

Review

Bimetallic Fenton-like Catalysts in the Remediation of Dyes

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Abstract: Remediation of organic dyes in natural waters is a significant environmental need under active study. This review analyzes bimetallic catalytic degradation systems that are based on the Fenton chemistry concept and that generate reactive oxygen species (ROS) as the agent of dye breakdown. Recently developed advanced oxidation processes (AOPs) take advantage of bimetallic heterogeneous catalysts to facilitate rapid rates and full degradation. Catalysts based on two metals including iron, copper, molybdenum, cobalt and magnesium are discussed mechanistically as examples of effective radical ROS producers. The reactive oxygen species hydroxyl radical, superoxide radical, sulfate radical and singlet oxygen are discussed. System conditions for the best degradation are compared, with implementation techniques mentioned. The outlook for further studies of dye degradation is presented.

Keywords: dye degradation; radical oxygen species; transition-metal catalysts; environmental remediation

1. Introduction

The contamination of natural waters is a growing problem, which is largely due to industrial wastewater discharge and to agricultural runoff [1]. The United Nations' sustainable Development Goals (SDGs) include the availability and sustainable management of water and sanitation for all [2]. A significant measure of the status of freshwater is the Planetary Boundary analysis, which places freshwater use presently at a level of ca. 2600 km³ year⁻¹, which is below an estimated planetary boundary of 4000 km³ year⁻¹, but local boundaries are being exceeded at parts of the planet in North America, Asia, and Europe [3]. The dye contamination of waters is common from a variety of industries, including textiles, food production, printing services, and more. Presently, 20% of wastewater contamination is attributed to dye utilization [4]. The treatment of dye waste is a challenging problem [5–9]. The dye coloration of natural waters may damage ecosystems by filtering sunlight as well as being unappealing to the eye. Dyes of the azo group in particular are toxic, carcinogenic and mutagenic [10]. The chemical inertness that results in the robust tinting of materials such as fabrics is also an inertness to natural degradative processes. Due to the persistence of these dyes, numerous biological, chemical and physical remedial processes have been tested. Many of the biological techniques that degrade dyes leave smaller undesirable or toxic molecules in their wake [11]. Physical processes that fully degrade dyes, such as irradiation, are often energy-intensive and costly [12]. Additionally, these physical processes are feasible for water treatment, but not for environmental remediation.

This review aims to highlight the successful remediation of these organic dyes through oxidation processes with bimetallic catalysts, with a focus on examples from the past five years. This will be carried out through an introduction to oxidative remediation processes, followed by an examination of these oxidative processes for a variety of metals. Next, we detail the dye decomposition mechanisms in terms of catalyst efficiency and organic radical reactions. The review concludes with an environmental outlook on the impacts and future prospects of bimetallic Fenton-like reactions in the remediation of dyes in water systems.



Citation: Milam, L.R.; Planalp, R.P. Bimetallic Fenton-like Catalysts in the Remediation of Dyes. *Colorants* **2024**, *3*, 1–16. <https://doi.org/10.3390/colorants3010001>

Academic Editor: Anthony Harriman

Received: 7 August 2023

Revised: 10 December 2023

Accepted: 12 December 2023

Published: 21 December 2023



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1.1. Oxidative Degradation Processes

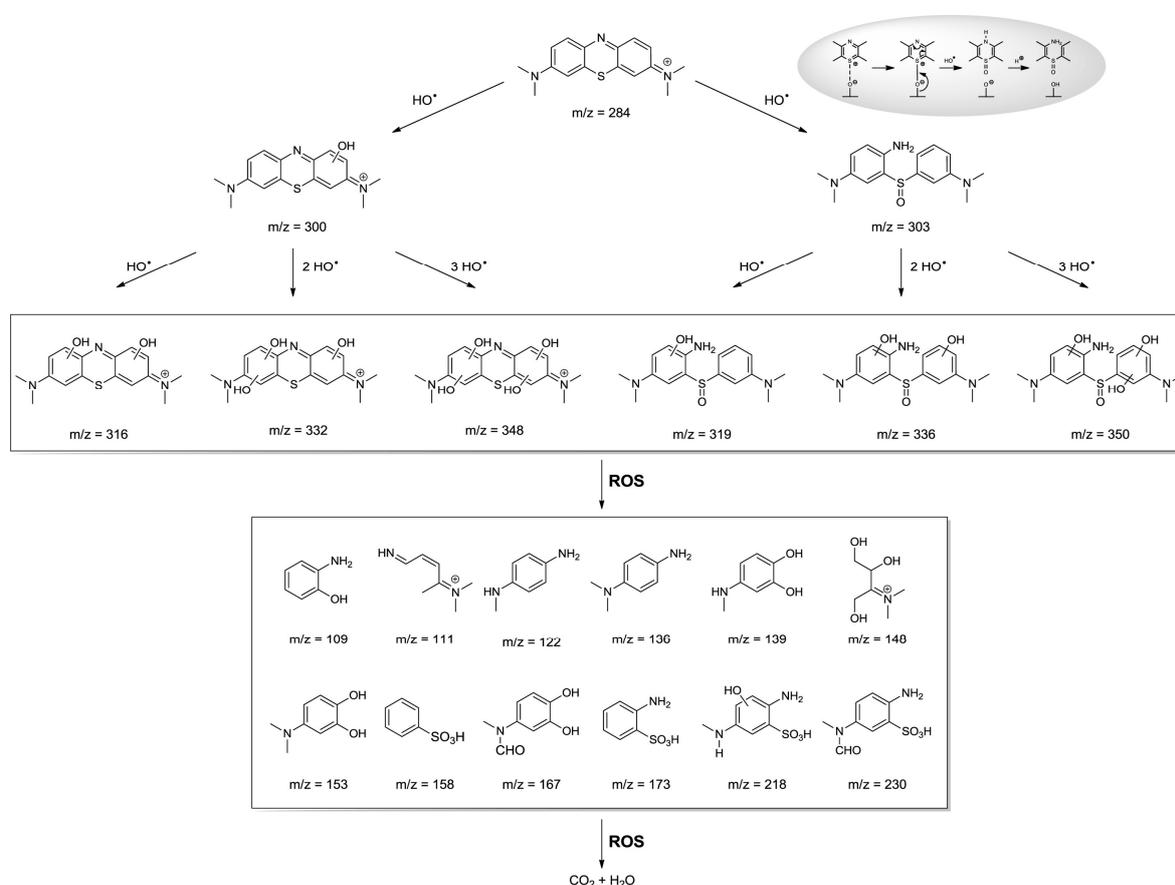
Processes that apply catalyzed radical production to oxidatively degrade environmentally undesirable substances are known as advanced oxidation processes (AOPs) [13]. We introduce classic Fenton chemistry as the forerunner to the development of AOPs, and detail several radical species which are produced to accomplish degradation. Thereafter, we describe “Fenton-like” oxidation processes in terms of a general set of reaction steps based on the Fenton process. The mechanistic steps that arise from the presence of two metals are treated in preparation for the consideration of specific systems.

1.2. Classic Fenton Chemistry

A common type of AOP utilizes Fenton chemistry, which is the redox-catalytic conversion of hydrogen peroxide to hydroxide ion and hydroxyl radical (Equation (1)). The hydroxyl radical then degrades organic pollutants through radical chain reactions. The Fenton process has existed since the 1890s [14] and has withstood the test of time, still being the most popular method to initiate the breakdown of organic compounds using H_2O_2 .



Hydroxyl radicals have been demonstrated to be effective in this regard, for example, in the breakdown of methylene blue via oxygen-based radicals as shown in Scheme 1 [15]. The process begins either through the addition of a hydroxyl radical to the ring, or the oxidation of the sulfur atom, which simultaneously severs the nitrogen–carbon bond. After several hydroxyl additions to the phenyl rings, the ring structure is broken into phenolic moieties. These will undergo ring-opening steps, followed by further oxidation to carbon dioxide and water [16].



Scheme 1. Example mechanisms of methylene blue degradation by hydroxyl radicals. Reproduced with permission from [15]. Copyright Elsevier, 2018.

1.3. Radical and Reactive Oxygen Species

The hydroxyl radical belongs to a large family of reactive oxygen species (ROS) which are either oxygen-containing, highly reactive free radicals or precursor molecules from which radicals may be made [13,17]. A variety of ROS are depicted in Scheme 2, being both reactive radicals and their precursors.

(a) radical ROS	(b) corresponding precursor for radical-generating metal reaction
O_2^{\bullet}	O_2
$HO^{\bullet}, HOO^{\bullet}$	H_2O_2
$S_2O_8^{\bullet-}, SO_4^{\bullet-}$	peroxydisulfate ($S_2O_8^{2-}$)
$SO_4^{\bullet-}, SO_5^{\bullet-}$	peroxymonosulfate ($SO_5H^{\bullet-}$)
1O_2 (*)	O_2^{\bullet}

Scheme 2. (a) Representative radical reactive oxygen species (ROS); (b) corresponding representative ROS precursors. (*) Although not a radical, singlet oxygen, 1O_2 , possesses electrophilic radical-like reactivity.

1.4. The Challenges of Fenton Cycling with Homogeneous Iron Catalysts

Following the generation of HO^{\bullet} via iron, it is necessary to reduce Fe^{3+} back to Fe^{2+} for continued ROS production. Equation (2) satisfies this requirement for a Fenton chemistry process; however, it is very slow [18,19]. Thus, conventional Fenton chemistry is not catalytically feasible for the bulk remediation of organic materials.

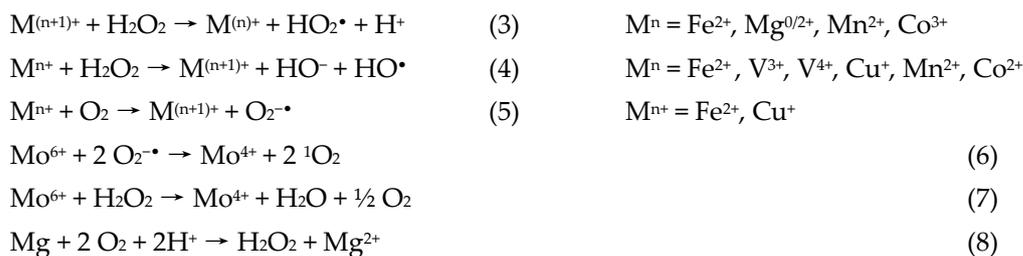


The initial studies of Haber and Weiss [20] indicated that the reactions $HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$ and $Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+$ result in the iron-catalyzed conversion of H_2O_2 to $O_2 + H_2O$, an undesired process that consumes the HO^{\bullet} intended for degradation. Kinetic studies indicate that these reactions may be avoided if the concentration of H_2O_2 is limited relative to iron [21,22]. With this constraint on H_2O_2 concentration, a rapid turnover of the iron catalyst is necessary.

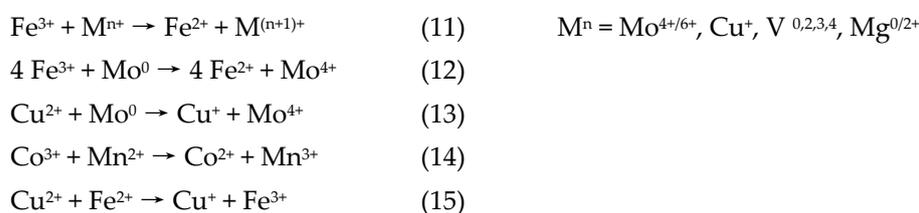
Additionally, the aqueous speciation of Fe^{3+} at pH levels near 7 is such that water bound to Fe^{3+} is hydrolyzed to insoluble iron hydroxide, $[Fe(OH)_3]_x$, with the release of $H^+(aq)$. The precipitated hydroxide is called "iron sludge", which is inactive and depletes the iron catalyst. Thus, conducting conventional Fenton chemistry for remediation requires acidification to a pH of 4 in order to suppress the hydrolyzed precipitate, followed by neutralization to restore the natural pH after degradation.

1.5. Bimetallic Catalyst Systems and the Modularity of Fenton-like Reactions

In Fenton-like reactions, researchers have varied three parameters, identified as the radical-generating metal reaction (Scheme 3), the reactive oxygen species (Scheme 2), and the cycling reduction reaction (Scheme 4). Intrinsic to the changes is a variation of the catalytic metal and, in the focus of this review, a process that engages two metals. It is also useful to classify the processes as homogeneous vs. heterogeneous.

Oxygen radical-generating metal reactions:**Sulfur-oxygen radical-generating metal reactions:**

Scheme 3. Examples of the modularity of Fenton-like chemistry: varied activating metals, Equations (3)–(5); generation of the radical ROS species hydroperoxyl radical, hydroxyl radical, superoxide and singlet oxygen, Equations (3)–(6); examples of sulfur-based ROS, Equations (9) and (10).



Scheme 4. Example of cycling reduction reactions to regenerate the reducing species Fe^{2+} , Cu^+ and Co^{2+} .

1.5.1. Homogeneous and Heterogeneous Fenton-like Processes

Homogeneous catalysts act only in the solution phase. To prevent iron hydroxide precipitation, an iron ligand can be used to solubilize iron. This has the benefit of raising the pH range for catalysis; however, the redox potential of the iron complex, $[Fe^{II}L]$, is also modified relative to $Fe^{2+}(aq)$, which may inhibit the reaction of Equation (1). Iron ligation also introduces the ligand as a secondary contaminant that may interfere with the recycling of spent catalysis [23]. Heterogeneous catalysts are often metal oxides or sulfides, which may be coated onto a support, such as silica, to provide a composite material [24]. Heterogeneous catalysts have the advantage of separability from the treated water, unlike the Fenton reaction, in which the homogenous iron catalyst is dissolved into a solution. In a heterogeneous system, a small amount of catalyst does dissolve, which contaminates the water; a challenge referred to as “leaching” [25].

1.5.2. The Radical-Generating Metal Reaction

Recent developments in the field have shown great improvements and further opportunities for increased ROS production by varying the metal ion to find improved electron transfer and redox cycling to generate ROS (Scheme 3, Reactions (3)–(6)). Other metal ions besides Fe^{2+} are sufficiently reducing to carry out the reaction $H_2O_2 + e^- \rightarrow HO\cdot + HO^-$, whose potential is estimated at 0.39 V at pH 7 [26]. Although Fe^{3+} has a redox potential of 0.77 V under standard conditions of pH 0, 1 M concentration, at pH 7 the presence of hydroxide ions and other oxygen-based ligands that stabilize Fe^{3+} indicates an adjusted reduction potential, with $pE(w)$ close to 0.0 V [27].

1.5.3. The Reactive Oxygen Species

Peroxyulfates are gaining increased use relative to hydrogen peroxide as the ROS precursor in the reaction. The sulfur ROS formed ($SO_4^{\cdot-}$, $SO_5^{\cdot-}$, $S_2O_8^{\cdot-}$) possess a lifetime of ca. 300 μs relative to a hydroxyl radical’s lifetime of less than 40 μs [28]. Reactive oxygen species may combine or produce other radicals in complex ways; for example, $HO\cdot$ can also

be formed from peroxyulfates, resulting in a mix of radical oxidizing agents [29]. Therefore, studies seek mechanistic information through the use of selective radical-quenching tests to determine the effect of radical removal upon the rate of degradation. The radical quenchers *tert*-butanol, thiobarbituric acid and potassium iodide [30] are selective for the hydroxyl radical [5,31–33], while PO_4^{3-} is selective for the $\text{SO}_4^{\cdot-}$ radical [25]. Other quenchers include *p*-benzoquinone for $\text{O}_2^{\cdot-}$ [30–33], catalase for hydrogen peroxide [31] and lastly tryptophan [33] or 2,2,6,6-tetramethylpiperidine (TEMP) for singlet oxygen [31,32].

1.5.4. The Cycling Reduction Reaction

In order to cycle Fenton-like chemistry, it is necessary to regenerate the activating metal species, for example, to accelerate Equation (2). An emerging area of Fenton-like degradation systems are bimetallic; that is, they utilize a second metal as a co-catalyst to facilitate the reduction of Fe^{3+} or another metal ion analogous to Equation (2). Examples of such reactions are shown in Scheme 4.

1.6. The Advantages and Prospects of Bimetallic Fenton-like Catalysts

The introduction of a second metal to Fenton-like chemistry opens a host of reaction mechanisms, which have been partially analyzed in the literature of AOPs. Scheme 4 illustrates the bimetallic reactions that will be considered. Several further redox processes and catalytic processes are possible in a bimetallic system, with two scenarios being concurrent ROS generation by both metals and the co-catalysis of ROS production [24,31]. Thus, concurrent ROS generation implies that two metals may function simultaneously as radical-generating catalysts. In the second case, one of the two metals promotes radical generation via the second metal by binding to the ROS precursor. Many studies that identify an advantage of the bimetallic system refer to a “synergistic effect” in the system. In light of the complexities, we will consider synergy as a phenomenological term in this review.

2. Metal Catalysts for Dye Degradation

2.1. A Co-Catalytic Effect for the Cycling of Iron

Part 2.1 covers bimetallic systems, in which the first metal ion conducts the activating reaction to produce ROS. The second metal has the cycling reduction reaction role which regenerates the reducing state of the first metal ion and overall accelerates the catalysis. These systems are often referred to as co-catalytic. Noting that the reduction of Fe(III) to Fe(II) is slow in classic Fenton cycling (Equation (2)), the bimetallic iron system uses the second metal ion to regenerate Fe(II) from Fe(III). In most cases, the second metal ions are then reduced under the reaction conditions so they may repeat the cycling reduction reaction; these include Mo, Cu and V. Others, such as Mg^0 or Fe^0 , are stoichiometrically consumed.



2.1.1. Iron with Molybdenum

Molybdenum is the most common co-catalyst in bimetallic Fenton-like systems because it is largely nontoxic and is able to reduce Fe^{3+} by cycling between Mo^{4+} and Mo^{6+} as well as from Mo^0 [34]. Often, molybdenum is introduced to the system in a solid form, such as Mo powder, MoS_2 , MoO_2 , or a nonstoichiometric mixed-metal catalyst; for example, FeMoO_4 (Figure 1) [5]. Most systems are heterogeneous, and release minimal iron into the solution [33]. Additionally, there is minimal leaching of Mo into the solution, increasing the recyclability of the catalyst and its continued ability to reduce iron. This effective system has been used by various groups, degrading Rhodamine B, Lissamine Rhodamine B, Methylene Blue, Orange G, and acid orange 7, showing increased degradation rates with all dye models in comparison to mono-metal reactions [23,32,33,35].

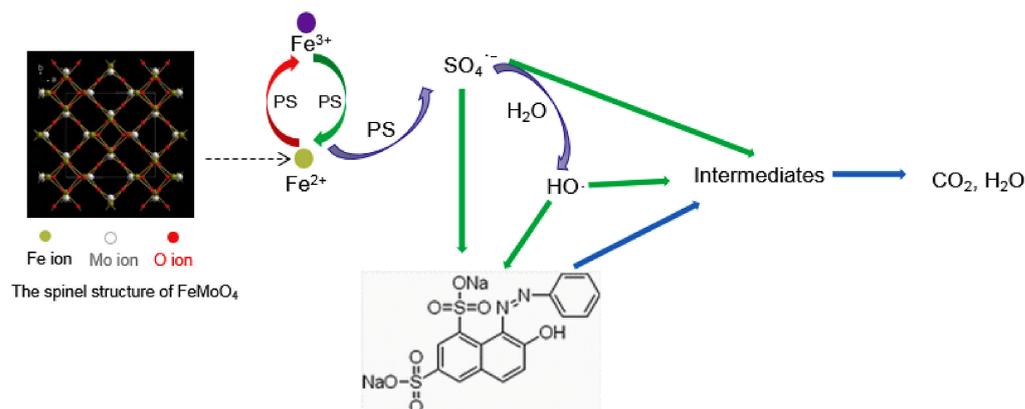
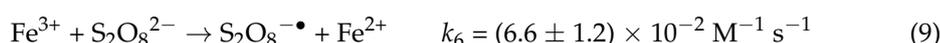


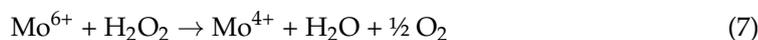
Figure 1. Proposed pathways for persulfate activation on FeMoO₄ surface according to Lin et al. [5]. Reproduced with permission from [5]. Copyright Elsevier, 2019.

While the classic Fenton reagent is the most common (H₂O₂ reduced to HO•), this bimetallic catalyst pair has also been shown to successfully activate persulfates, such as peroxymonosulfate (SO₅H⁻) or peroxydisulfate (S₂O₈²⁻). These persulfates form the SO₄^{-•} radical, which will oxidize and degrade dyes in a similar manner to the hydroxyl radical. However, it has been reported that the concentration of the catalyst must be closely monitored, as too much will abdicate the efficiency of the dye degradation by the consumption of the radical species [33]. If the catalyst concentration is too high, the sulfate radicals will be lost to a combination reaction [5].

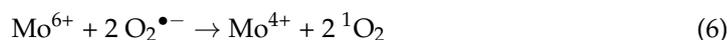
When the oxidant of the system is persulfate, the Mo species is present as a supported co-catalyst. In heterogeneous catalysts such as MoO₂, Mo⁶⁺ is reduced to Mo⁴⁺ on the surface of the catalyst, allowing for its continued recyclability [36]. Interestingly, this system is reported to degrade Rhodamine B (RhB) much faster than methylene blue or other non-dye phenyl-based substances. This system is shown to successfully improve the cycling of iron because peroxydisulfate reduces iron with a rate constant (Equation (9)) of 10⁻² M⁻¹s⁻¹, producing the S₂O₈^{-•} radical [35].



In hydrogen peroxide systems, the usage of MoS₂ as the solid heterogeneous catalyst is often seen. Many report that the sulfides of various co-catalytic metals perform extraordinarily well, with Mo showing the best degradation rates, as well as being the preferred metal due to its low toxicity and cost [33,37]. When using the MoS₂ solid, the Mo active sites are exposed when H₂S is formed. With MoS₂ as the catalyst, it has been suggested that Mo⁶⁺ is reduced via the disproportionation of hydrogen peroxide into water and O₂ (Equation (7)) [23,37].



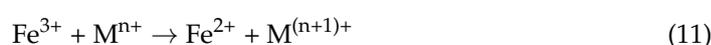
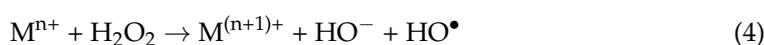
Other systems, specifically using Mo⁰ powder and homogeneous iron, have emphasized that the main contributor to the degradation of dyes such as rhodamine B is singlet oxygen (¹O₂) [32,33], with some conflicting mechanisms for the proposed formation of singlet oxygen. Most propose that the formation of ¹O₂ results from the superoxide reduction of Mo⁶⁺, as seen in Equation (6) [31,32]. Tungsten has also been investigated as a co-catalyst [38].



2.1.2. Iron with Copper

Many report that Cu⁺ is able to reduce Fe³⁺ to cycle the Fenton reaction. The classic Fenton reaction may also be carried out with copper in place of iron. A copper-based Fenton reaction has the advantages of environmental nontoxicity, cost, and solubility at higher pH levels [11,39,40]. That being said, the reduction of Cu²⁺ back to Cu⁺ is also

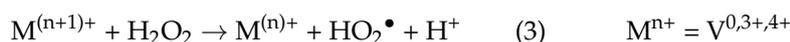
very slow, and so a means to accelerate the cycling of Cu is needed [41]. The iron–copper combination may demonstrate synergy, in this case being the cycling of Fe^{3+} back to Fe^{2+} by Cu^+ , which happens quickly, relative to classic Fenton chemistry. The greater solubility of $\text{Cu}(\text{OH})_2$ also allows for a higher pH operating condition [42]. Interestingly, copper functions as both a co-catalyst to iron, and a radical ROS generator itself (*vide infra*) [24,42]. Fe–Cu oxides allow for a charge transfer between the metals and the oxygen, which allows for both metals to be active catalysts for H_2O_2 , forming $\bullet\text{OH}$ or $\bullet\text{OOH}$. This reaction has not been reported using other oxidants such as persulfates, but its remarkable efficiency suggests that a persulfate system would be equally effective and improve degradation rates. Effectively used to degrade methylene blue and orange II, both Fe^{2+} or Cu^+ reduce H_2O_2 , forming HO^- and $\text{HO}\bullet$, and either metal can co-catalytically reduce the other in order to facilitate cycling [24,42]. (Equation (4) ($\text{M}^n=\text{Cu}^+$), Equation (11) ($\text{M}=\text{Cu}^+$) and Equation (15).) This system of iron and copper shows better degradation rates for dyes than other organics such as antibiotics [43].



2.1.3. Iron with Vanadium

Vanadium is not a common catalyst seen in the literature, but when seen it boasts of high degradation rates, efficiency and overall success as a co-catalyst. With four common oxidation states, vanadium is an outstanding transition metal for redox activity and the transfer of electrons [19].

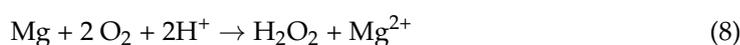
Because Fe–V systems are uncommon, the mechanism of ROS production is rather uncertain; it appears that the vanadium has a dual function, in which it helps to cyclize iron while also producing $\bullet\text{OOH}$ radicals on its own, as well (Equations (3), (4) and (11)) [19]. While vanadium assists in iron cycling, it occurs on the surface of vanadium particles, and so it is uncertain which vanadium redox couple is present. V^0 , V^{3+} and V^{4+} appear to contribute to redox the most, however.



Leaching does occur with vanadium catalysts, but it is effectively handled by filtration, allowing the vanadium to be recovered. The filtration strategy allows the catalyst to be recycled up to five times [19]. Vanadium has proven to be a strong catalyst, as vanadium oxides have been reported to produce ROS on their own. This emphasizes its excellence for bimetallic studies and the complementary support of iron.

2.1.4. Iron with Magnesium

Combined systems of iron with magnesium as a co-catalyst have been used in order to degrade dye processing waste [44]. Interestingly, this system does not report to use hydrogen peroxide as the oxidant, but O_2 , as aerated through the solution. The hydroxyl radical was still deemed the active oxidation species, as tested through quenching the solution and testing degradation rates. This leads to the proposed mechanism that magnesium reduces oxygen to hydrogen peroxide (Equation (8)), which then undergoes Fenton chemistry (Equation (1)).



The mechanism of this reaction is uncertain, but it appears that the magnesium catalyst exists to create the oxidant (hydrogen peroxide), such that the Fenton reaction can occur.

Magnesium does not support in the cycling of iron, however. Both magnesium and iron are solid particle catalysts, such that they are constantly being oxidized, and there is a low level of cycling. Some cycling occurs when solid magnesium reduces two iron ions at a time. Because of this, however, there is low to no recyclability, and high levels of iron and magnesium leaching [44]. This system was not used to degrade dyes, but rather phenolic moiety byproducts from the production of dyestuffs. It is a unique alternative to H_2O_2 for HO^\bullet production.

2.2. The Systems of Two Radical-Generating Metals

In this section, we will discuss use of two metals simultaneously generating radical ROS species.

2.2.1. Iron with Copper

Iron with copper systems have shown each metal acting as co-catalyst for the other (Section 2.1.2). In this section, we consider iron and copper acting independently as radical-generating metals. For example, iron and copper may independently generate radical ROS while also acting as co-catalysts for each other as shown in a report by Li et al. (Figure 2). This inexpensive bimetallic combination has shown to degrade methylene blue [24] as well as a host of non-dye phenolic compounds. This is a pH-dependent process, in which iron is the major catalyst when the pH is under 4. Between pH 4 and 6, copper becomes the active catalyst [45]. This dual catalyst effect allows for a significantly increased pH range.

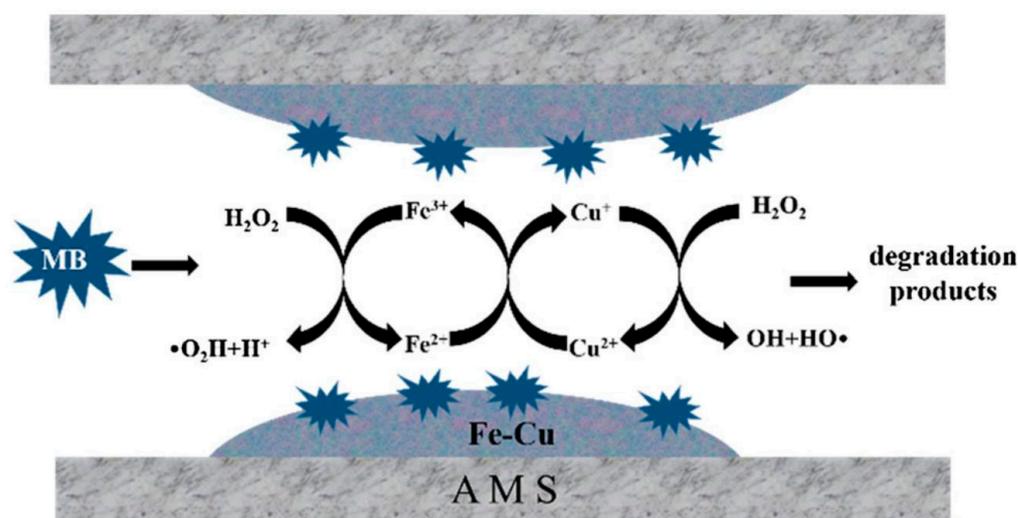


Figure 2. Iron and copper acting as independent radical ROS generators as well as co-catalysts for methylene blue degradation. Reproduced with permission from [24]. Copyright Springer Nature, 2016.

This system is almost exclusively reported as solid oxides, but some catalyst adjustments can create a system which is both heterogeneous and homogeneous by the inclusion of iron or copper particles on the surface of the heterogeneous catalyst [46]. However, this system allows for a substantial amount of leaching of the metal particles, which is less than ideal.

2.2.2. Iron with Molybdenum

While molybdenum is an excellent co-catalyst to iron, and greatly catalyzes iron cycling (Section 2.1.1), the metal can also generate HO^\bullet itself. When molybdenum and iron are paired as MoS_2 and Fe_3O_4 , the system generates HO^\bullet from H_2O_2 faster than iron alone, resulting in more rapid dye degradation. In addition to HO^\bullet , superoxide ($\text{O}_2^{\bullet-}$) has been detected as a major ROS to degrade dyes, as measured via quenching studies [30].

This system was additionally tested on other organic dyes, such as methyl orange and Congo red. While the system was slower to degrade methyl orange and Congo red, after 30 min they were 90%+ degraded, while methylene blue reached 100% degradation [30].

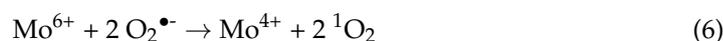
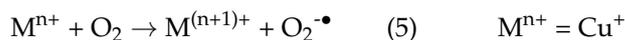
This shows that the system can effectively degrade a variety of structural organic dyes (azo or thiazine) efficiently. After five cycles, this system retained 75% of its degradation capacity.

2.3. Iron-Free Bimetallic Catalysts

Iron-free catalysts avoid the problems of slow $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ cycling and iron hydroxide precipitation. This section explores less common approaches to dye degradation in bimetallic systems that do not include iron.

2.3.1. Copper and Molybdenum

Molybdenum is largely the only metal observed to create singlet oxygen from superoxide. Zheng et al. have presented an original system for the generation of $^1\text{O}_2$ using Cu^+ to reduce O_2 to $\text{O}_2^{\bullet-}$ (Equation (5)), followed by the oxidation of superoxide to singlet oxygen via Mo^{6+} (Equation (6)) [31]. Although few details of catalyst preparation are provided, this system appears to utilize Mo particles of 1–2 μm size coated with Cu. Analysis by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) shows that the Mo particles were coated with amorphous Cu, and the species present were Cu^0 , Cu^+ , Cu^{2+} , Mo^0 , Mo^{4+} and Mo^{6+} . Thereby, the authors inferred that Mo^0 reduces Cu^{2+} to Cu^0 and Cu^+ , and that Mo^{6+} oxidizes $\text{O}_2^{\bullet-}$ to singlet oxygen that is active in degrading molecules, including RhB. This system lost only ca. 4% of activity after four cycles, and degraded 90% of the rhodamine dye in 120 min. The authors note that the rate of O_2 reduction to $\text{O}_2^{\bullet-}$ via Cu^+ was substantially greater at $k = 3.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ than the rate of O_2 reduction via Fe^{2+} , $k = 0.013 \text{ M}^{-1} \text{ s}^{-1}$. Copper is able to produce radical ROS catalytically by cycling between Cu^+ and Cu^{2+} , and it possesses low toxicity to mammals.

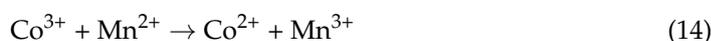
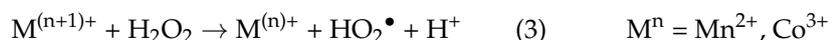


2.3.2. Manganese and Cobalt

Because of cobalt's toxicity to the environment, it is often used sparingly in environmental remediation. Cai et al. have studied the sulfur-doping of the spinel metal oxide CoMn_2O_4 [25] to produce, for example, a spinel containing 5% sulfur, designated as S- CoMn_2O_4 (5.00%). These catalysts are prepared by a sol-gel synthetic method from citric acid, cobalt nitrate and manganese acetate, by firing at 600 °C with a gradual addition of elemental sulfur. Oxygen vacancies are formed by sulfur doping, which creates a greater reactivity due to more open sites for reactivity, such that the lattice oxygens, as well as absorbed oxygens, are easily turned into radical ROS. Because of this process, sulfur-doped catalysts are shown to be more effective than those without sulfur (Figure 3).

Hazarika et al. have reported a degradation system designated as $\text{Mn}_2\text{O}_3\text{-Co}_3\text{O}_4/\text{C}$, in which the carbon is carbon black as a support for the catalyst. This system is seen to efficiently produce oxygen-based radicals both from H_2O_2 and from persulfates, forming the expected HO^\bullet and HOO^\bullet from H_2O_2 , and $\text{SO}_4^{\bullet-}$, HO^\bullet and $\text{O}_2^{\bullet-}$ from the persulfate system [25,47].

Manganese and cobalt are believed to independently perform redox cycling in these systems, where H_2O_2 oxidizes the metal creating HO^\bullet , and H_2O_2 reduces the metal to produce HOO^\bullet (Equations (4) and (3), respectively). In addition to this, Mn also helps to cycle Co via electron transfer (Equation (14)). While it is not explicitly stated that Co also catalyzes the cycling of Mn, the data presented appear consistent [47].



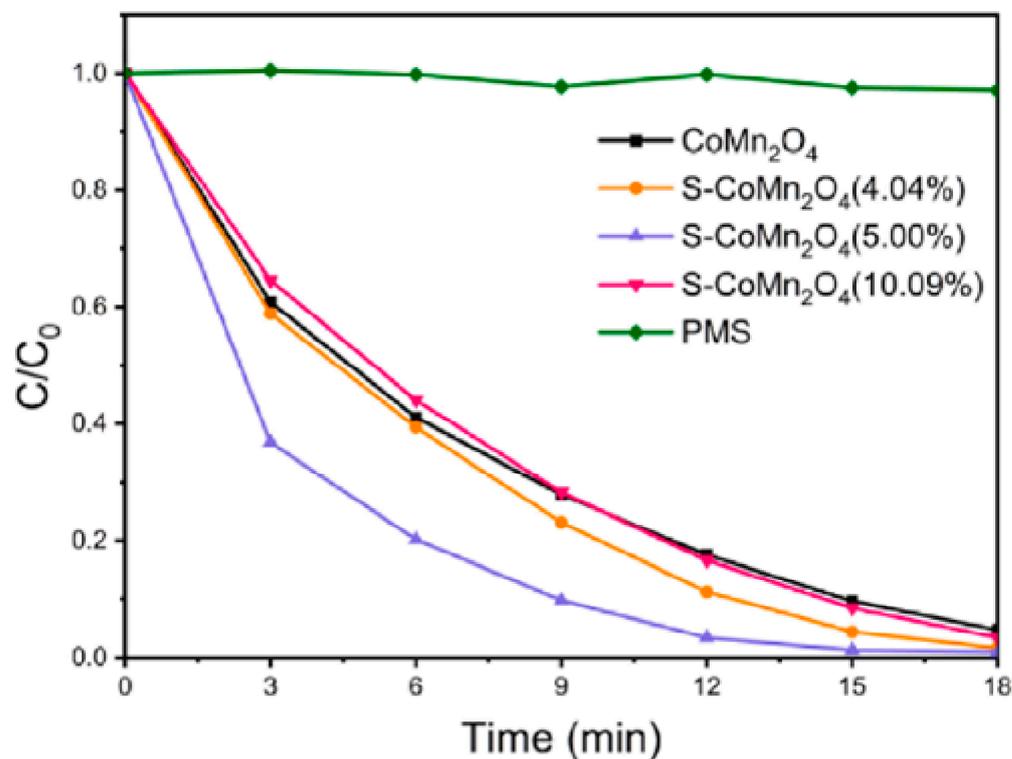


Figure 3. Progress of Rhodamine B degradation via various cobalt–manganese catalysts. Reproduced with permission from [25]. Copyright Elsevier, 2023.

The Mn-Co system proved to be significantly more efficient than the Fenton reaction, due to its ability to function at a significantly larger pH range. This system was largely used to degrade xanthene dyes, such as rhodamine B, but was also shown to degrade diazo dyes, such as Congo red. Rhodamine B was degraded from pH levels of 3 to 9.5. When pH was increased to 11, 25% of the rhodamine B was still degraded, showing significantly decreased rates, but not a complete inability to create radical species [25]. This may have occurred due to metal hydroxides forming, but it is more likely that it was due to the self-decomposition of the oxidant, peroxymonosulfate, without the formation of radicals, leading to no ROS to facilitate degradation at these high pH values [25].

In sum, the Mn/Co system can effectively degrade a variety of undesirable phenolic compounds, slowly breaking them down into small molecules and eventually to carbon dioxide and water.

2.3.3. Niobium and Zinc

Zinc appears to be an uncommon metal for Fenton-like reactions because Zn^0 is strongly reducing, such that a Zn^0-Zn^{2+} cycle would be unfavorable. However, a system has been studied based on a Nb–Zn couple [15]. Niobium pentoxide reacts with hydrogen peroxide to produce superoxide, a reaction that was accelerated, but was found to have higher rates of degradation when another metal was added to the composite (Figure 4). Zn was also found to exist as Zn peroxide, which is analogous to the Fe–Mg system of Section 2.1.4, where the reductive power of Mg serves to produce hydrogen peroxide from oxygen.

A problem with this system, however, is that the dye shows a high affinity to absorb onto the catalyst, instead of being degraded. In this case, the dye is still removed from the system, but has not been broken down, and still needs to be disposed.

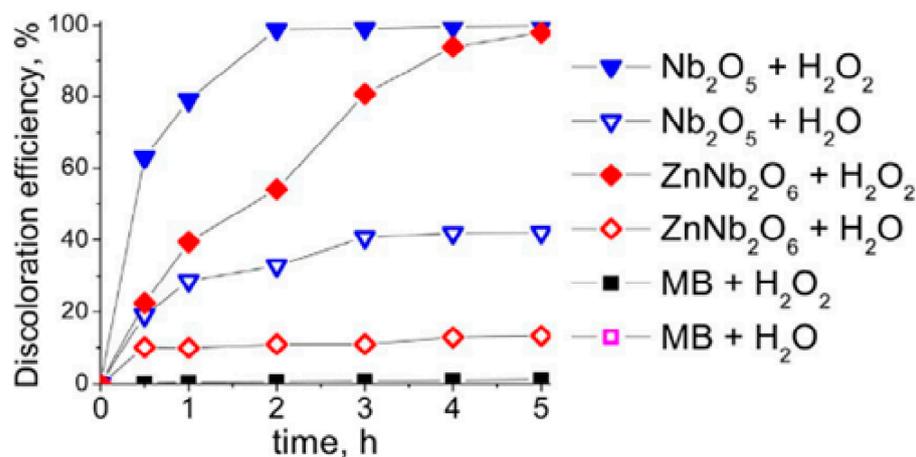


Figure 4. Efficiency of methylene blue degradation via various niobium and zinc catalysts. Reproduced with permission from [15]. Copyright Elsevier, 2018.

2.4. Case Studies: Iron–Cobalt and Iron–Copper Heterogeneous Systems Exploiting Metal–Metal Synergy and the Facile Reclamation of Catalysts

Here, in two case studies, we highlight the demonstrated rapid dye removal and careful mechanistic study of ferromagnetic heterogeneous bimetal catalysts. Ferromagnetic or ferrimagnetic catalyst particles are easily removed from the medium. The inclusion of iron as zerovalent iron or as Fe₃O₄ is presented in these case studies.

2.4.1. A Fe₃O₄–CoS₂–(S, O)_x/HSO₅[−] Catalyst System with Oxygen or Sulfur Vacancies

Qiu et al. have leveraged several properties of iron-oxide-cobalt sulfide nanoparticles to demonstrate dye and antibiotic degradation by multiple ROS generated from peroxymonosulfate, HSO₅[−] (PMS) [48]. Their design of a Fe₃O₄–CoS₂-based catalyst is based on the demonstrated very high catalytic activity of Co²⁺ for the conversion of HSO₅[−] to ROS [49] in homogeneous systems. Fe₃O₄ is ferrimagnetic, allowing a facile separation of the catalyst. Extensive radical trapping studies demonstrated four active ROS derived from HSO₅[−], being, in order of importance, ¹O₂ > SO₄^{−•} > O₂^{−•} > HO[•]. The innovation in this work centers on their careful formulation and characterization of “Fe₃O₄–CoS₂–0.4”, where “–0.4” refers to the degree of defects, being O and S vacancies in the particles. Their method was the hydrothermal growth of CoS₂ upon Fe₃O₄, in the presence of the surfactant polyvinyl pyrrolidone, to generate vacancies. The material was thoroughly characterized, including using X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and electron paramagnetic resonance (EPR) to determine the degree of the O and S vacancies. This system demonstrated 100% to 96% removal of methylene blue (MB) in 5 min under the conditions of 1 mM SO₅^{2−}, 100 mg/L catalyst, 20 mg/L MB at 298 K and pH 7. A synergistic effect of Fe²⁺ promoting Co³⁺/Co²⁺ cycling was observed.

2.4.2. A Reduced Iron–Copper Spinel Catalyst Containing Zerovalent Iron and Copper

Qin et al. [46] sought to improve upon iron oxide nanoparticle catalysts which activate H₂O₂ for oxidative degradation. They noted that such catalysts show modest electron-transfer rates, while zerovalent iron is a productive ROS generator. They reported a modification of the iron-copper spinel, CuFe₂O₄, which contains zerovalent iron and copper. A reduction with hydrogen at 400 °C afforded a modified spinel, “reduced CuFe₂O₄”, which was shown by X-ray diffraction to contain zerovalent iron and copper. This catalyst showed significant increases in degradation rates when compared to CuFe₂O₄, which was without the zerovalent pockets of metals. While the common concentration and pH studies were performed, Qin et al. additionally discussed the adsorption/desorption studies that were performed in order to gain a better understanding of the properties of reduced CuFe₂O₄. Confirmed via thiobarbituric acid radical inhibition tests, hydroxyl radicals were formed

from H_2O_2 and were measured to have degraded 74% of the methylene blue within 25 min. This catalyst is stable, and was said to be effectively reusable for at least five trials.

3. Dye Degradation Mechanisms and Products

3.1. Effects of Reaction Conditions on the Catalysis

While various bimetallic systems have differing system conditions, general correlations between the degradation and the system temperature, the stoichiometry of the oxidant (radical ROS precursor), substrate, catalyst and the catalyst lifetime can be identified. As is consistent with most chemical reactions, when the system temperature increases, hydroxyl radical generation occurs more rapidly, resulting in faster dye degradation. A positive correlation is observed between the oxidant stoichiometry and the rate of degradation, for both hydrogen peroxide and persulfate-based oxidants. In some cases, lower oxidant stoichiometry cannot completely degrade dyes; conversely, if the oxidant stoichiometry is too high, degradation rates will plateau due to radical coupling or secondary reactions between radicals and catalysts, such as the Haber–Weiss process [5,20,21]. A small catalyst:substrate ratio will slow the degradation as active sites saturate, and while the rate will remain steady, complete degradation times will increase [47]. This must be balanced against the need to avoid water contamination of the catalyst. A typical lifetime of bimetallic catalysts is about five cycles with a good percentage of dye removed being greater than 75% (Figure 5).

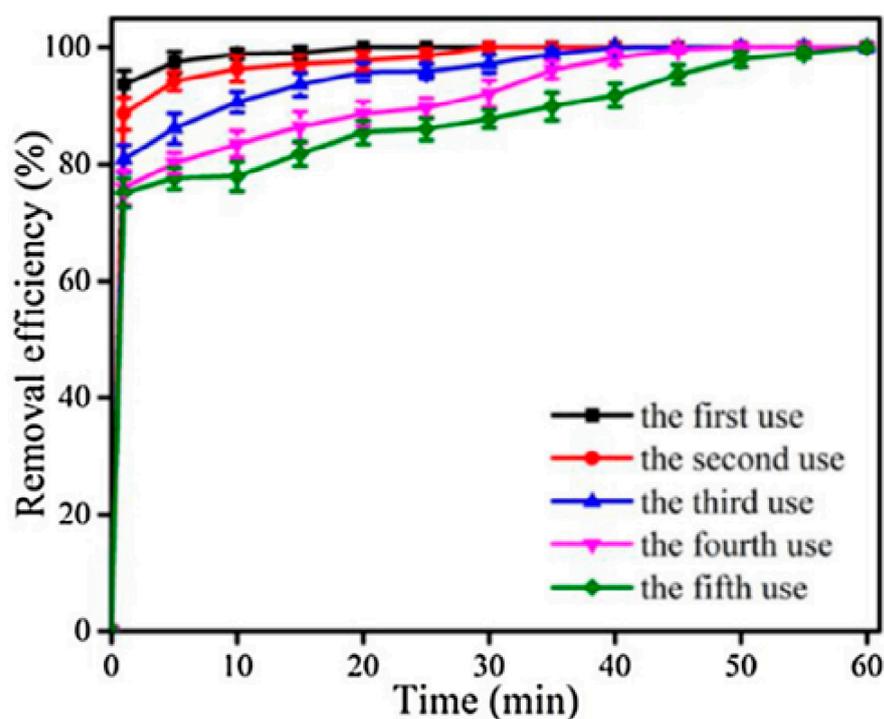


Figure 5. Progress of methylene blue degradation via $\text{MoS}_2\text{-Fe}_3\text{O}_4$ over several cycles of reuse. Reproduced with permission from [30]. Copyright Elsevier, 2020.

Operation at a neutral pH range is possible for Fenton-like reactions that utilize divalent or monovalent catalytic metals due to a good solubility of the metal ion or its hydroxide. Whereas, the classical Fenton reaction utilizing $\text{Fe}^{2+}/\text{Fe}^{3+}$ will precipitate $\text{Fe}(\text{OH})_3$ at pH 7. Some bimetallic systems are shown to function effectively in basic conditions, with a pH as high as 9 [18,30,35,36] or even 11 [25]. Despite the resilience of some catalysts, pH control can be significant. Within a closed system, a buffer may be necessary to control pH, which introduces the further issue of buffer removal after treatment. On the other hand, in a flow system of natural waters, the dilution effect will limit the rise in pH.

3.2. Dye Degradation Reactions and Products

Among the bimetallic systems considered, several different dyes appeared to be the most common substrates, although ROS should be able to degrade any organic dye. This system is often used in order to remove various pharmaceuticals, or other contaminants such as BPA. The majority of the bimetallic catalysts cited herein were used to degrade methylene blue, rhodamine B, or acid orange 7. In general, bimetallic systems can be used to degrade azo, sulfonate, and xanthene dyes. Dyes often contain S- or N-substituted aromatic rings. Radicals, as oxidants, tend to attack bonds involving electron-rich groups, such as the diazo group [5]. This attack leads to phenolic, anilino, and aryl sulfoxide groups. For example, methylene blue contains nitrogen- and sulfur-aryl groups and is broken down into substituted HO^- , N^- and $\text{O}=\text{S}$ -substituted arene groups (Scheme 1 [15]). Orange II is broken into phenolic moieties prior to complete mineralization to carbon dioxide and water [43,47]. Rhodamine B has been degraded with a four-step mechanism: N-deethylation, followed by chromophore cleavage, ring opening and finally mineralization [25].

In general, degradation studies favor the complete mineralization to CO_2 and H_2O . Upon chromophore cleavage, the dye is decolorized, resolving the aesthetic and light-filtering properties of the pollutant. However, the reactivity of molecules formed in limited breakdown raises concerns for toxicity [11].

3.3. Matrix Effects

The medium carrying the target dye contains other chemical species, known as the matrix. Ions in the matrix are the greatest concern, in particular, chloride. Chloride may scavenge the hydroxyl radical to $\text{Cl-OH}^- \bullet$, resulting in Cl^\bullet [25]. The sulfate radical is also scavenged by chloride, affording Cl^\bullet . The chloride radical is generally not effective in dye degradation. Opinions vary [50,51] regarding the influence of other matrix ingredients, including humic acid, bicarbonate, sulfate and nitrate. Some ions, like nitrate, are oxidizing agents, but other ions, such as phosphate, have lesser oxidizing abilities, which will reduce the degradation of dyes (Figure 6) [25].

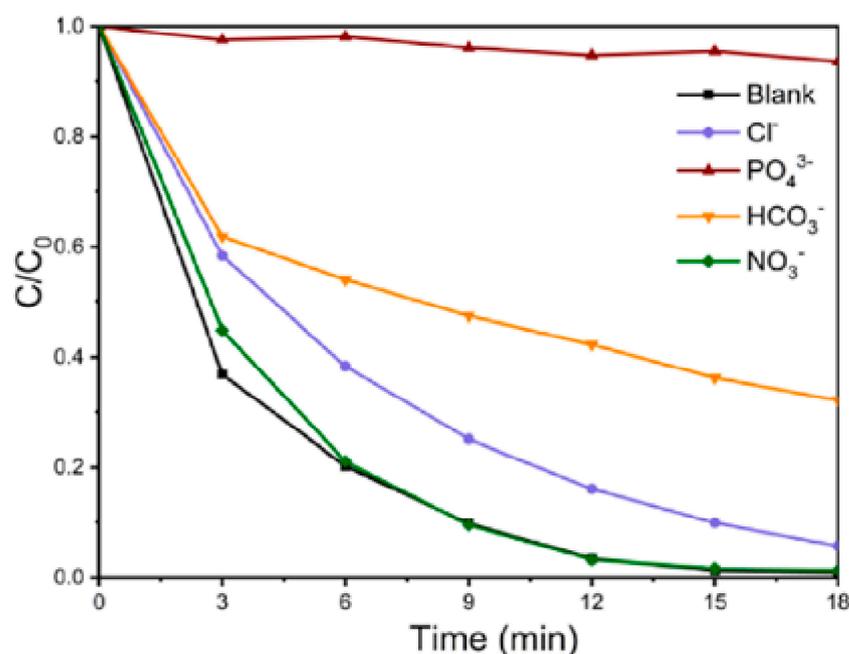


Figure 6. The effect of different matrix ions on degradation rates. Reproduced with permission from [25]. Copyright Elsevier, 2023.

4. Implementation and Environmental Challenges

The remediation of dyes may take either the path of wastewater treatment or that of the remediation of dye in the environment. Wastewater treatment would likely involve the flow of the water over a supported catalyst, which is best conducted with a heterogeneous catalyst. If the environment has already been contaminated, the Fenton-like system would more likely be added to the environment, although flowing natural contaminated water through a treatment system is also possible. Either homogeneous or well-dispersed heterogeneous catalysts may be used. In the environmental treatment scenario, the toxicity of the catalyst is a crucial factor given that catalyst separation is not feasible.

A vision for greater efforts in dye remediation is the breakdown to nontoxic substances that are consumed in the environment by biogeochemical processes. In the treatment of dye contaminants, there is a distinction between the degradation of the dye and the remediation of the dye. Degradation is taken as any breakdown of the dye, and will most likely destroy its chromophore. Remediation implies that the pollutant has been completely dealt with and is no longer a problem. Thus, remediation implies the conversion of the molecule into substances that are harmless to the ecosystem. Remediation, by the breakdown to carbon dioxide and water, known as mineralization, ensures no direct toxicity to the environment but does create a greenhouse gas.

A concern in radical-based degradation is the persistence of radicals and the possibility that the radicals will damage other molecules in the ecosystem, possibly converting them into toxic or carcinogenic materials. The oxygen and sulfur-oxygen radicals considered herein have lifetimes generally of microseconds, thus, persistence appears not to be an issue [5]. The possibility of ROS reactions with other environmental substances has not been examined in detail to our knowledge, and is worthy of further study.

5. Conclusions

The bimetallic Fenton-like processes for the remediation of dyes in natural waters are a diverse and growing field. Reviewing a selection of recent bimetallic dye degradation catalysts leads to an assessment of the desirable properties and criteria for future research in the field. It was shown that metal redox properties are paramount to effective degradation. Relative to classic Fenton chemistry, bimetallic catalysts demonstrate improved rates, a wider range of active radicals, and an extended operable pH range in the degradation process. It is recommended that redox mechanism and dye degradation mechanism receive greater study. For use in natural waters, it would be useful to investigate the interaction of radicals with native dissolved organic matter. In sum, the advancements in the field show great promise for solving the environmental challenges in dye degradation.

Author Contributions: Conceptualization, L.R.M. and R.P.P.; methodology, R.P.P.; formal analysis, L.R.M. and R.P.P.; investigation, L.R.M. and R.P.P.; writing—original draft preparation, L.R.M.; writing—review and editing, R.P.P. and L.R.M.; supervision, R.P.P.; funding acquisition, R.P.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Dennis Chasteen Undergraduate Research Fellowship and the University of New Hampshire Department of Chemistry. Chemical structures were created with help from the Marvin Suite (www.chemaxon.com accessed on 15 December 2023).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing not applicable.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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