally friendly technologies that can degrade the variety of organic pollutants [56]. In recent years, the use of ozonation in wastewater treatment has enhanced significantly. Interest in the use of ozone is due to the various benefits of this method, including the high oxidation power of ozone (2.08 V) even at low concentrations, high efficiency in the decomposition of organic matter, and the production of nontoxic residues [57,58]. Furthermore, ozonation is the preferred method for the removal of colored materials that have chromophore groups with conjugated double bonds. These substances can be easily broken down into smaller molecules by the ozone process in direct and indirect ways [59]. Hoigne et al. studied the mechanism of ozone reaction [60,61]. These studies showed that direct ozonation includes the reaction of double bonds or aromatic systems of reactive dyes with molecular ozone in acidic pH [61,62]. The degradation mechanism of organics dyes is investigated throughout hydroxyl radicals under basic pH. The hydroxyl radicals are generated through the radical chain reactions, which react with the organic compounds [63]. Sometimes, the ozone process cannot entirely oxidize the organic dyes to CO₂ and H₂O. This is due to the generation of partial oxidation products. In this case, the combination of ozone with homogeneous or heterogeneous catalysts is proposed for the improvement of organic compounds elimination [64].

Wijannarong et al. studied the wastewater treatment of reactive dyes with ozone in a batch reactor at 35 °C. In this experiment, the effects of time reaction and pH on the

Non-photochemical	Photochemical
Ozonation	Photocatalytic oxidation, UV/Catalyst
Ozonation with hydrogen peroxide (O_3/H_2O_2)	UV/H ₂ O ₂
Fenton and related processes (Fe ²⁺ or Fe ³⁺ /H ₂ O ₂)	UV/O ₃
Wet air oxidation (WAO)	UV/O ₃ /H ₂ O ₂
Electrochemical oxidation	Photo-Fenton and related processes (Fe ²⁺ or Fe ³⁺ /H ₂ O ₂ /UV)
Catalytic wet air oxidation (CWAO)	Heterogeneous photocatalysis oxidation: UV/ZnO, UV/SnO ₂ , UV/TiO ₂ , UV/TiO ₂ /H ₂ O ₂

Table 2: Classification of Advanced Oxidation Processes.

decolorization efficiency was investigated. The decoloration efficiency enhanced from 32.83% to 56.82% after two hours. In addition, color reduced by more than 92% after six hours [65].

The commercial reactive azo dyes with different structures were treated by ozone in a semi-batch reactor. The optimized conditions for decolorization were obtained in pH 10 and COD removal 95-99% for different dyes due to the complexity of their structures. This ozonation reaction revealed a significant technique for dyecontaining wastewater treatment. The kinetics of reaction achieved pseudo-first-order [66].

Wu et al. used the catalytic ozonation process for the removal of organic pollutants. The organic pollutants were effectively removed at initial pH values of 7.18-7.52 with the iron shavings. The COD value was reduced from 142 to 70 mg/L. The toxicity effect decreased from 51% to 33% that was due to hydroxyl radical oxidation, co-precipitation and oxidation by other oxidants. Therefore, this method was introduced as a favorable method for the removal of organic [67].

Asgari et al. investigated a catalytic ozonation process to remove the reactive black 5 (RB5) dye using a bonechar (BC) ash improved with MgO-FeNO₃. Experimental parameters such as initial RB5 concentration, catalyst dosage, pH, and reaction time were optimized by the Taguchi method. The optimal conditions were achieved at an initial RB5 concentration of 10 mg/L, pH 10, 0.1 g/L catalyst dosage, and 15 min reaction time. The initial RB5 concentration had a considerable influence on RB5 elimination efficiency (54.03%), but the reaction time had a lower impact (2.04%) [68]. So far, numerous studies have established that dyes can be effectively degraded by ozone and ozone-based methods. In this regard, some of the results are summarized in Table 3.

Fenton's Reagent Oxidation

Fenton and Fenton-based oxidation processes have attracted attention as a favorable and remarkable AOPs technology. This reagent contains a mixture of a strong chemical oxidizer, hydrogen peroxide, and ferrous ions as a catalyst that is called Fenton's Reagent. It was introduced by Henry Fenton as an oxidant reagent in 1890. The catalytic chemical reaction between hydrogen peroxide and Fe²⁺ or Fe³⁺ ions under an optimum pH condition produced the hydroxyl free radical, which is the main component of Fenton's reagent [84,85]. The generation of hydroxyl radicals in Fenton reactions was determined by spin-trapping analysis [86]. The iron (III) ions are produced during the oxidation stage that promoting the elimination of pollutants through coagulation and sedimentation. In this process, the pollutants were converted to harmless compounds like carbon dioxide and water. The important advantages of this reagent are simplicity, the cost-effective source of hydroxyl radicals, and the lack of toxicity of the reagents [87]. The homogeneous or heterogeneous conditions can be utilized for Fenton oxidation. The traditional homogeneous Fenton oxidation was extensively utilized in degradation organic compounds. However, there are two important limits in this process, including acidic pH 2-4 and high amounts of iron ions. The iron ions should be separated at the end of the reaction that needs additional elimination procedures [88-92]. In recent years, the use of heterogeneous Fenton and the Fenton-like process has been increasingly regarded [91-97].

The Fenton process using Fe^{3+} or other metals at low oxidation states like Cu^{2+} and Co^{2+} is the so-called Fenton-like reaction that has a slower rate compared to the Fenton reaction [96]. *Abo-Farha et al.* studied the degradation of C.I. Acid Orange 8(AO8) and C.I. Acid Red 17(AR17)

Entry	Dye	Time (min)	Catalyst	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.
1	Textile Dyeing Industrial Effluent	240-360	-	92	-	-	[65]
2	Commercial reactive azo	30-40	-	60-90	95-99	-	[66]
3	Textile auxiliaries and dye intermediates	120	Iron shavings	BOD ₅ /COD=0.17	46	-	[67]
4	Reactive black 5 (RB5)	5-20	MgO-FeNO ₃	90	60	-	[68]
5	C. I. Reactive Blue 5	-	LaCoO ₃	-	-	100	[69]
6	Acid Red 88	0.5-6	-	98	64	-	[70]
7	Acid Red B	60	Fe-Cu oxide	90	70	-	[71]
8	Acid black 1 (AB1), Acid yellow 19 (AY19), Acid orange 7 (AO7)	-	-	80-98	-	-	[72]
9	Reactive Blue 19	90	-	-	55	17	[73]
10	Procion red MX-5B	30	Metal ions	97	-	75	[74]
11	C. I. Acid Blue 113, C. I. Reactive Yellow 3, C. I. Reactive Blue 5	< 10	Activated carbon, cerium oxide, ceria-activated carbon composite	100	-	-	[75]
12	RR198	9	MgO nanocrystal	100	-	-	[76]
13	Reactive Blue 19	10	-	BOD ₅ /COD=0.33	-	-	[77]
14	Bomaplex Red CR-L	10-30	-	100	35-56	-	[78]
15	Acid, Direct and Reactive	180	-	100	66	-	[79]
16	Red X-GLR	120	-	100	5.7-35	-	[80]
17	Remazol Black B	2-60	-	96	-	-	[57]
18	Remazol Black 5	360	-	-	40	25	[81]
19	Reactive red X-3B	30	MnO ₂	99	85	59	[82]
20	C. I. Direct Black 22	160	-	70-83	-	33	[34]
21	Direct Blue 86 (DB-86)	35	-	98	62	-	[83]

Table 3: Summary of ozonation studies in the removal of dyes.

with Fenton and Fenton-like processes. The color was reduced 93% for AO8 and 98% for AR17 with Fenton oxidation under the optimum conditions, while were obtained 89% and 78% using the Fenton-like process [95]. Furthermore, the Fenton oxidation process was used for the degradation of Direct Blue 71 (DB71). The parameters such as dosages of Fe²⁺ and H₂O₂, pH, temperature, and dye concentration

in the color removal and COD reduction were studied. The color was reduced 94% and COD 50.7% under the optimum conditions of pH 3.0, 3 mg/L Fe²⁺, 125 mg/L and 100 mg/L H_2O_2 after 20 min [98].

Sohrabi et al. investigated the degradation of Carmoisine dye from aqueous solutions through the Fenton process. The effect of operating parameters such as pH,

Fe²⁺, H₂O₂, and dye concentration were optimized by Taguchi fractional factorial design. The optimal conditions for the Fenton oxidation were obtained equal to 0.015 mmol Fe²⁺, 0.15 mmol H₂O₂, 20 mg/L initial dye concentration, and pH 3.5. The color was reduced 92.7% for the Fenton in optimal conditions [99].

The heterogeneous Fenton system such as green Fe(II)/Fe(III) oxides/hydroxides nanoparticles with hydrogen peroxide was used for dye removal in less than 3 h of reaction. In this study, the effect of hydrogen peroxide concentration, pH, catalyst dosage, and temperature were investigated. The decolorization was obtained equal to 80% at 50°C in 14 min and 40% at 25°C [100].

The Fe(II) supported on Y-Zeolite (Fe(II)-Y-Zeolite) catalyst and hydrogen peroxide (heterogeneous Fenton process) were studied for the decolorization and mineralization of the azo dye C.I. Acid Red 14 by Idel-Aouad et. al [101]. The catalyst was prepared from a commercial Y-Zeolite by ion exchange with Fe^{2+} . The effect of operating parameters such as initial pH, H₂O₂ concentrations, temperature, and dosage of catalyst on the decolorization efficiency was investigated. The percentage of decolorization and mineralization of dye was obtained equal to 99.3±0.2% and 84±5% in pH 5.96, the initial concentration of 50 ppm dye, 8.7 mM H₂O₂, 80°C temperature, the catalyst concentration of 15 g/L and 6 min contact time, respectively. In addition, the synthesized catalyst easily filtered from the solution without iron into the solution. This method was effective for the degradation of dye [102].

Daud and Hameed studied the decolorization of the azo dye reactive black 5 (RB5) using a Fenton-like oxidation process in the presence of Fe(III) immobilized on Montmorillonite K10 (MK10) catalyst and hydrogen peroxide (H₂O₂). The effect of various parameters such as catalyst dosage, temperature, the initial concentration of H₂O₂, iron ions loading on the supported catalyst, pH was investigated. The decolorization efficiency was obtained equal to 99% with 3.50 g/L of 0.11 wt. % Fe(III) oxide on MK10 catalyst, 12 mM of H₂O₂ at pH 2.5 within 150 min [103]. Some studies, including Fenton's reagent oxidation of dye contaminant, are shown in Table 4.

Catalytic Wet Air Oxidation (CWAO)

Wet Air Oxidation (WAO) is an environmentally friendly process for the treatment of organic pollutants

in wastewater. It was firstly introduced by Zimmerman over 50 years ago. This method oxidizes the organic compounds using oxidative functions such as air or oxygen at pressures (0.5-20 MPa) and high temperatures (175-320 °C) [111,112]. The wet air oxidation oxidizes the organic contaminants to dioxide carbon, NH₃ and inorganic salts [108]. In recent years, Catalytic Wet Air Oxidation (CWAO) processes were studied and used in the treatment of wastewater. This method has moderate reaction conditions and higher efficiency compared to conventional World Health Organization (WHO). The higher oxidation rates are obtained with the use of the catalysts. These catalysts involve homogenous and heterogeneous types. In the CWAO process, the organic contaminants oxidize to inorganic compounds like dioxide carbon, dissolved ions, and water at lower pressures and temperatures [113,114].

Liu and *Sun* synthesized a new Fe₂O₃-CeO₂-TiO₂/g-Al₂O₃ catalyst and used it for degrading the methyl orange in the CWAO process. The results showed that 98.09% of color and 96.08% of Total Organic Carbon (TOC) could be eliminated in 2.5 h. The catalyst had high stability and activity [113].

Zhang et al. prepared a new polyoxometalate $Zn_{1.5}PMo_{12}O_{40}$ catalyst and used it for the catalytic wet air oxidation of the Safranin-T. The Safranin-T (ST) is a hazardous textile dye. This catalyst showed good catalytic activity. The color was reduced 98% and 95% of COD was eliminated in 40 min under atmospheric pressure and room temperature. Total Organic Carbon (TOC) decreased 92%. In this method, the organic contaminants were converted to inorganic species such as Cl⁻, HCO₃⁻ and NO₃⁻ [115].

Kumar Kondru et al. investigated the removal of congo red dye using modified Y-zeolite in catalytic wet peroxide oxidation. The effects of various parameters such as pH, temperature, hydrogen peroxide concentration, and catalyst dosage were studied. The optimum conditions were obtained at pH 7, 0.6 mL H₂O₂, and 1 g/L catalyst. The color removal and COD reduction were found 100% in 45 min and 58% in 4 h. Therefore, the Fe exchanged Y-zeolite was introduced as an excellent catalyst for dye removal [116].

Hua et al. studied the catalytic effect of CuO/Y-Al₂O₃ on the wet air oxidation of three azo dyes (Methyl Orange, Direct Brown, and Direct Green) (2013). The COD removal, Total Organic Carbon (TOC) reduction, and decolorization were investigated. The color, TOC, and COD were removed 100%, 80%, and 70% in 2 h, respectively.

Entry	Dye	Time (min)	[H ₂ O ₂]	[Fe ²⁺]	Catalyst	pН	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.
1	Reactive Black 5	-	4.0 mM	-	iron (III) impregnated on rice husk ash	3.0	89.18	-S	-	[88]
2	Alcian Blue	-	$[H_2O_2]/$ $[Fe^{2+}] =1$	$[H_2O_2]/$ $[Fe^{2+}] = 1$	-	2.5	93.2	-	54.1	[89]
3	Acid Red 1 (AR1)	180	12 mM	1.0 %	Fe–ball clay (Fe–BC)	2.5	99	-	-	[92]
4	C.I. Acid Orange 8, (AO8), C.I. Acid Red 17 (AR17)	55	10 mM	$\begin{array}{c} 1.0\times10^{-5}\\ M\end{array}$	-	3.0	89-99	-	-	[95]
5	Direct Blue 71 (DB71)	20	125 mg/L	3 mg/L	-	3.0	94	50.7	-	[98]
6	Carmoisine edible dye	12	0.15-0.3 mmol	0.012- 0.015 mmol	-	3.5	92-95	-	-	[99]
7	C. I. Acid Red 14	6	8.7 mM	15 g/L	Fe (II)-Y Zeolite	5.96	99	-	-	[101]
8	Reactive Black 5	150	12	3.5 g/L 0.11 wt%	Montmorillonite K10	2.5	99	-	-	[102]
9	Yellow drimaren, Congo red, Methylene blue	30-120	-	0.5 mM	-	3.0	100	89	-	[91]
10	Remazol Black 5 (RB5), Remazol Red RB (RR), Remazol Yellow 84 (RY), Remazol Brilliant Blue (RB)	22	0.05-1.25 mM	0.05-1.25 mM	-	2.5- 4.0	>90	>90	-	[104]
11	Methyl Orange, Reactive Black 5, Fuchsin Acid	1260	-	-	-	2.0	42.68	-	46.57	[105]
12	Reactive Black 5	15	7.3×10^{-4} mol/L	$\frac{1.5\times10^{-4}}{mol/L}$	-	3.0	97.5	21.6	-	[32]
13	Reactive Blue 19	5	300 mg/L	30 mg/L	-	3.0	80.2	41.8	-	[106]
14	Acid Red 1	120	8.0 mM	0.070 wt%	iron ions loading on rice husk	2.0	96	-	-	[107]
15	Direct Blue 15	50	$\begin{array}{c} 2.8\times10^{\text{-3}}\\ \text{mol/L} \end{array}$	$\begin{array}{c} 2.8\times10^{\text{-5}}\\ \text{mol/L} \end{array}$	-	4.0	100	-	-	[108]
16	Remazol Red RR, Remazol Blue RR and Remazol Yellow 84 (RY)	120	1000 mg/L	600 mg/L	-	3.0	98	94	-	[109]
17	Reactive Red 198 (RR- 198)	90	50 mg/L	100 mg/L	-	3.0	92	-	-	[110]

 Table 4: Summary of Fenton's oxidation process studies in the removal of dyes.

The hydroxyl radicals oxidized the chromophoric groups of azo-benzene conjugated in the dye molecule. The oxidized molecules were converted to water and carbon dioxide [33].

Ovejero et al. investigated the removal of Crystal Violet (CV) dye using a nickel catalyst (7 wt.%) supported over Mg-Al mixed oxides. The effects of different parameters like pressure, dye concentration, gas flow, and temperature were studied in this process. The dye removal was obtained 86.1% at 180°C and 44.7% at 120°C. The Total Organic Carbon (TOC) varied from 59.5% to 18.7% and dye removal from 62.6% to 18.4% in an initial dye concentration of 10 to 50 mg/L [117].

MA et al. studied the Catalytic Wet Oxidation (CWO) process for the removal of the methyl orange and methyl blue using a new CuOMoO₃-P₂O₅ catalyst at atmospheric pressure and lower temperatures (35° C) (2007). The dye removal of MB was obtained equal to 99.26% at pH 7 and an initial concentration of 0.3 g/L within 10 min at 35° C. The color removal achieved 55% for methyl orange and 99.65% for MB under the same conditions [118]. Some studies on wet air oxidation of dye contaminants are listed in Table 5.

Electrochemical Oxidation

Electrochemical treatment is one of the advanced oxidation methods for the degradation of dyes. This method was increasingly applied in recent years due to its exclusive features, like energy efficiency, versatility, stability, and cost-effectiveness [128]. The electrochemical oxidation process is used in situ generations of hydroxyl radicals. Thus, it is introduced as an environmentally friendly process. In this technique, electrons are the main reagents that are produced on the surface of electrodes and consumed. Furthermore, the electrons are introduced as the "Clean Reagent". Electrochemical oxidation pollutants are performed by electrode reactions. The reactions depend on the anode material's effectiveness in the electrochemical treatment of the organic contaminant. Up to now, the electrodes such as Au, C, and Pt are used [129]. The mechanism of electrochemical treatment is complicated and can be categorized as direct or indirect. Direct oxidation is performed on the surface of the anode, while indirect oxidation is distant from the anode surface. The contaminants in the direct anodic oxidation are absorbed on the anode surface and then degraded by electron transfer reaction in the anode. In indirect oxidation, the oxidants were generated by electrochemical oxidation in electrolysis reactions. Then, these oxidants destroy the pollutants [130].

Rajkumar and Kim investigated chlorine-mediated electrochemical oxidation for degrading the reactive dyes. The chlorine was generated in situ by using the titaniumbased Dimensionally Stable Anode (DSA). The Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) in electrochemical oxidation were measured. The COD and TOC were obtained from 39.5% to 82.8% and 11.3% to 44.7% for various dyes. The diazo compounds with higher molecular weight such as triazines need more time for degradation compared to the mono azo. The effects of various parameters such as pH, current density, temperature, initial dye concentration, and NaCl concentration were studied in mixed dyes. The optimum conditions were obtained: pH 6.5, 72.2 mA/cm² current density and 4 g/L NaCl concentration. The COD and TOC reduction were obtained equal to 73.5% and 32.8% in 120 min, respectively [131].

Jovic et al. studied the electrochemical oxidation of reactive textile dyes such as Reactive Blue 52, Reactive Black 5, Reactive Green 15, and Reactive Yellow 125 using the platinum electrode. In this study, the electrolysis reaction was performed in cells involving a standard membrane. The supporting electrolyte was determined 0.1 M sodium sulfate. The voltages of 6, 12, and 24 V were considered due to the effect of a membrane on electrolysis. The best dye removal was obtained at 12 V. The COD reduction achieved 57.95% with membrane and 35.28% without membrane after 60 min [132].

In the other study, Morsi et al. investigated the electrochemical oxidation of three types of textile dyes using lead dioxide anode. The effect of temperature, time, pH, current density, initial dye concentrations, and salt concentration were investigated. The optimum conditions were achieved in 20 mA/cm², pH 3, 30°C temperature, and sodium chloride (3 g/L). In this method, the color removal and COD removal was obtained equal to 100% [129].

In 2017, Najafpoor et al. studied the electrochemical oxidation process for decolorization of reactive red 120 (RR120) using graphite anodes and cellulosic separator. Designing the experiments was performed by central composite design. The experimental factors were sodium

Entry	Dye	Time	P (MPa)	T (°C)	Catalyst	pН	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.
1	Methyl Orange Direct Brown Direct Green	120 min	-	-	CuO/Y-Al ₂ O ₃	-	99	-	70	[32]
2	Methylene Orange	150 min	1.0	25	Fe ₂ O ₃ -CeO ₂ -TiO ₂ /Y-Al ₂ O ₃	-	98.09	-	96.08	[111]
3	Congo red	-	-	70	Y-Zeolite	7	100 (45 min)	58 (4 h)	-	[115]
4	Crystal Violet (CV)	350 h	-	180	nickel catalysts supported over Mg-Al mixed oxides	-	86.1	-	59.5	[116]
5	Methylene Blue	10 min	1.0	35	CuO-MoO ₃ -P ₂ O ₅	5	99.26	-	-	[118]
6	Safranin-T (ST)	40 min	1	25	$\begin{array}{c} Polyoxometalate \\ Zn_{1.5}PMo_{12}O_{40} \end{array}$		98	95	92	[119]
7	Orange II	100 min	0.6- 3.0	160- 290	$\begin{array}{c} H_4SiW_{12}O_{40},\\ Na_2HPW_{12}O_{40} \end{array}$	-	-	-	92	[120]
8	Congo red	60 min	-	70	Y-Zeolite	2	99.52	88	-	[121]
9	Safranin-T	18 min	1.0	25	ZnO/MoO ₃	6.89	98	95	99.3	[122]
10	Reactive Black 5	90 min	-	70	Commercial activated carbons (AquaSorb 5000 P)	3	92	-	-	[123]
11	Orange II (OII) and Chromotrope 2R (C2R)	150 min	1	27	Activated carbon xerogels (ACXs)	3	49-67	-	-	[124]
12	Reactive Dye Solution	120 min	1.0	135 165	CoAlPO ₄ - 5 CeO ₂	-	95 100	90 95	-	[125]
13	Chromotrope 2R	-	2.5	100- 180	Ni/MgAlO	-	-	-	82	[126]
14	Cationic red GTL	60 min	1.0	25	Mo-Zn-Al-O catalyst	-	80.1	-	50.9	[127]

Table 5: Summary of catalytic wet air oxidation studies in the removal of dyes.

chloride (2500-12500 mg/L), dye concentration (100-500 mg/L), electrolysis time (7.5-37.5 min), and current intensity (0.06-0.3 A). The results showed that current intensity was the most important factor in RR120 decolorization. The optimum conditions were achieved equal to 200 mg/L RR120, 0.12 A current intensity, 7914.29 mg/L NaCl, and 30 min reaction time. The dye was removed 99.44% *via* electro-oxidation and 32.38% by the electro-reduction process [133]. Table 6 shows a brief account of the research for dye mixtures using the electrochemical oxidation process.

Photocatalytic oxidation

The irradiation of UV-Visible light is essential to generate photochemical changes in the compound. The wavelengths between 400 and 800 nm are related to the visible spectrum. The UV range is involved four regions: UV-A (λ = 315-400 nm), UV-B (λ = 280-315 nm),

UV-C (λ = 190-280 nm) and VU-V (<190 nm). Generally, the reaction rate of AOPs is increased in comparison with the same technology in the absence of light. The lower reaction temperatures, higher reaction rate, and selectivity control are the photochemistry advantages compared to conventional treatment methods [143]. The photochemical processes like photocatalytic oxidation, photocatalytic ozonation (UV/O₃), hydrogen peroxide (UV/H₂O₂), and ultraviolet irradiation are presented below.

Photocatalytic oxidation can involve direct photolysis through the interaction of light with molecules without the adding of chemical reagents. In this method, irradiation leads to homolytic or heterolytic breakages in the molecules. Therefore, a molecule is transmitted from the fundamental state to an excited singlet state. Such excited states can lead to heterolysis, homolysis, or photoionization processes. In most cases, radicals are produced by homolytic dissociation. Generally, the radicals are hydroxyl and superoxide.

Entry	Dye	Time (min)	Current Density (mA/cm ²)	pН	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.
1	Reactive dyes	120	72.2	6.5	>95	73.5	32.8	[131]
2	Reactive Textile Dyes	60	12	8	-	57.95	-	[132]
3	Textile dyes	20	20	3	100	100	-	[129]
4	Reactive red 120 (RR120)	30	0.12 A	-	99.44	-	-	[133]
5	Dye effluents	420	2.5 A/dm ²	2	99.48	100	-	[134]
6	Methylene Blue	300	1.75	-	-	62	-	[135]
7	Textile dyes	300	40	9	90	50	-	[136]
8	Textile dyes and dyehouse effluents	180	5	3	90	55	-	[137]
9	Textile effluent	50	3 A/dm ²	4.5	-	25	-	[138]
10	Dye effluents	-	2 A/dm ²	-	95	92	-	[139]
11	Textile Dyes	30	120	5	91	87	-	[140]
12	Synthetic dyes	60	350 mA		72.9	70.6	-	[141]
13	Reactive Black 5 (RB5)	160	100 A/m ²	6	-	33	18	[142]

Table 6: Summary of Electrochemical oxidation studies in the removal of dyes.

These can be broken down into various types of organic compounds to water, CO_2 , and mineral salts [144]. In this process, the photocatalysts such as TiO₂, ZnO, Fe₂O₃, WO₃, ZnS, and CdS were used for the degradation of organic pollution. In this regard, nano-titanium dioxide is applied more than the other ones due to its low cost, electrical and optical properties, chemical stability, nontoxicity, photo corrosion resistance, and remarkable photocatalytic activity [145].

Li et al. studied the photodegradation of rhodamine B and 4-(*p*-nitrophenylazo) resorcinol (Magneson I) using the TiO₂ hollow microspheres. This photocatalyst exhibited a higher photocatalytic activity compared to P25. A much higher photodegradation percentage for rhodamine B was obtained in the mixed solution. The catalyst degraded the two dyes with high efficiency. These results showed that the TiO₂ hollow microspheres would be very useful for use in wastewater treatment [146].

Nezamzadeh-Ejhieh et al. investigated the photodecolorization of a mixture of the rhodamine B and methylene blue cationic dyes using CuO/nano-zeolite X catalyst in solar irradiation. The photocatalyst was synthesized by hydrothermal process. The particles sizes were determined in the ranges of 7-10 nm and 75-85 nm

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using XRD and SEM analysis, respectively. The effects of different parameters such as catalyst dosage, pH, the initial dyes concentrations, and the amount of loaded CuO were studied. The decolorization efficiency was achieved by 12.5 mg/L MB, 12.5 mg/L RhB, pH 5.3, 0.1 g/L of catalyst, and the CuO loaded onto the zeolite X 88 mg [147]. The same group was also parallelly studied the photodecolorization of a mixture of Methyl Orange and Bromocresol Green was studied using CuS incorporated into an Iranian clinoptilolite (CuS-Cp) under sunlight irradiation. The effect of various parameters such as the amounts of the catalyst, pH, initial dye concentration, and contact time were studied. The COD reduction was obtained about 91.3% in pH 7, 20 mg/L of dyes mixture, and 0.1 g/L of CuS-Cp catalyst during 480 min irradiation [148]. In 2014, the effectiveness of CuO incorporated into clinoptilolite nanoparticles was investigated in the photodecolorization of Methylene Blue and Bromophenol Blue by Nezamzadeh-Ejhieh and Zabihi-Mobarakeh. They showed that the best results can be obtained at pH 5.9, 0.2 g/L catalyst dosage and 4.9% loading of CuO. The decolorization percentage for MB and BPB were respectively achieved 61% and 32% during 180 min irradiation [149].

Entry	Dye	Time (min)	T (°C)	UV Intensity mW/cm ²	Catalyst Type	pН	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.
1	Rhodamine B and Magneson I	60-120	-	-	TiO ₂ hollow microspheres	-	66.7 MgI- 88.6 RhB	-	-	[146]
2	Methylene blue and Rhodamine B	180	-	-	CuO incorporated nanozeolite-X	5.3	68 MB- 45 RhB	-	-	[147]
3	Methyl Orange and Bromocresol Green	480	-	-	CuS-nano- clinoptilolite	7	-	91.3	-	[148]
4	Methylene blue and Bromophenol blue	180	-	75 W	CuO-nano- clinoptilolite	5.9	61 MB- 32 BPB	-	-	[149]
5	Methylene blue (MB) Real textile wastewater (TW)	120	25	15 W	Silver doped titania	6.8	-	99 MB- 98 TW	-	[150]
6	Reactive Blue 2	-	-	32 W	Nano-titania	3	95.22	-	92.52	[151]
7	Acid Red 27	120	25	8	Nano ZnO	7	-	83.3	-	[152]
8	Orange II and Methyl orange	3600	25	5.14	P25 TiO ₂ -ZnO	6	88 OII 41 MO	-	-	[153]
9	Acid Black 2	15	25	250 mW	ZnO	8.17	97	-	-	[154]

Table 7: Summary of photocatalytic oxidation studies in the removal of dyes.

Sahoo et al. investigated the photodegradation of methylene blue dye (MB) in an aqueous solution using Ag^+ doped TiO₂ under UV irradiation. The comparison of TiO₂ and Ag^+ doped TiO₂ showed that Ag^+ doped TiO₂ was an efficient catalyst. The effect of various parameters like the dosage of catalyst, initial dye concentration, pH, and contact time were studied. The Langmuir-Hinshelwood pseudo-first-order rate law was obtained for the degradation kinetics. The decolorization percentage was achieved 99% in 20 mg/L MB, 2 g/L of Ag^+ doped TiO₂ in 180 min while with untreated TiO₂ was 86% after 240 min. The COD removal was obtained 98% after UV irradiation for 420 min with 1 g/L Ag^+ doped TiO₂ [150].

Alvia et al. synthesized the ZnO nanostructures through low-temperature solution methods and used them for the photodegradation of rhodamine B (RhB) (2017). The average diameter of nanostructures was 80-100 nm. The rapid photodegradation of RhB dye was obtained 97% in 120 min [151]. Some of the recent studies in photocatalytic oxidation of dyes are summarized in Table 7.

Photocatalytic Ozonation (UV/O₃)

The combination of ozone with UltraViolet (UV) radiation is an effective method to remove organic compounds. A larger quantity of hydroxyl radicals (OH°) is produced under UV radiation. In this process, the starting radicals are generated through electron transfer

from photocatalyst to oxygen. Thus, the important difference between photocatalyst/ozone degradation and ozone degradation is the initiation step of the reaction [155].

Rajendiran et al. studied the photocatalytic-ozonation of textile dye using $(UV/TiO_2/O_3)$ processes. The dyes in textile industries are one of the major pollutions. The COD changed from 760 to 2080 mg/L and Total Organic Carbon (TOC) from 210 to 458 mg/L in this process. The COD removal was obtained 64% after 30 min of treatment with the maximum oxidation [156].

Mahmoodi investigated the photocatalytic ozonation of Reactive Red 198 (RR198) and Reactive Red 120 (RR120) using copper ferrite (CuFe₂O₄) nanoparticles. The nanocatalyst was prepared by the co-precipitation method. The effect of different parameters like the dosage of nanocatalyst, pH, salt (inorganic anions), and initial dye concentration were studied. The dominant aliphatic intermediates were determined formate, oxalate, and acetate anions. The mineralization products of dyes were obtained from nitrate and sulfate [157]. In another research, the same researcher studied the photocatalytic ozonation of Reactive Red 198 (RR198) and Direct Green 6 (DG6) dyes using nickel-zinc ferrite magnetic nanoparticle (NZFMN). The dyes were degraded 100% by hotocatalytic ozonation in the presence of NZFMN [158]. Furthermore, the photocatalytic ozonation (UV/O3) of Reactive Red 198 (RR198) and also Direct Green 6 (DG6) dyes were investigated

			1							
Entry	Dye	Time (min)	T (°C)	Catalyst Type	pН	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.	
1	Textile dyeing industries	30	-	TiO_2	10	98	64	-	[156]	
2	Reactive Red 198 (RR198) and Reactive Red 120 (RR120)	20	25	Copper ferrite (CuFe ₂ O ₄) nanoparticle	3	66.7 MgI- 88.6 RhB	-	-	[15 ^v]	
3	Reactive Red 198 (RR198) and Direct Green 6 (DG6)	20	25	Nickel-zinc ferrite magnetic nanoparticle (NZFMN)	3	100	-	-	[158]	
4	Reactive Red 198 (RR198) and Direct Green 6 (DG6)	-	25	Multiwalled carbon nanotube (MWCNT)	3	100	-	-	[159]	
5	Aniline (ANL) aqueous solutions	60	25	TiO ₂ -carbon composite	5.6	-	-	70	[160]	
6	Orange II	60	90	Bi ₂ O ₃ and Au/Bi ₂ O ₃ nanorods	5.3	75	-	-	[161]	
7	Phenazopyridine (PhP)	35		TiO ₂ nanoparticles coated on ceramic plates	7	85	-	-	[162]	

Table 8: Summary of photocatalytic ozonation studies in the removal of dyes.

by Mahmoodi in the presence of a MultiWalled Carbon NanoTube (MWCNT). The optimal conditions were achieved in an initial RB5 concentration of 150 mg/L, pH 3, and 0.03 g/L catalyst dosage at room temperature $(25^{\circ}C)$ [159].

Orge et al. studied the photocatalytic ozonation of aniline (ANL) using multi-walled carbon nanotubes (MWCNT), neat titanium dioxide (TiO₂), and a composite of TiO₂ and MWCNT. 50 g/m³ of ozone was consumed in photocatalytic and catalytic ozonation of aniline in 15 min. The total aniline conversion was obtained by using commercial TiO_2 , P25, and the composite of P25/MWCNT 80:20 (w/w) in longer reaction times. The TOC removal was 70% in all photocatalytic ozonation processes. The oxalic acid (OXA) was completely removed by photocatalytic ozonation, while oxamic acid remained [160]. The Combination of photocatalysis and ozonation for degradation of the organic dyes is introduced as an efficient method. Some of the recent studies in the photocatalytic ozonation of dyes are summarized in Table 8.

Photo-Fenton (Fe^{2+} or $Fe^{3+}/H_2O_2/UV$)

The Fenton processes usually lead to uncompleted mineralization, reduction of the recycling of Fe (III), and other competitive reactions. The reaction of Fe(III) with organic compounds gives stable Fe(III) compounds. Thus, further oxidation and mineralization will be difficult. One of the ways for high mineralization is the photo-Fenton's method. The Fenton processes can be considerably increased under ultraviolet light that called photo-Fenton's method. The complexation of ferric ions generates extra hydroxyl radicals under irradiation. These ions react with more H_2O_2 compounds in the Fenton reaction [163-167].

Shaban et al. studied the photo-Fenton oxidation of Congo red dye by natural chromite (FeO.Cr₂O₃). The effect of different parameters like the illumination time, dosage of catalyst, pH, and initial dye concentration were studied. The optimal conditions for photocatalytic degradation of Congo red dye were achieved at 12 mg/L of the dye concentration, 0.14 g of the chromite dosage, pH = 3, and 11 h of the illumination time. In addition, the percentage of degradation was observed 100% with 13.5 mg/L of the dye concentration, 0.10 g of the chromite dosage, pH 3, and 11 h of the illumination time. The chromium oxide and ferrous oxide generate the binary oxide system in Fe-chromite. The photocatalytic properties were obtained by H₂O₂ under photo-Fenton oxidation and UV irradiation. The percentage of degradation was observed with H2O2 59.4% after 8 h and 54.6% after 12 h in the absence of H₂O₂. The second-order rate law was obtained for photocatalytic degradation and photo-Fenton oxidation kinetics. The photo-Fenton oxidation of Congo red dye in the presence of natural chromite was more effective than the photocatalytic degradation. Thus, the values of kinetic rate constants were great for the photo-Fenton oxidation in the competition of the photocatalytic degradation [168].

The magnetic diatomite/Fe₂O₃/TiO₂ composite was used as an efficient catalyst for the degradation of

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Entry	Dye	Time (min)	[H ₂ O ₂]	[Fe ²⁺]	Catalyst	pН	Color Removal (%)	COD Removal (%)	TOC Removal (%)	Ref.
1	Congo red	600	1 mL	0.1 g	FeO.Cr ₂ O ₃	4	100	-	-	[168]
2	Methylene blue (MB)	40	1.2 mL	2 mg/L	diatomite/ Fe ₂ O ₃ /TiO ₂ composites	7	98.86	-	65.5	[169]
3	Rhodamine B (RhB)	60	40 mM	1 g/L	Iron molybdate Fe ₂ (MoO ₄) ₃ nanopowders	-	97	-	-	[170]
4	Malachite green (MG)	60	90 mM	0.1 g/L	Double shell hollow Fe ₂ O ₃	-	99.9	-	-	[171]
5	Reactive black 5 (RB5)	60	11 mM	-	-	3	100	-	-	[172]
6	Carmoisine edible dye	12	0.3 mmol	0.0125 mmol	-	3.5	95.8	89	-	[99]
7	Rhodamine B (RhB)	120	10 mM	1 g/L	Graphene oxide (GO)-FePO ₄ composites	2.18	93	-	-	[173]
8	Rhodamine B (RhB)	60	6 mM	0.4 g/L	Iron modified rectorite	3	99	-	-	[174]
9	Rhodamine B (RhB)	100	12 mM	2 g/L	Poly-hydroxyl-iron/sepiolite (H-Fe-S)	2.5	99.8	86.1	38	[97]
10	Acid Blue 193, Reactive Black 39	45	35 mM	1.5 mM	-	3	99	83	58	[175]

Table 9: Summary of photo-Fenton's oxidation process studies in the removal of dyes.

methylene blue dye under the photo-Fenton system by *Barbosa et al.* This reaction was performed under neutral pH. The catalyst was synthesized by the co-precipitation method in the presence of diatomite. Then, the catalyst was saturated with TiO₂. The optimal amount of the catalyst was obtained 2.0 g/L for photodegradation degradation. The percentage of the degradation of methylene blue was observed 98.86% with 2.0 g/L of the catalyst after 40 min at 75°C. Therefore, this procedure is very striking for industrial application in oxidative methods with an effective catalyst [169].

Rashad et al. studied the photo-Fenton-Like removal of Rhodamine B dye using iron molybdate $Fe_2(MoO_4)_3$ nanopowder under visible light irradiation. The catalyst was synthesized by co-precipitation and sol-gel autocombustion methods. The highest photo-Fenton catalytic activity was exhibited 97% for the degradation of RhB dye after 60 min. These results are related to the strong absorption and the high surface area of $Fe_2(MoO_4)_3$ in visible light [170].

The degradation of Carmoisine edible dye by photo-Fenton and Fenton processes from aqueous solutions through Taguchi orthogonal design investigated by *Sohrabi et al* [99]. The effect of operating parameters such as the dosage of H₂O₂, pH, the dosage of Fe^{2+,} and initial dye concentration were studied. The optimal conditions for photo-Fenton of Carmoisine edible dye were achieved 0.3 mmol H₂O₂, 0.0125 mmol Fe²⁺, 20 mg/L of the initial dye concentration, pH 3.5. The percentage of degradation was observed 95.1% for the photo-Fenton processes in optimal conditions. Some studies using photo-Fenton's reagent oxidation of dyes are illustrated briefly in Table 9.

UV/Chlorine

The chlorine solutions are consumed in swimming pools under direct sunlight as a disinfectant [176]. The effect of chlorine solutions can be considerably increased under ultraviolet light as the UV/chlorine process. The hydroxyl radicals are the predominant active species of the UV/chlorine process [176]. Chatib et al. studied the decolorization kinetics of Ponceau S dye under sunlight/chlorine and UV/chlorine processes [50]. The decolorization rates of Ponceau S solutions were obtained 47.6%, 52.4%, and 99.2%, respectively in dark/chlorine, sunlight/chlorine, and UV/chlorine processes at pH 4.5. The efficacy of UV in combination with chlorine dioxide (UV/ClO₂) for color degradation of the azure C dye in an aqueous solution was investigated by Habeeb and Khayoon [177]. The maximum color removal of 93.8% was achieved under optimal conditions at a dosage of

Entry	Dye	Time (min)	T (°C)	UV Intensity mW/cm ²	Condition	pН	Color Removal (%)	TOC Removal (%)	Ref.
1	Ponceau S dye (PS)	5	25 ± 2	-	UV/Chlorine/	4.5	99.2	-	[50]
2	Ponceau S dye (PS)	5	25 ± 2	-	Sunlight/Chlorine	4.5	52.4	-	[50]
3	Ponceau S dye (PS)	5	25 ± 2	-	Dark/Chlorine	4.5	47.6	-	[50]
4	C.I. Reactive Red 2 (RR2)	6	25 ± 2	2	UV/Chlorine	7	97.9	-	[178]
5	Rhodamine-B (RhB)	75	30 ± 2	0.7	UV/Chlorine	7	98.5	40	[179]
6	Azure C	60	25 ± 2	173.7	UV/Chlorine	8	93.8	-	[177]

Table 10: Summary of UV/Chlorine process studies in the removal of dyes.

 1×10^{-5} M of azure C, 173.7 mW/cm² of light intensity, 25 ± 2 °C of temperature, and pH of 8 at 60 mins. Some studies using UV/chlorine of dyes removal are illustrated briefly in Table 10.

CONCLUSIONS

In this review, the efficiency of AOPs techniques based on green approaches for successful wastewater treatment was discussed. The optimum operating parameters were differed due to the wastewater quantity and quality. The efficiency of degradation in many results was observed with high yields. However, the invention of new approaches with high efficiency and low environmental effect for the decolorization of the mixture of dyes is a challenge. Therefore, the introduction of new methods for the decolorization of the mixture of dyes is under investigation by many research groups.

THE RESEARCH METHODE

This review is presented according to library research involving the reviews, books, and literature.

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