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The Use of Peroxides as Green Oxidants for Color Removal from Textile Industry Wastewater

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Abstract

The textile industry is known as one of the most water-intensive industries and discharges a wide range of complex chemicals into its effluents which depend on a variety of factors including the type of wet processes used as well as the dyes and dye auxiliaries applied in the fabric dyeing stage. The main environmental issue the textile industry is confronted with is the persistent and strong color in dyehouse effluent. Several treatment alternatives have been proposed for efficient color removal including advanced treatment processes and operations; however most of the time with limited success. Among these, the so-called "Advanced Oxidation Processes (AOPs)" have particularly proven to be successful in the degradation of dyestuffs and dye auxiliary chemicals. "Green peroxides", such as the well-known Hydrogen Peroxide (HP) as well as Persulfate (PS), Peracetic Acid (PAA) and Percarbonate (PC), have more recently received attention. These have been used together with powerful oxidants such as ozone (O_3) or were activated thermally (at elevated temperatures), electrochemically, photochemically by short ultra-violet (UV-C) light, etc. This review paper provides a brief summary of recent experimental work where green oxidants (peroxides) were used in AOPs for color removal from aqueous dye solutions, textile wastewater and dyehouse effluent. The treatment performance in these studies was evaluated in terms of color, Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) removals besides other parameters being important/typical for the textile industry. However, a crucial factor in real-scale applications remains the techno-economic optimization of AOPs since these are very energy-intensive processes.

Keywords: Color removal; Peroxides; Textile industry; Dyebath effluent; Advanced oxidation processes

Abbreviations: AOPs: Advanced Oxidation Processes; ($CH_3C(O)O\bullet$): Acetyloxy Radical; ($CH_3C(O)OO\bullet$): Acetylperoxy Radical; BOD_5 : 5th Day Biochemical Oxygen Demand ($mg\ O_2\ L^{-1}$); COD: Chemical Oxygen Demand ($mg\ O_2\ L^{-1}$); $CO_3^{\bullet-}$: Carbonate Radical; E^0 : Reduction Potential (eV); $HCO_3^{\bullet-}$: Bicarbonate Radical; $HO_3\bullet$: Hydridotrioxxygen Radical; $HO_2\bullet$: Hydroperoxy Radical; HP: Hydrogen Peroxide; H_2O_2 : Hydrogen Peroxide; $HO\bullet$: Hydroxyl Radical; k : First-and Second-Order Reaction Rate Constant (min^{-1}); O_3 : Ozone; O_3/H_2O_2 : Hydrogen Peroxide-Assisted Ozonation; O_3/PAA : Peracetic Acid-Assisted Ozonation; O_3/PC : Percarbonate-Assisted Ozonation; O_3/PS : Persulfate-Assisted Ozonation; PAA: Peracetic acid; PC: Percarbonate; PMS: Peroxymonosulfate; PS: Persulfate; $S_2O_8^{2-}$: Peroxydisulfate/Persulfate Ion; $SO_4^{\bullet-}$: Sulfate Radical; TOC: Total Organic Carbon ($mg\ C\ L^{-1}$); UV-C: Short Ultra Violet (light, irradiation); UV-C/peroxide: Treatment Based on UV-C Photolysis of Peroxides

Introduction

Among industries, the textile industry is known for the variety of chemicals used as well as its extremely high water consumption, which is typically exceeding several hundred cubic meters per day. In fact, textiles require between 80-400 L water/kg of fabric produced, making the textile business one of the most water-intensive industries [1]. Additionally, the quality of water is seriously endangered by effluent discharge from textile preparation, dyeing and finishing activities into receiving water bodies. Particularly textile dyes and associated dye assisting chemicals such as surfactants, salts, sequestering agents and biocides are posing a serious risk in the aquatic environment [2]. The pollution discharge in terms of chemical oxygen demand (COD) is 115-175 kg COD/t of finished textile product, besides a high salinity, low biodegradability and resistant color [3-5]. These have been applied with partial success and there is an urgent need to address the removal of resistant color from dyehouse effluent using efficient, but at the same time economically attractive and environmentally friendly treatment alternatives. Coming back to the problem of color in industrial effluent; the production of more than 10,000 dyestuffs annually has led to the release of significant volumes of colored effluent into wastewater by a variety of industrial processes including textile, tannery, paint, pigments, pulp and paper manufacturing [6]. Dyes, once released into the aquatic environment without proper treatment, might reduce light penetration, alter photosynthetic activity and once subjected to anoxic/anaerobic conditions could be converted to potentially harmful (carcinogenic) dye metabolites such as aromatic amines [7]. Among the textile dyes, fiber reactive dyes have received special attention due to their high production and release rates. Reactive dyes are used to dye cotton, regenerated cellulose, cellulose acetate and wool fibers [8]. They constitute up to 50% of the total textile dye market and are intentionally designed to resist biodegradation as well as photochemical/thermal decomposition. Further, reactive dyes cannot be reused after the dyeing process and remain in their spent, hydrolyzed form. Hence, their removal becomes a major challenge to the textile dyer and finisher [9,10].

Color in Dyehouse Effluent and Advanced Treatment Alternatives

Over 100,000 dyes are thought to be commercially accessible [11]. They are categorized based on their source, color, use and chemical structure [12]. The chemical structure-based dye classification categories include azo, anthracene, indigo, phthalocyanine, sulfur, nitro, and nitroso, among others, while the fiber application-based groups are reactive, disperse, acid, basic, direct and vat [13,14]. They contain chromophores which impart dyes their color. Auxochromes which are substituents that donate or withdraw electrons and cause the color of the chromophores, may also be present [13-15]. Azo, carbonyl, methane, nitro and quinoid groups are the most prevalent dye chromophores [16], whereas amine, carboxyl, sulfonate and hydroxyl groups are the most significant dye auxochromes [17,18]. The most popular textile dyes are the azo(-N=N-) type because they are used in the synthesis of most colors [19]. Additionally, several dye auxiliaries are used to assist the dyeing process [20]. When reactive dyes are applied for dyeing, the alkali dye fixation rate onto the fibers is typically less than 80%, causing more than 20% of the applied dye to get lost into the exhausted dyebath in its hydrolysed (exhausted), unfixed form. Due to intensive reactive dyeing activities, textile wastewater has a high pH, high salinity due to the extremely high concentrations of

NaCl, Na₂CO₃, Na₂SO₄ and NaOH used in these processes [21-23]. For the removal of textile industry dyes from dyehouse effluent several physical, chemical and biological methods have already been developed and used such as activated carbon adsorption, membrane operations (nanofiltration, ultrafiltration, reverse osmosis), chemical precipitation, coagulation-flocculation, ozonation, electrochemical oxidation, fungal treatment, activated sludge, biofilms as well as many others [3-5]. However, most of these have shown rather limited success and/or were economically not feasible for efficient color removal from dyehouse effluent. It should be also noted here that textile dyeing and finishing activities are mainly practiced in developing countries that face serious financial problems. Hence, the search for more effective and at the same time affordable, sustainable, ecotoxicologically safe treatment alternatives remains a serious technical challenge for this industrial sector. Among these advanced treatment alternatives, the so-called Advanced Oxidation Processes (AOPs) have been used for the removal of biologically resistant and/or toxic/harmful pollutants through the generation of highly reactive oxidizing species (free radicals) from water and wastewater. AOPs involve conventional oxidants such as O₃ or H₂O₂ (HP), short ultra violet (UV-C) light, (photo)catalysts (metal oxides, semiconductors), power ultrasound (sonolysis) or thermal energy to produce free radicals such as the hydroxyl radical (HO[•]). By the use of AOPs it is expected to enhance oxidation rates, reduce toxicity and/or increase the biodegradability [24,25]. More recently, sulfate radicals (SO₄^{•-})-based AOPs have also been explored as alternative, advanced treatment processes. Originally introduced for soil and groundwater remediation in the early 2000's to overcome some technical limitations of HP, persulfates (PS) has been activated as HP; however this time to initiate SO₄^{•-}-based reactions. Inherent advantages of PS-mediated AOPs can be given as a higher free radical formation yield, higher selectivity of SO₄^{•-} and the reduced storage and transportation costs associated with the use of PS [26,27]. Moreover, SO₄^{•-}-based AOPs are known to be less sensitive towards reaction conditions (pH, environmental parameters, etc.). In particular, green oxidants such as the peroxides HP and PS, but also peracetic acid (PAA) and percarbonate (PC) have recently been used in combination with activators for the treatment of water and wastewater. These have been briefly reviewed in this paper for color removal from textile effluent.

The Use of Green Peroxides for Color Removal from Dyehouse effluent

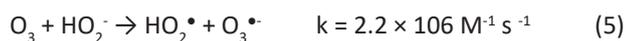
H₂O₂ (HP) and Combinations

As one of the strongest oxidants ($E^0 = 1.78$ eV), the peroxide H₂O₂ is commonly applied for the removal of reduced sulfur species, cyanides and some organic chemicals [29]. It is also used as a bleaching agent in some industries [2,3]. Commercially, it is offered in aqueous solution with concentrations ranging from 35% to 70% on weight basis. At all ratios, HP infinitely dissolves in water. Depending on the temperature, solution pH and the presence of organic contaminants including phenolic compounds and stabilizers, it decomposes exothermically into H₂O and O₂ [29]. HP decomposes in the presence of ozone, ferrous ions and UV radiation to produce free radicals which are known as strong oxidants. There are several examples in the scientific literature for employing the peroxone (O₃/HP) process for color removal from textile wastewater, old landfill leachate treatment and for volatile organics removal from groundwater [30,31]. HP is a weak acid; at highly alkaline pH it is dominant in its dissociated (ionized) form (pK_a = 11.74). In the presence of

ozone, it initiates free radical chain reactions to produce HO• at alkaline pH. Further, excessive HP concentrations might lead to HO• scavenging reactions as shown below;



For ozonation at alkaline pH and the presence of HP, the three phases of the free radical chain reactions, namely initiation, propagation and termination can be shown as below [30-32];



Several studies were reported for color removal by AOPs involving HP. The effect of ozonation (HP-assisted ozonation), electrolysis, electrolysis combined with HP, and combinations thereof were examined for the decolorization of the dye crystal violet (CV) from aqueous solutions (applied ozone dose = 2 mg L⁻¹ min⁻¹, pH = 3-9 (optimum found as pH = 9), reaction time = 30 min at an initial CV concentration of 25-200 mg L⁻¹. Results indicated that peroxone and electrolysis combined with peroxone were more effective in terms of color removal than the others. Color removal was always above 90% and compared to the parent pollutant, the CV breakdown products formed during peroxone treatment were more toxic towards *E. coli* bacteria [33]. In another study, ozonation and peroxone processes were applied to degrade synthetic wastewater bearing the dye Direct Red 80 (100 mg L⁻¹) and the effect of several process variables on color removal efficiency was examined via UV-visible spectrometry, three-dimensional fluorescence spectroscopy and ion chromatography. A Direct Red 80 degradation pathway was proposed. 99% color and 27% COD removals were obtained at pH = 12 for mere ozonation. COD removal increased to 40% when HP was added at a mass ratio of 1:10,500 to ozone. When the pH was increased to 13, the COD removal improved to 43%. These findings indicated that HP and elevated pH values increased oxidation rates appreciably [34]. In another study, the addition of 100 mg L⁻¹ HP during ozonation of an aqueous Direct Black 22 (DB22; 100 mg/L) dye solution (t = 30 min; pH = 3-11; ozone dose = 5 g/h for 30 min) resulted in a COD removal of 66% instead of 40% COD removal for mere ozonation. HP alone was capable of only 23% color removal from 100 mg L⁻¹ DB22 solution. Color removal increased from 72% (ozonation alone) to 90% for the same dye solution once coupled with 5 mg L⁻¹ HP [35]. Perkowski *et al.* [36] reported color removals of 98% and 100% for ozonation of a dyebath effluent containing Acid Blue 62, Direct Yellow 44 and Direct Brown 2 after 60 min and 120 min ozonation at a rate of 5 mg min⁻¹, respectively. In that study, HP enhanced color removal appreciably. However, according to several other works, HP had no positive effect on color removal during ozonation of dyes or dyebath effluents. Arslan and Balcioglu [37] investigated O₃ and O₃/HP treatment of a simulated reactive dyebath effluent. The effect of pH, initial dye concentration, HP concentration and dye assisting chemicals was studied. At pH = 11, which is nearly the pH of the simulated reactive dyebath effluent, color and COD removals increased considerably; and increasing the dyestuff (Reactive Black 5) concentration had a negative impact on oxidation rates. The addition of soda-ash had an inhibitory effect on ozonation, acting as a free

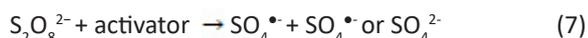
radical scavenger. As compared to ozonation alone at varying pH which increased with increasing pH, the addition of HP had a negligible (practically no) effect on color as well as COD removals rates and efficiencies [37]. Swaminathan *et al.* [38] studied ozonation of the dye surrogate H-acid at varying pH values and ozone doses. pH = 11.5 was most efficient for color (99%) and COD (88%) removals (30 min ozonation with 4.33 mg L⁻¹ ozone). Nitrate and sulphate being released during ozonation served as evidences for oxidative degradation of H-acid. The study also demonstrated that HP addition had no positive effect on color and COD removals. A pseudo-first order kinetics were determined for ozonation of H-acid. The biodegradability indicated as the BOD₅/COD ratio increased during ozonation. Wang *et al.* [39] studied the effect of HP on ozonation of dye-house effluent in the concentration range of 1-100 mg L⁻¹. They concluded that HP generally speaking had a negative impact on COD removal efficiencies compared to ozonation both in terms of color and COD parameters. The effect of HP was attributed to its free radical scavenging effect at elevated (excessive) concentrations. In another study, a synthetic wastewater containing the dye Bomaplex Red CR-L was subjected to treatment via ozone, peroxone and soda-ash/ozone. For all examined treatment processes, high color (99%) and COD removals (> 50%) were achieved after 30 min ozonation at a dose of 5 g h⁻¹. When compared to the ozonation process the O₃/HCO₃⁻ process had a positive impact on COD removal efficiency, while the O₃/HP process had a negative impact [40]. According to Aleboye *et al.* [41] the optimum operating conditions for the HP/UV-C process of the acid dye Acid Orange 7 (AO7; 17.5 mg L⁻¹) for 100% color and 95% TOC removal were 25 min and 120 min UV-C radiation, respectively. However, in comparison to the O₃/HP process, the optimum HP concentration for HP/UV-C treatment was 50 times higher. In order to remove 100 mg L⁻¹ Acid Red 27 from aqueous solutions, the traditional Fenton's reagent (Fe²⁺/HP) and its modification [42] using zero-valent iron-activated HP (ZVI/HP) were employed. Under optimized treatment conditions (Fe²⁺/HP; pH = 3.5, Fe²⁺ = 18 mg L⁻¹, HP = 60 mg L⁻¹, t = 15 min, ZVI/HP; pH = 3, ZVI = 80 mg L⁻¹, HP = 40 mg L⁻¹, ZVI = 80 mg L⁻¹, t = 15 min) COD removals were obtained as 71.5% and 69.2% for the traditional Fenton and its modification, respectively. The *Vibrio fischeri* acute toxicity test results indicated that the toxicity (relative inhibition) value decreased to < 25% after treatment. Color removals were high and the final, effluent COD values ranged between 49-53 mg L⁻¹. Red Cl-5B dye (100, 300 and 500 mg L⁻¹) was treated with UV-C, O₃, H₂O₂, HP/O₃ and HP/O₃/UV-C at an ozone dose of 75-450 mg min⁻¹, a reaction time of 30 min and 225 mg L⁻¹ HP. More than 90% color was removed via ozonation alone and could not be improved in the presence of HP. However, HP/UV was particularly effective since it provided 100% decolorization within 5 min treatment. When the dye concentration was increased from 100 to 300 mg L⁻¹, the decolorization rate reduced by half for all studied treatment processes. A comparison of color removal rate constants revealed that UV-C alone is four times slower than HP/UV-C. Because of HP overdosing, HP/O₃ treatment was three to four times slower than ozonation alone. In comparison to the other tried processes, HP/UV-C treatment appeared to be superior and more suitable in terms of color removal under all studied conditions. Complete color removal was obtained for Red Cl-5B solution within 30 and 50 min HP/UV-C treatment of 100 and 300 mg L⁻¹, respectively [43].

Arslan *et al.* [44] reported that HP/O₃ treatment of synthetic dyehouse effluent highly depended upon the reaction pH and ozone absorption increased from 11% at pH = 2.5 to 74% at pH

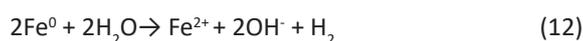
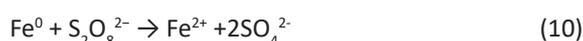
= 11.5 and in the presence of 10 mM HP due to enhanced ozone decomposition at elevated pH values and the presence of free radical chain initiators. In addition, more HP is dissociated into HO_2^- ions at $\text{pH} \geq 11.5$. In another related study, complete decolorization of C.I. Reactive Blue 220 and C.I. Reactive Yellow 15 was accomplished after 90 min ozonation at an ozone dose of 1.5 g h^{-1} [45]. Kurbus *et al.* [46], on the other hand, postulated that the same dyes could be completely decolorized in 20 min with the Fenton's reagent. The Fenton process was carried out at $\text{pH} = 3$, while peroxone treatment was conducted at $\text{pH} = 12$. In both treatment processes HP concentration was critical and exhibited an optimum value. The HP to O_3 mass ratio also affected the acute toxicity (here: microbial development). This ratio varied depending on the type of dye, from 0.3 to 0.6.

Persulfate (PS) and Combinations

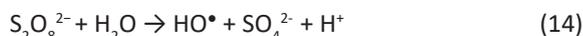
PS-based AOPs are also frequently used to degrade industrial pollutants found in water and wastewater. In PS-based advanced oxidation, activation is in most cases essential since PS alone has a limited capacity to oxidize organic contaminants. Therefore, numerous activation methods have been thoroughly researched in the past to increase its oxidation efficiency. Due to high reduction potential of the sulfate radical ($E^0 = 2.7\text{-}2.8 \text{ eV}$) which is comparable to that of the hydroxyl radical ($E^0 = 2.9\text{-}3.0 \text{ V}$) its potential for use as an alternative active oxidant to remove emerging pollutants has been explored [47]. PS or peroxymonosulfate (PMS) can be activated through alkaline reagents, thermally (by heat), microwave, ultrasound (US), as well as with photo- and electrochemically [48];



Fe(II) ions and ZVI (Fe^0) can also be used to activate PS as shown below [49];



PS activation with alkalinity is given below [50];



PS and PMS activation by UV-C irradiation results in its homolytic cleavage to sulfate radicals [48,51] according to equations (16)-(18);



Weng *et al.* [52] examined PS activated with Fe^0 for the decolorization of the azo dye C.I. Direct Red 23 (DR23). Heat was applied also applied to enhance the oxidation system. Thermal treatment (PS/ $\text{Fe}^0/55^\circ\text{C}$) considerably improved the decolorization rate of the oxidation system. At $\text{pH} = 6.0$, $\text{PS} = 5 \text{ mM}$, $\text{Fe}^0 = 0.5 \text{ g L}^{-1}$, about 95-100% decolorization of 0.1 mM DR23 was accomplished in 15 min that decreased to 10 min treatment for

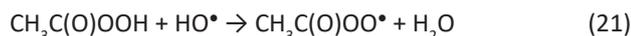
the $\text{Fe}^0/\text{PS}/55^\circ\text{C}$ treatment system. The degree of degradation and mineralization was confirmed via UV-Vis spectroscopy and TOC measurements. Color removal from aqueous Reactive Blue 52 (RB52) with PS/UV-C was also studied. After 30 min treatment at $\text{pH} = 3\text{-}4$, color removal increased from 55% to 99% when PS was increased from 5 mM to 15 mM [53]. PS/UV-C treatment of Acid Blue 129 (25 mg L^{-1}) was also reported. 2.5 mM PS/UV-C treatment resulted in 87% color removal within 60 min. Increasing the PS concentration to 10 mM decreased the color removal rate constant (obtained as 0.029 min^{-1} under optimized reaction conditions) due to peroxide overdosing. Acute toxicity bioassays of the oxidation intermediates indicated that these were less toxic/inhibitory than the parent pollutant-original dye solution [54]. The effectiveness of ZVI/PS oxidation on Remazol Golden Yellow (Reactive Orange 107; RO107) indicated that PS activation with ZVI appreciably enhanced color removal. The effects of pH, Fe^0 and PS concentrations as well as temperature on color removal were examined. Optimum RO107 treatment conditions for 100 mg L^{-1} were established as $\text{pH} = 6.0$, $\text{PS} = 0.5 \text{ mM}$, $\text{ZVI} = 0.5 \text{ g L}^{-1}$. Under these circumstances, 98% color removal occurred after 20 min treatment [55]. The effectiveness of PS/ O_3 treatment on color removal from Acid Orange 52 (AO52) solution was demonstrated. PS/ O_3 treatment outperformed ozonation and $\text{pH} = 2\text{-}6$, PS concentration (25-65 mM) and reaction time (3-25 min) had dramatic effects on COD removals. The highest COD removal of 75% (initial COD = 50 mg L^{-1}) was achieved after 60 min PS/ O_3 treatment (1.5 mL min^{-1} at 70 mg min^{-1}) compared to ozonation alone resulting in 65% COD removal [56].

Peracetic Acid (PAA) and Combinations

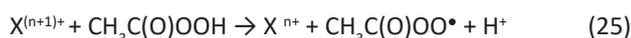
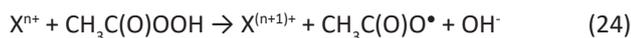
The reduction potential of peracetic acid ($\text{CH}_3\text{CO}_3\text{H}$; PAA) is relatively high ($E^0 = 1.81 \text{ V}$) and the reactive oxygen content is nearly 21% [57]. PAA is also be used as a disinfectant [57,58]. However, PAA has just recently been employed for water/wastewater treatment. The potential of PAA and other alternative oxidants became subject of interest in the late 1970's due to the rising awareness about the presence of harmful disinfection by-products (DBPs) being formed during chlorination [58]. PAA appears to be an attractive disinfectant and oxidant due to several reasons; its inherent selectivity, efficiency at room temperature, stability/long shelf-life, deodorizing capacity and acceptable price [59]. The peroxy radicals $\text{CH}_3\text{COO}^{\bullet}$ and $\text{CH}_3\text{CO}_2\text{O}^{\bullet}$, which play an important role in PAA-based AOPs, can react with organic compounds and initiate free radical chain reactions [60]. However, $\text{CH}_3\text{COO}^{\bullet}$ and $\text{CH}_3\text{CO}_2\text{O}^{\bullet}$ exhibit a higher selectivity for electron-rich sites than HO^{\bullet} [61]. As for the other peroxides, several activation methods exist for PAA to initiate indirect oxidation reactions of in-situ formed reactive species. When PAA is activated via transition metals, a primary electron exchange and not free radical pathway may occur. Reaction equations Nr. (19) and (20) demonstrate how the O-O bond in HP/PAA is broken in response to the high energy radiation delivered, producing HO^{\bullet} and $\text{CH}_3\text{C(O)O}^{\bullet}$. This is the crucial, preliminary stage of PAA activation which has a profound effect on the later stages as the reaction progresses. Additionally, a little quantity of HP is present in the PAA solution, which can be activated by an energy input (chemical, photochemical, thermal, sonolytic, etc.) to produce HO^{\bullet} that may take part in subsequent reactions;



The HO[•] abstracts hydrogen atoms from PAA and in this way generates free and organic radicals, of which CH₃C(O)OO[•] is the major reactive organic specie, as shown in Equations (21-23);



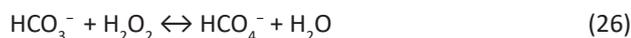
PAA can generate free radicals other than HO[•], which complicates the activation system of PAA-involving oxidation processes [62]. Homogeneous and heterogeneous catalysis, both of which use transition metals/metal oxides as catalysts have cyclic activation mechanisms because they can both gain and lose electrons as given in Equations Nr. (24) and (25);



It is generally accepted that R-O is the primary reactive specie once PAA is activated by metals. Scientists mainly work with free radical and charge transfer probe chemicals as well as electron paramagnetic resonance to identify the primary reactive species involved in transition metal/PAA oxidation systems. This approach is debatable because it depends on the free radical's predominant reaction. In these studies it has been evidenced that in metal/metal oxide-activated PAA involving treatment systems, charge transfer rather than free radicals are mainly involved in pollutant degradation [63]. Souza *et al.* [64] worked with PAA treatment alone, UV-C treatment alone, addition of PAA upstream and downstream of UV-C radiation (PAA/UV-C). According to the results of this study, PAA/UV-C treatment exhibited the highest oxidation efficiency. Furthermore, PAA/UV-C treatment might considerably reduce the disinfectant dosage and contact time [64]. Due to its great potential, its application for color removal from reactive dyebath effluent has recently been explored by our research group (unpublished work).

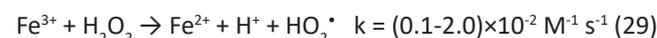
Percarbonate (PC) and Combinations

The use of PC as a cleaning agent and disinfectant offers several advantages such as a high and at the same time selective oxidative capacity, low sensitivity to pH, low toxicity and affordable price [65]. PC would not require additional recycling or regeneration procedures and costs as compared to other typical treatment approaches, including carbon-based adsorption methods [66]. In PC-based AOPs, activation is achieved via metal ions/oxides, discharge plasma, ozone and other methods to produce HO[•] and O₂^{•-}, besides two other important, less strong but more selective, powerful oxidants, namely carbonate (CO₃^{•-}) and bicarbonate (HCO₃^{•-}) radicals depending on the reaction pH [67]. With a structure similar to other peroxides like peroxyhydrate (H-O-O-NO) and PMS (H-O-O-SO₃), peroxymonocarbonate (PMC) is a real peroxide as opposed to PC. Nuclear magnetic resonance data revealed that the pre-equilibrium interaction between HP and HCO₃⁻ produces PMC. The reduction potential of the HCO₄⁻/HCO₃⁻ couple is 1.8 ± 0.1 eV [50,51]. The related reaction is shown below;



Iron compounds (salts, oxides, zero valent metal) are often used for PC activation, whereas cobalt compounds are used in homogeneous and heterogeneous catalytic systems to activate PMC [68-70]. Additionally, PC can be activated electrochemically, or with tetraacetyethylene diamine, ozone, buffered alkali

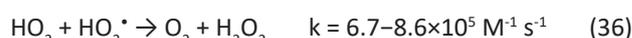
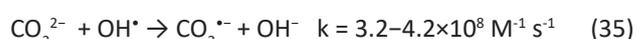
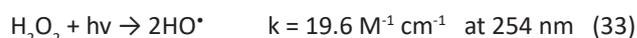
reagents and other substances to form a variety of reactive species for pollutant removal [71]. While a proper concentration of certain activators and initiators may enhance the formation of free radicals, some anions (chloride, phosphate, etc.) may have negative impacts on the degradation of pollutants acting as free radical scavengers [53,54]. Formation of active oxygen species and the Fenton reactions involved in PC-activation are given below [72];



PC activation occurs in heterogeneous (solid, catalyst) and homogeneous (UV-C, thermal, sonolytic) medium. Similar to homogeneous catalytic treatment systems, the majority of research on heterogeneous catalysts for PC activation focused on ZVI, bimetallic oxides, iron oxides and supported iron oxides [73,74]. In these modified-Fenton (Fenton-like) oxidation systems, Fe(II) could be effectively recovered and regenerated as given below [73];



PC/HP activation through semiconductors electrons, UV-C, discharge plasma, sonolysis and microwaves to produce a variety of free radicals [73] is shown in the following reaction equations;



HCO₃⁻ can form HCO₃^{•-} and enhances the conversion of HO to CO₃^{•-}, which has a lower reduction potential and higher selectivity than HO[•] (E⁰ = 2.9-3.1 eV), namely 1.57 eV [75]. In activated PC oxidation systems, typically the working pH is neutral to alkaline to produce bicarbonate/carbonate radicals. Upon careful optimization of the pH and other operating conditions it is possible to benefit from several active oxygen species such as HCO₃^{•-}, CO₃^{•-}, O₂^{•-} and HO[•]. Compared to other peroxides such as PS, the PC-based oxidation system exhibits a relatively modest degradation efficiency due to its moderate reduction potential.

PC has been employed for the oxidation and disinfection of water/wastewater recently. In one study, a low and high pressure UV-C/PC treatment system was used for color removal from textile wastewater. PC concentration (100-400 mg L⁻¹ for low pressure and 100-250 mg L⁻¹ for the high pressure system), the Fe²⁺/PC mass ratio (0.2-0.4), initial reaction pH (3 and 4) and reaction time (10-30 min) were investigated. The proposed treatment systems were quite effective in color removal under optimized treatment conditions. The optimum PC concentration and Fe²⁺/PC ratio were 400 mg L⁻¹ and 0.2, respectively, at pH = 3 and t = 20 min for the low pressure UV-C treatment system. The optimum PC concentration and Fe²⁺/PC mass ratio were 200 mg L⁻¹ and 0.33, respectively, at pH = 3 and t = 20 min for the high pressure UV-C treatment system. The final (effluent) concentration of the target dyestuff Acid Green 16 (AG16) was in the range of 0.64-0.96 mg L⁻¹ when the starting (initial)

pH was 3, and in the range of 0.80-6.87 mg L⁻¹ when the starting pH was 4.0 [76].

Conclusions

From this review it can be concluded that extensive research has been done with most of the above-mentioned peroxides on color (textile dye) removal from dyehouse effluent. However, most treatability studies are limited to single textile dye solutions in pure water. More research is needed to be carried out with real dyehouse effluent and textile industry wastewater to question the real-scale applicability of green peroxides for efficient color and organic matter removal. While HP- and PS-activation methods have frequently been reported on different water and wastewater samples, PAA and PC have been relatively less explored. Numerous studies were devoted to process optimization and kinetics, color and TOC removals, toxicity and biodegradability assessments; however, only a rather limited number of experimental studies mentioned the associated treatment (capital and operating) costs. Thus future research should focus on detailed feasibility and cost analyses of the more recently explored, promising treatment methods involving green peroxide activation. Cost analysis should be supported with a life cycle assessment procedure to have a clearer and broader picture of the proposed treatment alternatives.

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