

Article

Degradation of Textile Dye by Bimetallic Oxide Activated Peroxymonosulphate Process

Hera Rashid ^{1,2}  and P. V. Nidheesh ^{1,*} 
¹ CSIR-National Environmental Engineering Research Institute, Maharashtra, Nagpur 440020, India

² Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India

* Correspondence: nidheeshpv129@gmail.com or nidheesh@neeri.res.in

Abstract: The sulphate radical based advanced oxidation processes (AOPs) are highly in demand these days, owing to their numerous advantages. Herein, the Fe-Mn bimetallic oxide particle was used to activate peroxymonosulphate (PMS) for Rhodamine B (RhB) degradation. Three bimetallic catalysts were synthesized via the chemical precipitation method with different concentrations of metals; Fe-Mn (1:1), Fe-Mn (1:2) and Fe-Mn (2:1). The best performance was shown by Fe-Mn (2:1) system at optimized conditions; 96% of RhB was removed at optimized conditions. Scavenging experiments displayed the clear dominance of hydroxyl radical in pH 3, while sulphate radical was present in a large amount at pH 7 and 10. The monometallic Fe and Mn oxides were also synthesized to confirm the synergistic effect that was present in the bimetallic oxide system. The application of optimized condition in real textile wastewater was conducted, which revealed the system works efficiently at high concentrations of PMS and catalyst dosage.

Keywords: Rhodamine B; peroxymonosulphate; advanced oxidation process; bimetallic oxide catalyst; textile wastewater; de-ethylation; blue shift



Citation: Rashid, H.; Nidheesh, P.V. Degradation of Textile Dye by Bimetallic Oxide Activated Peroxymonosulphate Process. *Catalysts* **2023**, *13*, 195. <https://doi.org/10.3390/catal13010195>

Academic Editor: Grzegorz Boczkaj

Received: 30 November 2022

Revised: 9 January 2023

Accepted: 10 January 2023

Published: 13 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Water quality has become a global issue and the sustainable development goals (SDGs) have been focusing on the treatment of water and wastewater under goal six, “Clean water and sanitation”. There has been excessive deterioration of water quality by industries by their release of toxic and carcinogenic substances like dyes, pharmaceutical compounds, personal care products, etc. causing many health issues like gastrointestinal infection, respiratory problems, skin allergies and eye irritation, etc. [1,2]. World Bank data showcases that the textile industries contribute 17–20% of industrial wastewater [3]. Many organic dyes, having complex heterocyclic molecules, like Rhodamine B, a very stable xanthene dye [4] have high chromic properties owing to high toxicity, when left untreated can cause serious issues with public health [5].

Many chemical treatments like chemical precipitation, membrane systems, electrocoagulation, advanced oxidation processes etc. can be employed to treat these effluents. Out of these, advanced oxidation processes (AOPs) have served as a promising technology in the treatment of complex organic molecules like dyes because of their high efficiency in degradation with significant mineralization [6–9]. In addition to the depollution of water and wastewater, AOPs are also efficient at increasing in biodegradability index [10].

AOPs, a radical based process is classified as hydroxyl radical AOPs (HR-AOPs) or sulphate radical AOPs (SR-AOPs), based on the radicals predominantly responsible for degradation. In recent era, SR-AOPs have been gaining more importance than HR-AOPs as sulphate radical has a greater life time (30–40 micro seconds for $\text{SO}_4^{\bullet-}$ while $\bullet\text{OH}$ has 0.001 micro second) [11] and applicability in wide range of pH conditions where most of the HR-AOPs are limited to acidic pH [5]. Though $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ has similar redox potential (2.44 V | SHE and 2.8 V | SHE) [12], the sulphate radical is even effective at low

concentrations and possesses selectivity characteristics unlike $\bullet\text{OH}$, which is non selective in nature [13,14].

Both peroxymonosulphate (PMS) and peroxydisulphate (PDS) contribute to SR-AOPs, having a peroxide bond that makes them good oxidants, but the former generates more radicals; both sulphate and hydroxyl, it has a greater degradation efficiency than PDS [15]. Extensive studies have been done on PMS nowadays because of their high efficiency to degrade very stable organic compounds as well as their economical use [16]. PMS can be activated by physical as well as chemical methods; physical activation includes visible light irradiation, UV, ultra-sonication, microwave etc. while chemical activation is done by bases, metals; mainly transition metals as catalysts (Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ru^{3+} , Ag^{+}). Cobalt amongst all transition metals has proven to be the most efficient, but its drawback of having toxic properties and leaching lead prompted studies to tend towards safer metals [16]. Both manganese oxides and iron oxides as catalyst for activation of PMS are highly preferred owing low cost and environment friendly properties (Co being 10 times costlier than Mn) [16–18].

Compared to homogeneous AOPs, heterogeneous AOPs are considered to be more beneficial due to their reusability characteristics [19]. Additionally, a bimetallic system has proven to be more efficient than monometallic systems because of synergistic interaction of the two [20,21]. This paper showcases the Fe-Mn oxides of different ratios used to activate PMS for the effective degradation of RhB along with optimization of the condition by varying the catalyst dosage, PMS concentration and pollutant concentration.

2. Results and Discussions

2.1. Characterization of Catalyst

Figure 1 illustrates the XRD patterns of Fe_2O_3 - Mn_2O_3 bimetallic catalyst. The diffraction peaks obtained for Fe in samples are very similar to JCPDS: 25-1402; $2\theta = 18.157, 24.3, 29.09, 32.55, 35.62, 38.23, 40.33, 44.5, 54.0, 58.2, 60.18$ correspond to (113), (203), (206), (216), (209), (316), (0012), (2212), (1115), (2115) JCPDS: 25-1402 (Fe_2O_3), respectively. Diffraction peaks for Mn are $2\theta = 24.3, 32.581, 35.55, 40.33, 48.92, 54.0, 62.25, 64.75$ correspond to (012), (104), (110), (113), (024), (116), (214) and (030) for JCPDS: 33-0900, respectively (Mn_2O_3). Most of the peaks for Mn and Fe are co-existing at same degrees therefore, it is difficult to distinguish between them.

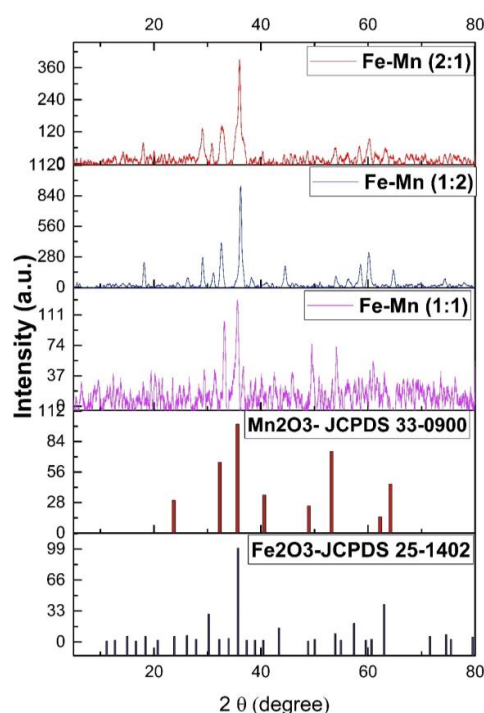


Figure 1. XRD pattern of Fe-Mn (2:1), Fe-Mn (1:2), and Fe-Mn (1:1) oxides.

Figure 2 illustrates peaks obtained in the FTIR spectra of $\text{Fe}_2\text{O}_3\text{-Mn}_2\text{O}_3$, which showcases peak 3433 cm^{-1} corresponding to OH^- [22], peaks around 621 cm^{-1} and 981 cm^{-1} corresponding to Fe-O [23] bonds and 507 cm^{-1} , 1627 cm^{-1} to Mn-O bonds [24].

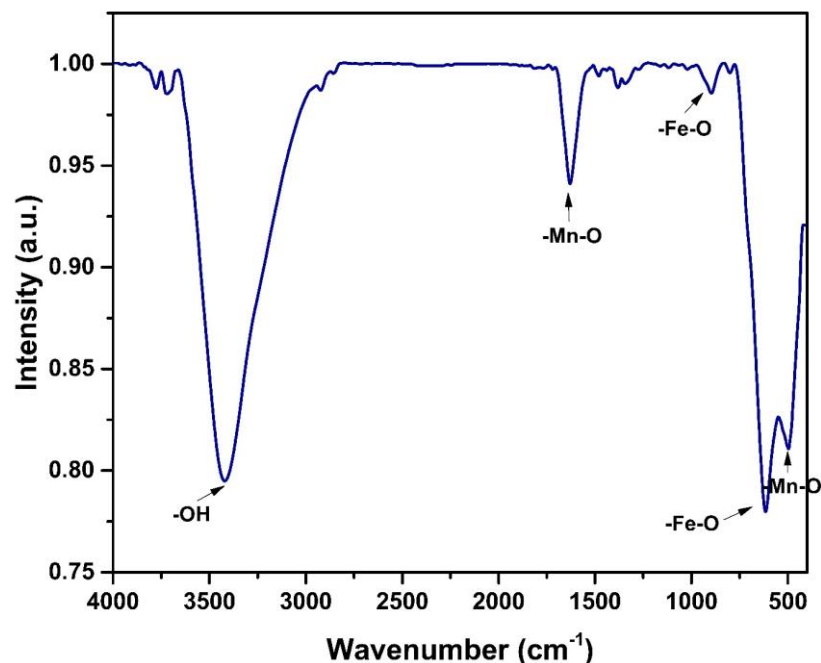


Figure 2. FTIR spectra of FeMn bimetallic catalyst.

To verify the microporosity, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images were used to examine the morphologies and microstructures of the synthesized Fe-Mn bimetallic catalyst. As can be observed from the FE-SEM picture in Figure 3a, the Fe-Mn bimetallic catalyst had aggregates that resembled spheres and were made up of nanoparticles. The bimetallic Fe-Mn catalyst as synthesized is made up of nanospheres with an average diameter of 20–40 nm, according to the TEM image (Figure 3b). The ring-like mode, which corresponds to the facet of Mn_2O_3 and the facet of Fe_2O_3 , is present in the inset of the TEM image (Figure 3b), which is in excellent agreement with the XRD result and offers greater clarity on the crystalline structure of the synthesized Fe-Mn catalyst.

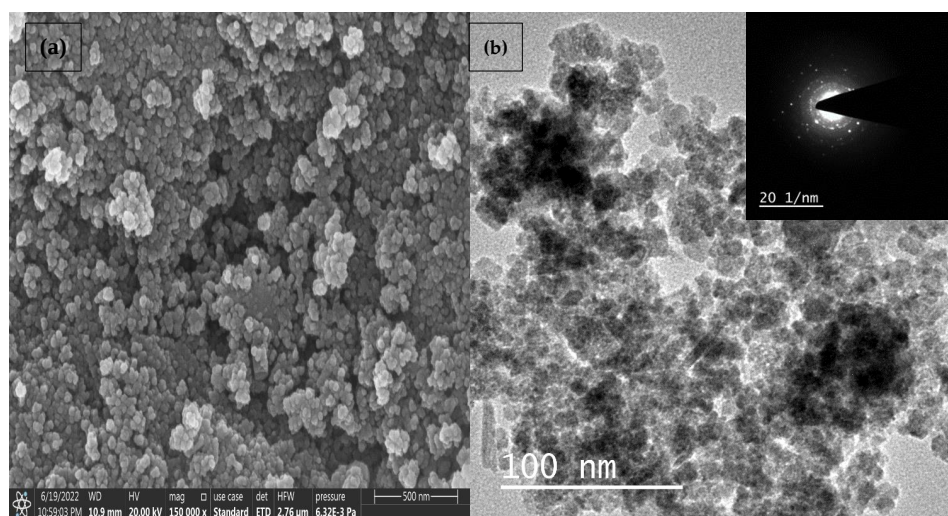
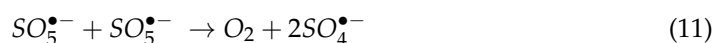
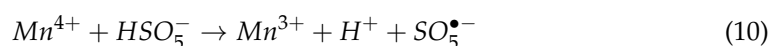
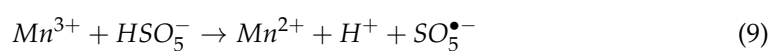
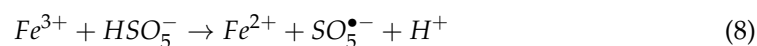
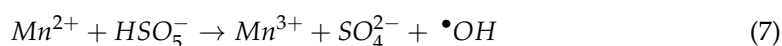
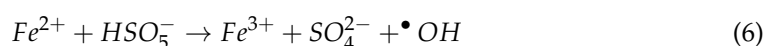
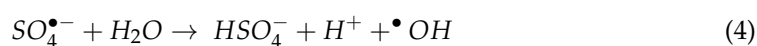
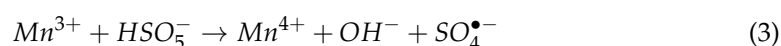
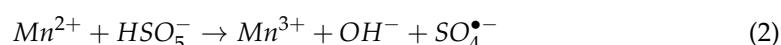
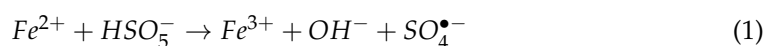


Figure 3. Shows (a) FE-SEM and (b) TEM of Fe-Mn bimetallic catalyst; inset of TEM image shows selected area electron diffraction (SAED) pattern.

2.2. Comparison of Catalysts Based on Performance at Different pH Conditions

The RhB degradations using PMS activated by three different catalysts were investigated at different pH conditions (pH 3, 7 and 10) (Figure 4). It was found that 0.25 mM PMS alone is not much effective for the degradation of RhB (19%—pH 10, 32%—pH 7, 41%—pH 3), even though it is having a redox potential of +1.81 V. Hence, the activation of PMS and the subsequent generation of sulphate radicals is necessary for the effective degradation of the pollutant. For this purpose, the efficiency of synthesized catalysts was tested at the 3 pH conditions and all three bimetallic oxides activated PMS process shown almost the same removal efficiency in a neutral medium (>90%). The following reactions may be predominately occurring in the system when Fe-Mn bimetallic oxide catalyst is used for activation of PMS [25–27].



Both Fe-Mn (1:2) and Fe-Mn (2:1) oxides show excellent performance (more than 95%) between the range of pH 3–10, which is contrary to previous works where the optimal performance of catalyst was observed in acidic conditions [28]. The catalyst Fe-Mn (1:1) oxide shows decreased performance in pH 3 (65%) and pH 10 (76%).

During the RhB degradation by PMS along with degradation, change of color from pink to light green was also observed. This is because the peak shift occurs from 554 nm to 498 nm; and is known as blue shift of RhB. During the blue shift, radicals attack the chromophoric groups present in RhB; N-ethyl groups and removing all four ethyl groups. Since the peak shift mainly occurs due to the removal of ethyl groups present in RhB, this is also known as de-ethylation [29]. The mutual interaction between RhB, catalyst and PMS plays the vital role in the degradation of RhB in this system. PMS is a weak acid while RhB is a weak base, hence there exists RhB^- in acidic medium and PMS as HSO_5^- at basic conditions [30]. Considering the overall performance of catalysts, Fe-Mn (2:1) oxides show the comparative better results amongst the three.

The reaction mechanism of RhB degradation depends on pH, a kind of reactive species attacking the pollutant, which in turn depends on the catalyst, and oxidant interaction. The absorption maximum of RhB was found to be 554 nm, which undergoes a blue shift (hypsochromic shift) with increased reaction time, which implies the de-ethylation of RhB by the attack of reactive species. The spectral changes in RhB with the PMS activation by Fe-Mn (2:1) oxide at different pH are provided in Figure 5. In general, hypsochromic shift of RhB occurs in stages [31]. RhB transforms to N,N-diethyl-N'-ethyl-rhodamine 110, N,N-diethyl-rhodamine 110, N-ethyl-N'-ethyl-rhodamine 110, and N-ethyl-rhodamine 110 sequentially and finally to rhodamine 110. Degradation of RhB occurs only after the removal of four ethyl groups and conversion to rhodamine 110. This was also observed with the decrease in absorbance after the hypsochromic shift.

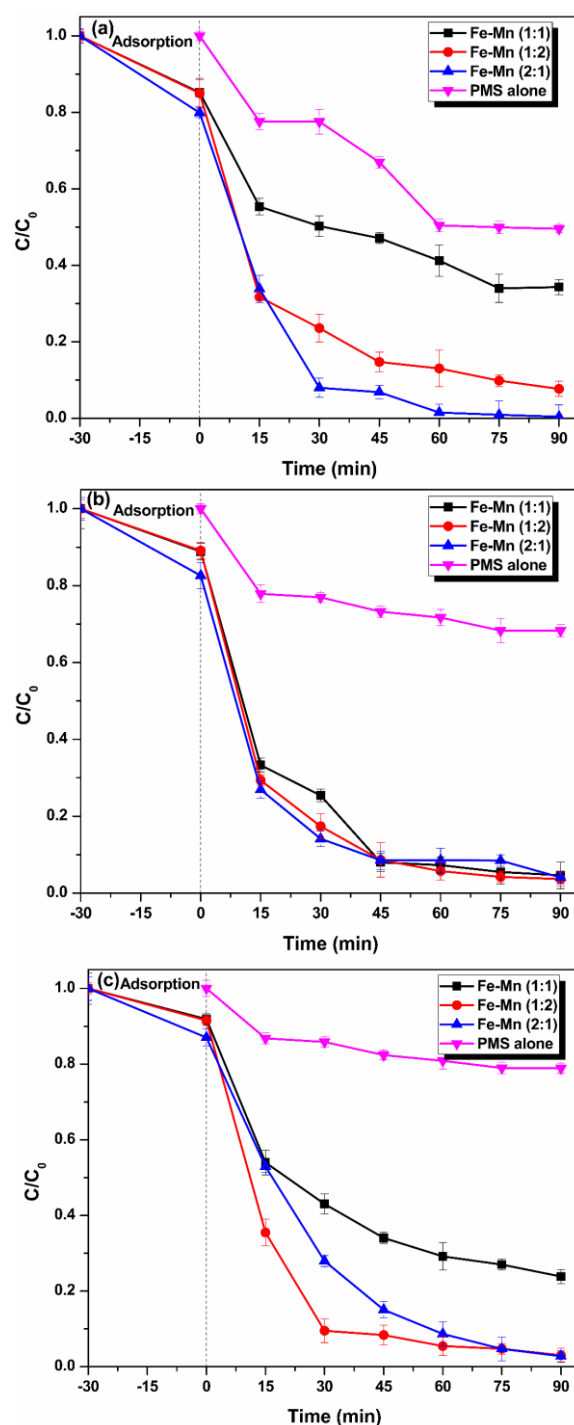


Figure 4. RhB degradation by the bimetallic oxides (100 mg/L) at different pH conditions: (a) pH 3; (b) pH 7; and (c) pH 10 using 0.25 mM PMS.

The shape of the curve reflects the relation between direct degradation of the chromophoric system and the de-ethylation process. The de-ethylation mechanism plays the key role in the total RhB degradation in case of catalyst Fe-Mn (2:1) oxide under neutral pH. As each de-ethylation step leads to a hypsochromic shift of about 15 nm, a maximum blue shift of 60 nm was obtained in case Fe-Mn (2:1) oxide and it can be attributed to the formation of four-fold de-ethylated RhB, that is, rhodamine 110 [32].

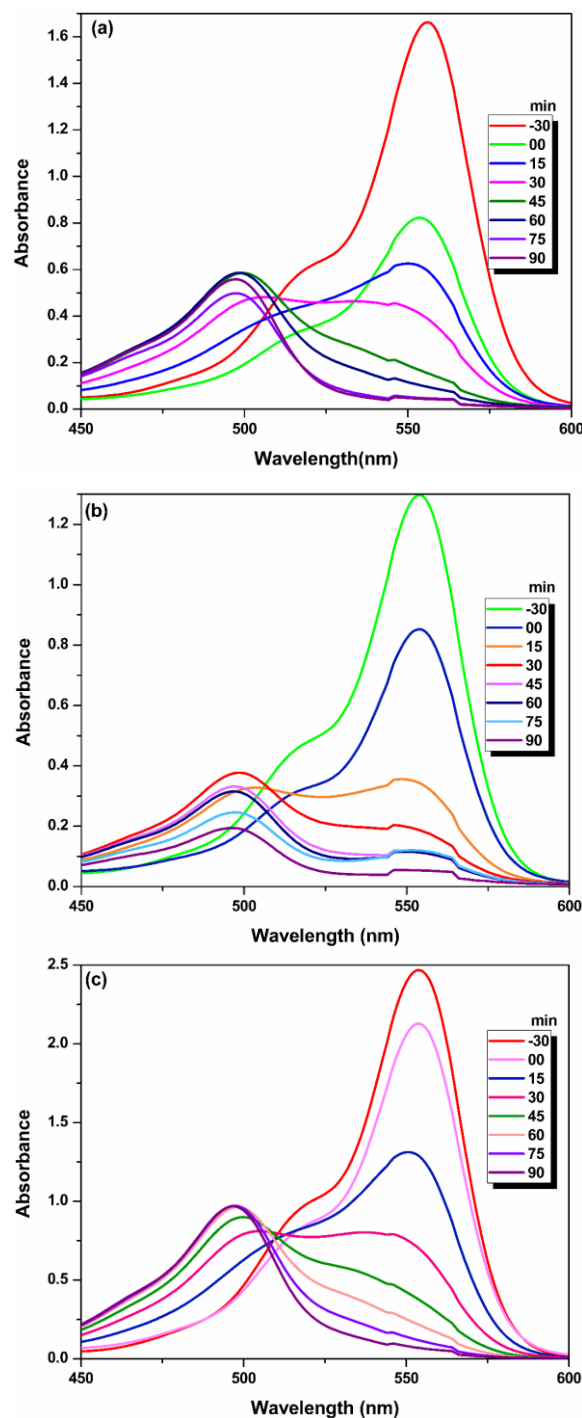


Figure 5. Changes in RhB spectrum with time, at (a) pH 3, (b) pH 7 and (c) pH 10.

2.3. Effect of Catalyst Dosage

The degradation results for RhB were investigated at different dosages of catalyst (50 mg/L, 100 mg/L, 200 mg/L and 300 mg/L) (Figure 6a). The dosage of 50 mg/L shows slow and a gradual degradation with adsorption of 8% and total degradation of 85%, which increases to 96% with 100 mg/L of catalyst due to the more active sites provided by the addition of more catalyst, which also enhances the adsorption of RhB [33]. Doubling the concentration to 200 mg/L causes no significant difference in degradation of dye, which might be because of the limiting of active sites playing its role in degradation after a certain amount of dosage [34]. When the catalyst dosage was increased to 300 mg/L, the total degradation (92%) decreased because of the scavenging of radicals [29] by Fe and Mn ions

in the system, as given below. Therefore, the optimum amount of catalyst required to give better activation of PMS for degradation of 10 ppm RhB solution, was chosen as 100 mg/L.

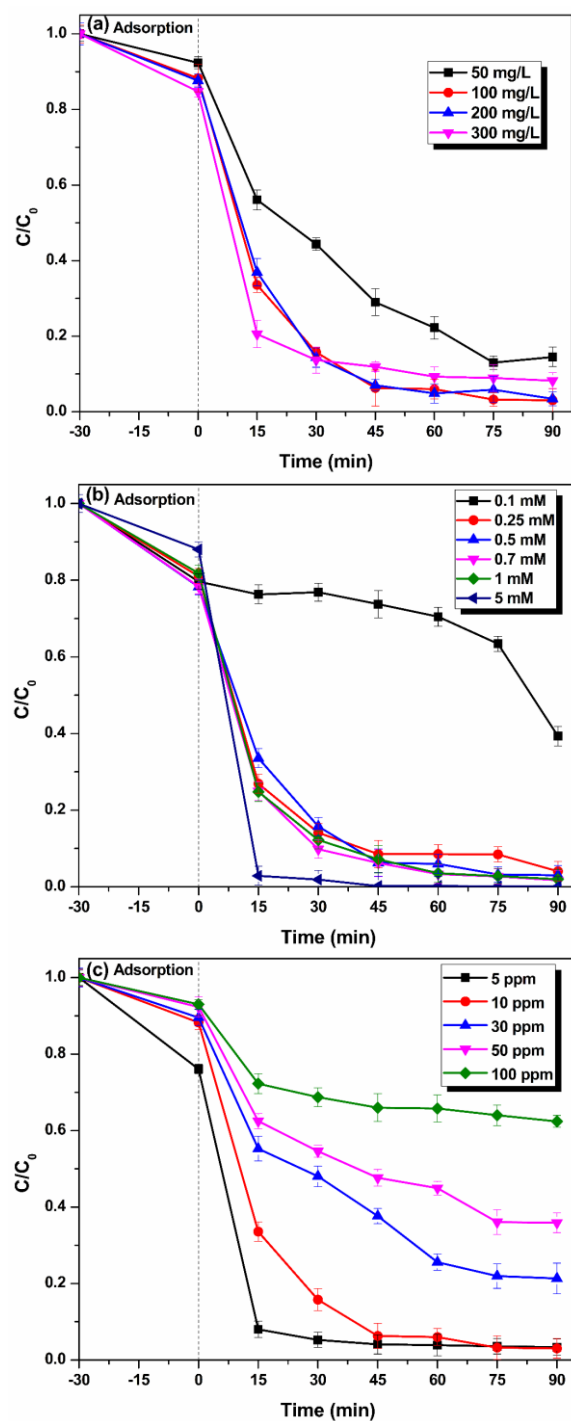
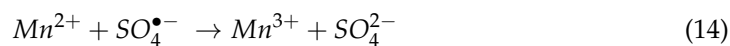
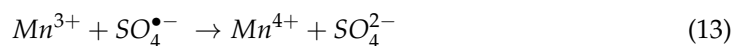
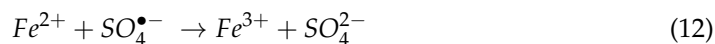


Figure 6. Effects of: (a) catalyst dosage using 0.25 mM PMS; (b) PMS concentration using 100 mg/L catalyst (c) initial pollutant concentration on dye removal efficiency using 0.25 mM PMS and 100 mg/L catalyst.

2.4. Effect of PMS Concentration

The RhB degradation was monitored at different PMS concentrations with 100 mg/L Fe-Mn (2:1) catalyst, 10 ppm RhB at neutral pH conditions. The PMS concentrations were taken as 0.1 mM, 0.25 mM, 0.5 mM, 0.7 mM, 1 mM and 5 mM. It was found that the degradation results increased from 61 % to 96 % (Figure 6b), when PMS dosage is increased from 0.1 mM to 0.25 mM. The degradation by 0.1 mM PMS was low because the amount of PMS was insufficient to generate enough radicals for the effective degradation of dye [35]. A further increase in PMS concentration to 0.25 mM resulted in sharp increase in the degradation which is because of the more reactive species present in the system [22]. The removal efficiency does not increase much after further addition of PMS, which may be due to saturation of available active sites provided by catalyst [36]. Similar results were observed by Xu et al. [37], Liu et al. [11], where increasing PMS dosage increases the removal efficiency till an extent following no longer increment in efficiency was observed.

2.5. Effect of Pollutant Concentration

The influence of pollutant concentration was also investigated using 100 mg/L catalyst and 0.25 mM PMS by varying the initial pollutant concentration as 5 ppm, 10 ppm, 30 ppm, 50 ppm and 100 ppm. It was noticed that increasing the pollutant concentration causes decreases in the degradation; from 97 % in 5 ppm to 38 % in 100 ppm (Figure 6c). The efficiency of AOPs decreases with increases in pollutant concentration, which indicates an insufficient amount of radicals available in the system [29]. Similar results of increasing pollutant concentration causing a decrease in removal efficiency was found by pyrite/ hydroxylamine system using PMS for RhB degradation [38] and Co-Fe-Cu ternary system [34].

Nonetheless, the percentage of dye removed was lessened with an increase in initial pollutant concentration, while the actual amount of dye removed was increased with an increase in initial pollutant concentration. For example, after 90 min of oxidation, 9.7 mg/L of dye was removed from its initial concentration of 10 mg/L; while it was 38 mg/L for 100 mg/L dye concentration. This increase in pollutant amount at its higher initial concentration is mainly due to the improved collisions at elevated pollutant concentrations. In all the experiments, the amount of radicals generated in the system is constant, as the constant amount of catalyst and PMS were added in each experiments. However, due to the lesser lifespan of radicals resulted in lesser effective collision between dye molecules and radicals generated, which ultimately leads to lesser pollutant removals. At the same time, for the higher initial dye concentrations, the effective collision between radicals and dye molecules will be higher, which resulted in higher amount of pollutant removals.

2.6. Scavenging

To determine the presence of active species dominating the PMS activation in this bimetallic system, quenching or scavenging experiments were carried out using various scavengers. While p-Benzoquinone (16.2 mg) is a super oxide scavenger, t-butanol (10 mL) can scavenge bulk hydroxyl radicals, ethanol (5.8 mL) is used to quench the activity of both hydroxyl and sulphate radicals together and sodium azide (9.5 mg) scavenges singlet oxygen [39]. All the scavenging experiments were conducted at optimized conditions: 100 mg/L catalyst, 0.25 mM PMS, 10 ppm RhB solution at room temperature.

Interpreting the reaction kinetics for all the scavenging experiments, it is found that all the reactions follow first order kinetics. A straight line graph obtained by plotting $\ln(C_0/C)$ vs. time confirms the first order reaction and the slope of the graph gives the rate constant. [Rate of reaction for first order is $kt = \ln(C_0/C)$]. Through the scavenging experiments carried out, it was found that hydroxyl radicals are predominantly present at pH 3 (60% contribution) ($k = 0.0091 \text{ min}^{-1}$) (Figure 7); while at pH 7 and 10, the hydroxyl radical contribution was less with rate constant of 0.0293 min^{-1} and 0.0212 min^{-1} (contribution- 9%, 15%, respectively). The experiments also showcase the sulphate radical dominance at pH 7 and 10 ($k = 0.0038 \text{ min}^{-1}$, 0.0021 min^{-1} , respectively) with a total count of 70% in both conditions, while at pH 3 its contribution remains very low; 13%, $k = 0.0048 \text{ min}^{-1}$.

Hence, in acidic conditions, hydroxyl radicals are the dominating species responsible for degradation of dye, while sulphate radicals play major role in neutral and basic conditions. A significant presence of singlet oxygen was observed in basic conditions contributing 65% of total species ($k = 0.0114 \text{ min}^{-1}$) but at neutral conditions, 25% ($k = 0.0196 \text{ min}^{-1}$) and acidic it is reduced to 16% ($k = 0.0278 \text{ min}^{-1}$). Superoxides were extremely ineffective in the system, contributing less in all pH conditions.

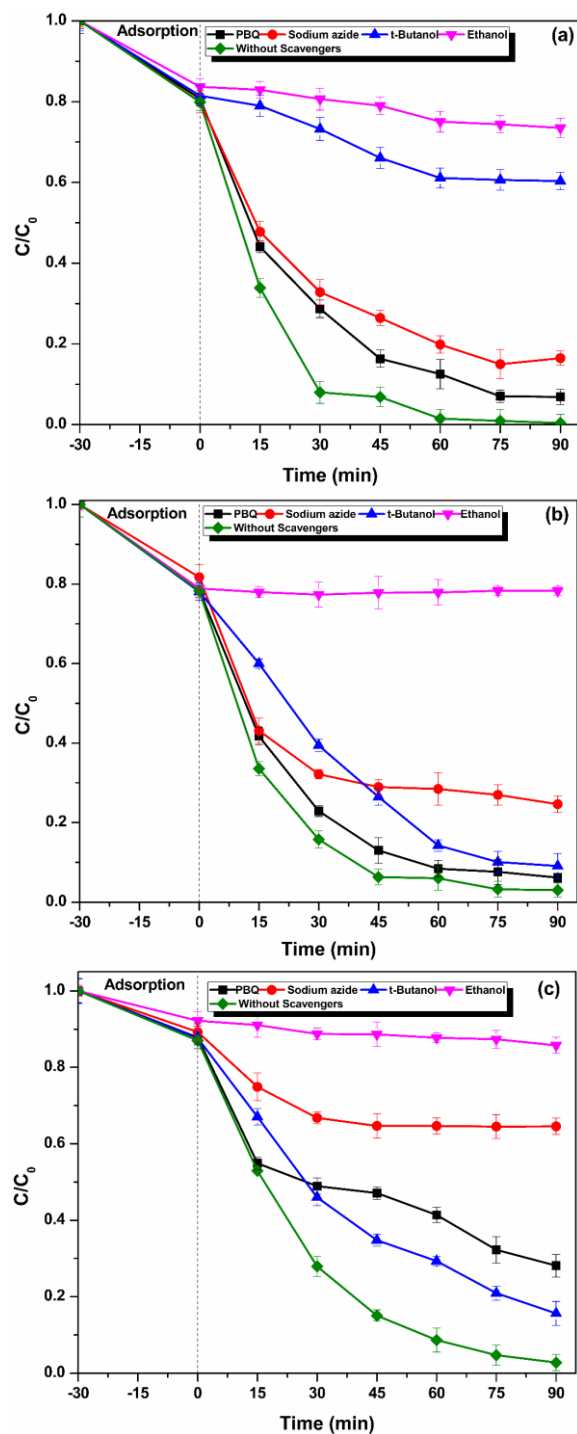


Figure 7. Cont.

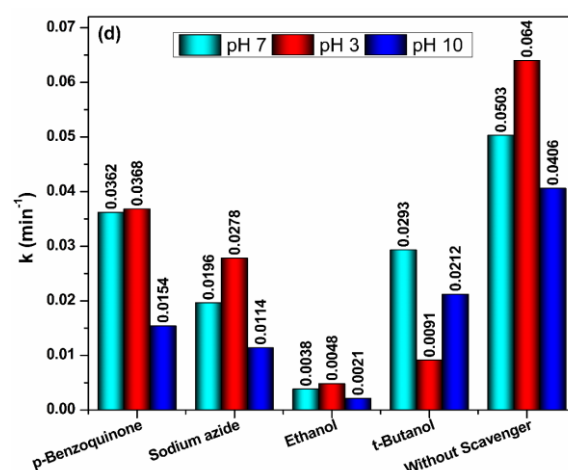
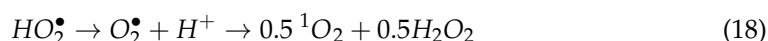
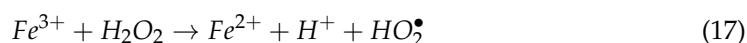
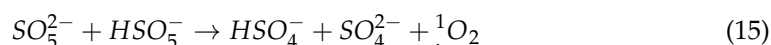


Figure 7. Radical scavenging experiments at (a) pH 3, (b) pH 7 and (c) pH 10, along with (d) the rate of reactions.

In general, sulphate radicals are predominant in PMS activation process at pH < 7 and hydroxyl radicals are predominant at pH > 9. Predominance of hydroxyl radicals at alkaline condition is mainly due to the reaction between sulphate radicals and hydroxyl radicals as provided in Equation (5). However, in the present study, predominance of hydroxyl radicals was observed in acidic conditions, instead of alkaline conditions. Thus, the reactions between PMS and metal ions are predominant in acidic conditions (Equations (6) and (7)). PMS reacts with divalent Fe^{2+} and Mn^{2+} of bimetallic oxides and generates sulphate ions and hydroxyl radicals along with the production of trivalent Fe^{3+} and Mn^{3+} ions.

It was found in our previous study that the blue shift used to occur by the attack of sulphate radicals, not by hydroxyl radicals [29]. In our recent study also, we didn't observe any blue shift of RhB during the electro-Fenton oxidation [40]. At the same time, blue shift was observed at pH 3, even with the predominance of hydroxyl radicals and with lesser contribution of sulphate radicals (13%). Similarly, blue shift of RhB was observed during its photooxidation at pH 4.3 [31] and photocatalytic oxidation at pH 2 [41].

Another interesting result observed was related to the formation of singlet oxygen and its predominance in alkaline conditions. Singlet oxygen generation during PMS was observed with the catalysts such as Fe-N co-doped carbon-based catalysts [42], Fe^0 -montmorillonite [43] and sillenite $\text{Bi}_{25}\text{FeO}_{40}$ [44]. The formation of singlet oxygen occurs in several ways. Self-decomposition of PMS as in Equation (15) is one of the way of singlet oxygen generation [44]. Another route of singlet oxygen generation is the production of $\text{HO}_2^\bullet$ and its consumption as provided in Equations (16)–(18). This may be the main singlet oxygen generation route, as the hydroxyl radical generated in alkaline conditions via Equation (5) are consumed for the production of singlet oxygen.



2.7. Comparison with Monometallic Systems

The bimetallic catalyst synthesized was compared with the monometallic catalyst at optimum conditions (Figure 8). The bimetallic catalyst activity for activating PMS causes a total degradation of 96% in 90 min at pH 7 with optimized conditions but the catalytic activity of iron oxide and manganese oxide were found as 66% and 71%, respectively. The degradation trend was gradual by Mn oxide catalyst but iron oxide, after 15 min, shows

very slow degradation. Kang and Hwang [45] also compared the monometallic Co and Mn systems with the bimetallic Co-Mn system. They found that Co monometallic caused 93% degradation in 1 h and Mn monometallic achieved just 36 % removal efficiency in 80 min in contrast to bimetallic system giving full degradation in 40 min [45].

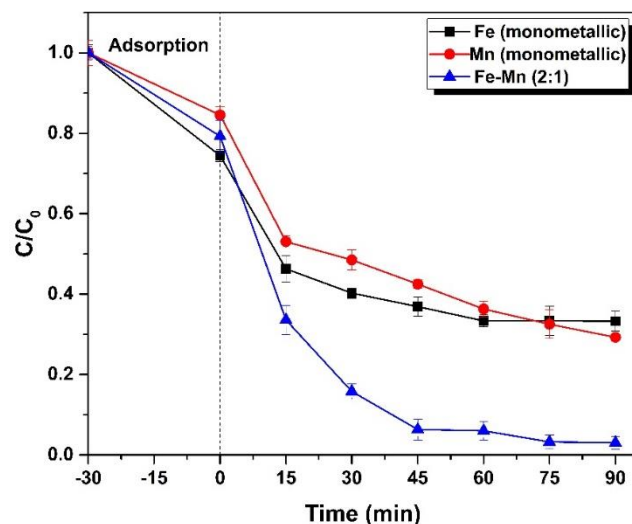


Figure 8. Comparison of bimetallic and mono metallic oxide catalysts for RhB removal.

2.8. Examining Real Textile Wastewater

The collection of real textile wastewater was done from an industry located in Mumbai. The sample (10 L) was collected and sealed tightly and refrigerated to store it for further analysis. Characteristics of the wastewater was provided in our previous study [40]. Color removal at 554 nm was monitored at pH 3 and pH 7 with 0.25 mM PMS and 100 mg/L catalyst dosage (Figure 9a). The results show only 5% color removal was observed in pH 3 while 2% in pH 7. This indicates that the optimized concentrations of PMS and catalyst are not sufficient for the treatment of real wastewater. The PMS concentration and catalyst dosage were optimized for 10 ppm RhB solution. In general, the dye concentration in real textile wastewater is in the range of 100 ppm. Therefore, experiments conducted at 10 folds optimized catalyst and PMS amounts ($10\times$) to examine the degradation efficiency (Figure 9b). Astonishingly, at these experimental conditions, it shows a sharp decline in absorbance, owing 98% color removal within 15 min of PMS addition, while 99.5% color removal was achieved at the end of 90 min (Figure 9b). Observing this trend, this study further examined that even on lowering the amount of catalyst and PMS to five times ($5\times$) under same experimental conditions, similar results were obtained (Figure 9c).

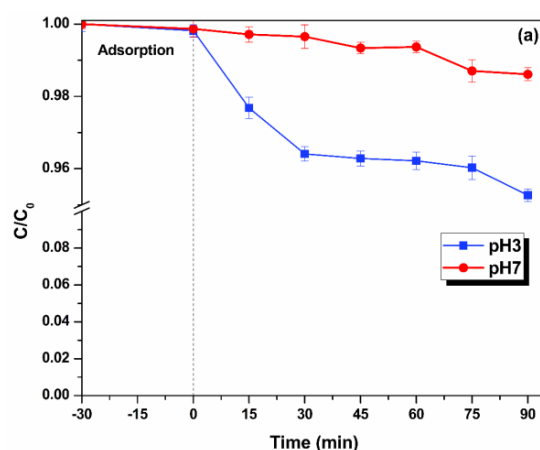


Figure 9. Cont.

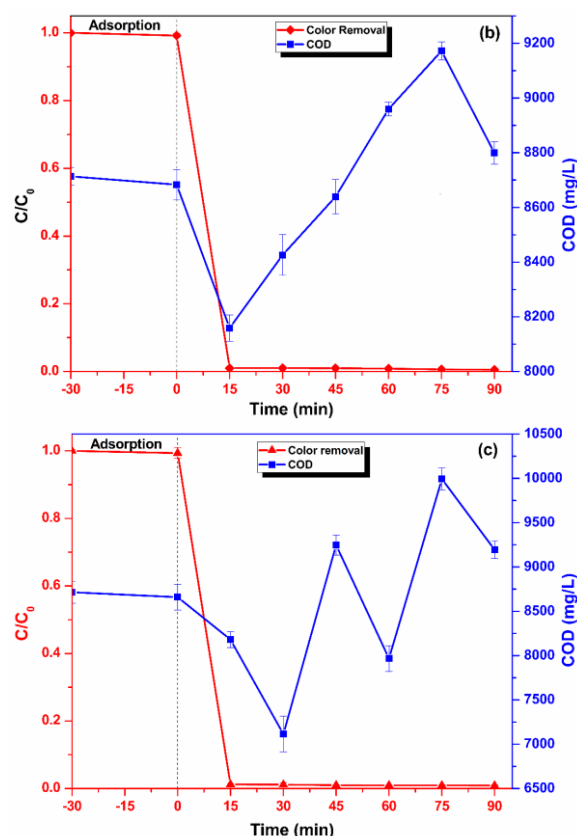


Figure 9. Treatment of real textile wastewater with: (a) 0.25 mM PMS and 100 mg/L catalyst dosage, (b) 2.5 mM PMS and 1000 mg/L catalyst dosage and (c) 1.25 mM PMS and 500 mg/L catalyst dosage.

The chemical oxygen demand (COD) analysis was also done for the system of $10\times$ and $5\times$ optimized conditions in real wastewater, and it was observed that the COD of the wastewater reduced until 15 min but then increased gradually in the next 75 min in $10\times$ system, while fluctuations were observed in $5\times$ system. In the $10\times$ system, the sudden decrease in COD in the initial stages indicates the degradation of pollutants, while the further increase COD after 15 min indicates the degradation of recalcitrant compounds (Which were not provided COD values) and the productions of by-products which are degradable by dichromate ions in acidic conditions. Similar results were observed in our previous study [40].

3. Materials and Methods

3.1. Chemicals

Analytical grade chemicals including RhB ($C_{28}H_{31}ClN_2O_3$) supplied by Loba Chemie (Mumbai, India) was used for the experiments. Iron nitrate nonahydrate ($Fe(NO_3)_3(H_2O)_9$), 25% ammonia (NH_3) purchased from Merck (Mumbai, India), manganese nitrate tetrahydrate ($Mn(NO_3)_2 \cdot 4H_2O$, 98%) purchased from Thermo Fisher Scientific (Lancashire, UK), cethyl trimethyl ammonium bromide (CTAB) ($C_{19}H_{42}BrN$) purchased from Amresco (Solon, OH, USA) were used for the synthesis of bimetallic catalyst. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$; PMS) was purchased from Avra (Secunderabad, India).

Other chemicals like potassium dichromate ($K_2Cr_2O_7$, $\geq 99.0\%$), silver sulphate (Ag_2SO_4 , $\geq 98\%$), t-butanol($(CH_3)_3COH$, $\geq 99\%$), sodium hydroxide ($NaOH$, $\geq 97\%$), sodium azide (NaN_3 , $\geq 99\%$), and p-Benzoquinone ($\geq 98\%$) were purchased from Merck (Mumbai, India). Ammonium acetate (CH_3COONH_4 , $\geq 98\%$) and hydroxyl amine (NH_2OH , $\geq 96\%$) were purchased from Qualigens (Mumbai, India).

3.2. Preparation of Catalyst

The Fe-Mn bimetallic catalyst of ratio 1:1 was prepared by using the chemical co-precipitation method. Amounts of 0.05 M of each metal precursor; iron nitrate nonahydrate (1.01 g) and manganese nitrate tetrahydrate (0.627 g), were added to the 50 mL distilled water with small amount of CTAB (0.0503 g), to avoid aggregation. The solution was agitated for about 2 h at 80 °C and 100 rpm on the magnetic stirrer. Following this, 25% ammonia solution was added until the pH reached 8, to cause the precipitation. The system was left for 2 h in the same experimental conditions. The precipitate obtained via vacuum filtration was dried for 9 h in muffle furnace. Catalyst thus obtained was ground using mortar and dried again for 1 h. In the same manner, Fe-Mn (1:2) and Fe-Mn (2:1) oxides were prepared taking metal precursors as 0.05 M:0.025 M (0.505g: 0.627g) and 0.025 M:0.05 M (1.01g: 0.313g) respectively. Since, the best catalyst examined is Fe-Mn (2:1) it was compared with the monometallic iron oxide catalyst and manganese oxide catalyst. Iron oxide was prepared in the same way, taking 0.05 M iron precursors with no manganese precursor in the system while manganese oxide catalyst prepared has a concentration of 0.025 M with no iron precursor following the same route of synthesis.

3.3. Characterization of Catalyst

The structural characterization of the catalyst prepared in the laboratory was done using X-ray powder diffraction (XRD, Bruker D8 Advance). Surface functional groups presence on the catalyst was detected by Fourier Transfer Infrared (FTIR) Spectroscopy (FTIR, Bruker, Germany). The size of the prepared catalyst was determined by Transmission Electron Microscope (TEM, Tecnai G2 20 S-TWIN).

3.4. Experimental Procedure

The RhB degradation experiment in stimulated water was performed in a 100 mL beaker at room temperature and 300 rpm on the magnetic stirrer. In detail, the catalyst was added at 10 ppm in 100 mL RhB solution for 30 min of stirring for adequate adsorption-desorption. It was followed by addition of PMS which marked the enhancement of degradation reaction. 0.1 N NaOH and 0.1 N H₂SO₄ were used for adjusting the pH (when required) and was monitored using Laqua pH meter (Horiba scientific). The samples were collected and filtered after every 15 min to observe the degradation pattern. Residual RhB concentration in the samples was analyzed using UV/Vis spectrophotometer (UV-1900I, Shimadzu, Japan) at 554 nm, which is the peak wavelength of the dye. The RhB degradation thus observed was analyzed on the basis of C/C_0 vs. time; where, 'C' is the concentration at time 't' while 'C₀' is the initial concentration. COD analysis of real textile wastewater was done according to the standard method [46]. The samples were initially digested in a closed reflux digester for a time period of 120 min at 150 °C, followed by the titration of digested solution, using ferrous ammonium sulfate as a titrant and ferroin as an indicator.

Performance of bimetallic catalyst is also compared with various catalysts used for activation of PMS (Table 1). Extensive research has been done to activate PMS using transition metals as catalyst to facilitate better degradation. Studies shows that copper metal can successfully degrade RhB using PMS in 20 min but copper oxide as catalyst, is required in fairly large concentration (three times than our work) as well as PMS concentration used are also greater [47]. Metal organic frameworks are also proven to cause full degradation of RhB assisted by PMS as in case of metal organic framework and bismuth sulphide binary system (MIL-100(Fe)/Bi₂S₃ (MIL-BS) + Visible light). However, synthesis of MOFs is not economical as the organic linkers used in the synthesis of MOFs are expensive. Cobalt and its oxides show excellent degradation of RhB when assisted by PMS. One of the studies where cobalt phthalocyanine on reduced graphene oxide [rGO-CoPc (1:1)] shows 100% degradation efficiency in 9 min [48]. In another study microporous activated carbon and cobalt phthalocyanine (Co-AC) could cause 97% degradation in 16 min. Though cobalt efficiency remains unmatched to any other transition metal catalyst in case of RhB degradation via PMS, toxicity caused due to excessive leaching and its tenfold cost compared to

manganese metal paves the way for cheaper and less toxic routes. Synergy of bimetallic have been proved efficient in various studies, cobalt manganese oxide supported on hollow activated carbon nano fibres ($\text{CoMn}_2\text{O}_4/\text{HACNFs}$) [45] and iron-cobalt bimetallic catalyst supported on graphene oxide ($\text{CoFe}_2\text{O}_4/\text{GO}$) [49] resulting in almost full degradation in 40 min and 12 min respectively. Herein bimetallic Fe-Mn oxide is able to achieve good efficiency in simulated as well as in textile wastewater in natural pH condition.

Table 1. Performance of PMS activated by various catalysts and its comparison with the present study.

Catalyst	Optimised Conditions	Removal Efficiency	Reference
Copper oxide synthesised using Sodium Citrate assisted by visible light ($\text{CuO-SC} + \text{Visible light}$)	120mg/L PMS, catalyst: 300mg/L	98% in 20 min	[47]
Metal organic framework and bismuth sulphide binary system ($\text{MIL-100(Fe)/Bi}_2\text{S}_3$ (MIL-BS) + Visible light)	150mg/L PMS, neutral pH, 25mg/L MIL-BS.	100%	[50]
Reduced graphene oxide (rGO) + ultrasonication	0.02mM RhB, 0.25mg/L rGO, 0.3mM PMS.	100% in 15 min.	[51]
Manganese oxide (Mn_3O_4)	0.05 mM RhB, 1mM PMS, 20 mg/L catalyst	36% in 80	[45]
Cobalt oxide (Co_3O_4)		93% in 1 h	
Manganese oxide supported on hollow activated carbon nano fibres ($\text{Mn}_3\text{O}_4/\text{HACNFs}$)		55% in 80 min	
Cobalt oxide supported on hollow activated carbon nano fibres ($\text{Co}_3\text{O}_4/\text{HACNFs}$)		100% in 1 h	
Cobalt manganese oxide supported on hollow activated carbon nano fibres ($\text{CoMn}_2\text{O}_4/\text{HACNFs}$)		100% in 40 min, $k = 0.093 \text{ min}^{-1}$	
Iron-cobalt bimetallic catalyst supported on graphene oxide ($\text{CoFe}_2\text{O}_4/\text{GO}$)	0.03 mM RhB, 0.1 mM PMS, 0.01 g catalyst	98% in 12 min, $k = 0.3260 \text{ min}^{-1}$	[49]
Magnetically recoverable iron oxide/ layered double hydroxides (LDHs) of cobalt-iron-copper ($\text{Fe}_3\text{O}_4/\text{CoFeCu-LDHs}$)	0.05 g/L RhB, catalyst 200 mg/L and 1 mM of PMS	100% in 20 min	[34]
Cobalt-doped $\text{g-C}_3\text{N}_4$	0.01 g/L RhB, 0.12 mM PMS, 1% Co loading, pH of 4.68.	99% in 25 min	[39]
Bismuth vanadate ($\text{BiVO}_4 + \text{visible light}$)	0.01 g/L RhB solution, 1 mM PMS, 500 mg/L catalyst, pH 3	92.4 % in 1 h	[52]
Manganese oxide ($\alpha\text{-Mn}_2\text{O}_2$)	0.02 g/L RhB, 200 mg/L PMS, 0.1 g/L catalyst	99% in 1 h	[11]
Cobalt phthalocyanine on reduced graphene oxide [rGO-CoPc (1:1)]	0.025 mM RhB, 0.1 mM PMS, 0.5 mg/mL catalyst	100 % in 9 min	[48]
Zero valent iron (ZVI) + ultrasound	50W US power, 1 mM PMS, 1 g/L ZVI catalyst, pH 4.5	99.76 % in 12 min	[53]
LaFeO_3 (LFO) + visible light	0.02 g/L RhB, 3.552 mM PMS, 1 g/L catalyst, pH 8.07	100% in 180 min	[30]
Cobalt sulphide supported on reduced graphene oxide (CoS-rGO)	The 0.03 mM RhB, 0.05 mM PMS of 0.25 g/L catalyst	100% in 8 min	[22]
Cobalt nanoparticles incorporated on N-doped carbon nanotubes (Co/NCNT-700)	20 mg/L RhB, PMS 60 mg/L, 20 mg/L catalyst, pH 5.67 at 25 °C.	98.8% in 7 min	[54]
Cobalt oxide supported on rice husk ash ($\text{Co}_3\text{O}_4/\text{rice husk ash}$)	20 mg/L RhB, PMS 500 mg/L, catalyst 100 mg/L	96.3% in 1 h	[55]
Iron oxide nanoparticle on biochar (5S@Fe-500)	0.05 g/L RhB, 600mg/L PMS, 600 mg/L catalyst, natural pH	97.27 % in 10 min.	[56]
Porous iron oxide ($\alpha\text{-Fe}_2\text{O}_3$)	0.05 g/L of RhB, 1.5 g/L catalyst, 1 mM PMS	100% in 1 h	[28]
Dumple shaped manganese oxide using gelatin as template ($\text{Mn}_2\text{O}_3\text{-G}$)	0.01 g/L RhB, 250mg/L PMS, 250 mg/L catalyst.	100 % in 30 min	[57]
Dumple shaped manganese oxide using carboxymethyl cellulose sodium as template ($\text{Mn}_2\text{O}_3\text{-C}$)		98.1 % in 30 min	
Dumple shaped manganese oxide using no template ($\text{Mn}_2\text{O}_3\text{-N}$)		29.6 % in 30 min	

Table 1. Cont.

Catalyst	Optimised Conditions	Removal Efficiency	Reference
Conjugated system of polyvinyl chloride and bismuth oxide (Bi_2O_3 /cPVC + visible light)	0.02 g/L RhB, 2% composite system, 3 mM PMS	100% in 150 min	[58]
Pyrite/ hydroxylamine ($\text{Fe}^{2+}/\text{Fe}^{3+}$)-pyrite/HA)	0.05 g/L RhB, 0.4 g/L catalyst, 1.6 mM PMS, 0.8 mM hydroxylamine, pH 4	100% in 30 min	[38]
Bimetallic oxide; Fe-Mn (1:1)	10 ppm RhB, 0.25 mM PMS, 100 mg/L, natural pH	95% in 90 min	This work
Bimetallic oxide; Fe-Mn (1:2)		96% in 90 min	This work
Bimetallic oxide; Fe-Mn (2:1)		96% in 90 min	This work
Bimetallic oxide; Fe-Mn (2:1)	Real textile wastewater, 2.5 mM PMS, 1000 mg/L, natural pH	98% in 15 min	This work
Iron oxide monometallic	10 ppm RhB, 0.25 mM PMS, 67 mg/L, natural pH	66% in 90 min	This work
Manganese oxide monometallic	10 ppm RhB, 0.25 mM PMS, 33 mg/L, natural pH	71% in 90 min	This work

4. Conclusions

Bimetallic Fe-Mn-oxides-activated PMS process was found efficient for the degradation of dyes from a water medium. Amongst all three bimetallic catalysts, Fe-Mn (2:1) oxide worked most efficiently at natural pH, showing 96% dye removal efficiency in 90 min in neutral medium, unlike other AOPs that work effectively in acidic pH through PMS activation and demonstrate a 20% adsorption level. XRD and FTIR characterization confirms the bimetallic oxide to be $\text{Fe}_2\text{O}_3\text{-Mn}_2\text{O}_3$ while FE-SEM and TEM results showcase its nano sizing and microporosity thus demonstrating clear morphological characteristics. The optimized conditions obtained for 10 ppm RhB degradation are 100 mg/L of catalyst dosage, and 0.25 mM PMS at natural pH. Additionally, scavenging experiments conducted at different pH conditions revealed the predominant contribution of hydroxyl radicals at pH 3, while sulphate radical was dominant in neutral and basic pH conditions. To confirm the synergistic effect of bimetallic catalyst, Fe monometallic and Mn monometallic oxide efficiencies for RhB degradation were confirmed to be 66% and 71%, respectively, in 90 min. The process was also found effective for the treatment of real wastewater with almost complete decolorization along with the mineralization.

Author Contributions: Conceptualization, P.V.N.; methodology, P.V.N.; investigation, H.R.; writing—original draft preparation, H.R.; writing—review and editing, P.V.N. and H.R.; supervision, P.V.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data is contained within the article.

Acknowledgments: The authors are thankful to Director, CSIR NEERI for the support.

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

References

- Bai, C.; Xiong, X.; Gong, W.; Feng, D.; Xian, M.; Ge, Z.; Xu, N. Removal of rhodamine B by ozone-based advanced oxidation process. *Desalination* **2011**, *278*, 84–90. [CrossRef]
- Forgacs, E.; Cserháti, T.; Oros, G. Removal of synthetic dyes from wastewaters: A review. *Environ. Int.* **2004**, *30*, 953–971. [CrossRef] [PubMed]
- Rafiq, A.; Ikram, M.; Ali, S.; Niaz, F.; Khan, M.; Khan, Q.; Maqbool, M. Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution. *J. Ind. Eng. Chem.* **2021**, *97*, 111–128. [CrossRef]
- Nidheesh, P.V.; Gandhimathi, R. Electrolytic removal of Rhodamine B from aqueous solution by peroxicoagulation process. *Environ. Sci. Pollut. Res.* **2014**, *21*, 8585–8594. [CrossRef] [PubMed]
- Su, S.; Guo, W.; Leng, Y.; Yi, C.; Ma, Z. Heterogeneous activation of Oxone by $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanocatalysts for degradation of rhodamine B. *J. Hazard. Mater.* **2013**, *244–245*, 736–742. [CrossRef]
- Nidheesh, P.V.; Gandhimathi, R.; Ramesh, S.T. Degradation of dyes from aqueous solution by Fenton processes: A review. *Environ. Sci. Pollut. Res.* **2013**, *20*, 2099–2132. [CrossRef]
- Nidheesh, P.V.; Zhou, M.; Oturan, M.A. An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. *Chemosphere* **2018**, *197*, 210–227. [CrossRef]

8. Nidheesh, P.V.; Divyapriya, G.; Ezzahra Titchou, F.; Hamdani, M. Treatment of textile wastewater by sulfate radical based advanced oxidation processes. *Sep. Purif. Technol.* **2022**, *293*, 121115. [\[CrossRef\]](#)
9. El-Hakam, S.A.; ALShorifi, F.T.; Salama, R.S.; Gamal, S.; El-Yazeed, W.S.A.; Ibrahim, A.A.; Ahmed, A.I. Application of nanostructured mesoporous silica/ bismuth vanadate composite catalysts for the degradation of methylene blue and brilliant green. *J. Mater. Res. Technol.* **2022**, *18*, 1963–1976. [\[CrossRef\]](#)
10. Syam Babu, D.; Nidheesh, P.V. A review on electrochemical treatment of arsenic from aqueous medium. *Chem. Eng. Commun.* **2021**, *208*, 389–410. [\[CrossRef\]](#)
11. Liu, C.; Pan, D.; Tang, X.; Hou, M.; Zhou, Q.; Zhou, J. Degradation of Rhodamine B by the α -MnO₂/Peroxymonosulfate System. *Water Air Soil Pollut.* **2016**, *227*, 92. [\[CrossRef\]](#)
12. Scaria, J.; Nidheesh, P.V. Comparison of hydroxyl-radical-based advanced oxidation processes with sulfate radical-based advanced oxidation processes. *Curr. Opin. Chem. Eng.* **2022**, *36*, 100830. [\[CrossRef\]](#)
13. Urán-Duque, L.; Saldarriaga-Molina, J.C.; Rubio-Clemente, A. Advanced Oxidation Processes Based on Sulfate Radicals for Wastewater Treatment: Research Trends. *Water* **2021**, *13*, 2445. [\[CrossRef\]](#)
14. Missaoui, K.; Ouertani, R.; Jbira, E.; Boukherroub, R.; Bessaïs, B. Morphological influence of BiVO₄ nanostructures on peroxy-monosulfate activation for highly efficient catalytic degradation of rhodamine B. *Environ. Sci. Pollut. Res.* **2021**, *28*, 52236–52246. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Lee, J.; von Gunten, U.; Kim, J.-H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* **2020**, *54*, 3064–3081. [\[CrossRef\]](#)
16. Waclawek, S.; Lutze, H.V.; Grübel, K.; Padil, V.V.T.; Černík, M.; Dionysiou, D.D. Chemistry of persulfates in water and wastewater treatment: A review. *Chem. Eng. J.* **2017**, *330*, 44–62. [\[CrossRef\]](#)
17. Zhou, H.; Peng, J.; Li, J.; You, J.; Lai, L.; Liu, R.; Ao, Z.; Yao, G.; Lai, B. Metal-free black-red phosphorus as an efficient heterogeneous reductant to boost Fe³⁺/Fe²⁺ cycle for peroxymonosulfate activation. *Water Res.* **2021**, *188*, 116529. [\[CrossRef\]](#)
18. Fei, J.; Cui, Y.; Yan, X.; Qi, W.; Yang, Y.; Wang, K.; He, Q.; Li, J. Controlled preparation of MnO₂ hierarchical hollow nanostructures and their application in water treatment. *Adv. Mater.* **2008**, *20*, 452–456. [\[CrossRef\]](#)
19. Nidheesh, P.V. Heterogeneous Fenton catalysts for the abatement of organic pollutants from aqueous solution: A review. *RSC Adv.* **2015**, *5*, 40552–40577. [\[CrossRef\]](#)
20. Khan, A.; Liao, Z.; Liu, Y.; Jawad, A.; Iftikhar, J.; Chen, Z. Synergistic degradation of phenols using peroxymonosulfate activated by CuO-Co₃O₄@MnO₂ nanocatalyst. *J. Hazard. Mater.* **2017**, *329*, 262–271. [\[CrossRef\]](#)
21. Scaria, J.; Nidheesh, P.V.; Kumar, M.S. Synthesis and applications of various bimetallic nanomaterials in water and wastewater treatment. *J. Environ. Manag.* **2020**, *259*, 110011. [\[CrossRef\]](#)
22. Amirache, L.; Barka-Bouaifel, F.; Borthakur, P.; Das, M.R.; Ahouari, H.; Vezin, H.; Barras, A.; Ouddane, B.; Szunerits, S.; Boukherroub, R. Cobalt sulfide-reduced graphene oxide: An efficient catalyst for the degradation of rhodamine B and pentachlorophenol using peroxymonosulfate. *J. Environ. Chem. Eng.* **2021**, *9*, 106018. [\[CrossRef\]](#)
23. Alangari, A.; Alqahtani, M.S.; Mateen, A.; Kalam, M.A.; Alshememry, A.; Ali, R.; Kazi, M.; AlGhamdi, K.M.; Syed, R. Iron Oxide Nanoparticles: Preparation, Characterization, and Assessment of Antimicrobial and Anticancer Activity. *Adsorpt. Sci. Technol.* **2022**, *2022*, 1562051. [\[CrossRef\]](#)
24. Najjar, R.; Awad, R.; Abdel-Gaber, A.M. Physical Properties of Mn₂O₃ Nanoparticles Synthesized by Co-precipitation Method at Different pH Values. *J. Supercond. Nov. Magn.* **2019**, *32*, 885–892. [\[CrossRef\]](#)
25. Jia, D.; Hanna, K.; Mailhot, G.; Brigante, M. A Review of Manganese(III) (Oxyhydr) Oxides Use in Advanced Oxidation Processes. *Molecules* **2021**, *26*, 5748. [\[CrossRef\]](#)
26. Deng, J.; Ya, C.; Ge, Y.; Cheng, Y.; Chen, Y.; Xu, M.; Wang, H. Activation of peroxymonosulfate by metal (Fe, Mn, Cu and Ni) doping ordered mesoporous Co₃O₄ for the degradation of enrofloxacin. *RSC Adv.* **2018**, *8*, 2338–2349. [\[CrossRef\]](#)
27. Yang, S.; Wang, P.; Yang, X.; Wei, G.; Zhang, W.; Shan, L. A novel advanced oxidation process to degrade organic pollutants in wastewater: Microwave-activated persulfate oxidation. *J. Environ. Sci.* **2009**, *21*, 1175–1180. [\[CrossRef\]](#)
28. Ji, F.; Li, C.; Wei, X.; Yu, J. Efficient performance of porous Fe₂O₃ in heterogeneous activation of peroxymonosulfate for decolorization of Rhodamine B. *Chem. Eng. J.* **2013**, *231*, 434–440. [\[CrossRef\]](#)
29. Nidheesh, P.V.; Rajan, R. Removal of rhodamine B from a water medium using hydroxyl and sulphate radicals generated by iron loaded activated carbon. *RSC Adv.* **2016**, *6*, 5330–5340. [\[CrossRef\]](#)
30. Meng, W.; Wang, Y.; Zhang, Y.; Liu, C.; Wang, Z.; Song, Z.; Xu, B.; Qi, F.; Ikhlaiq, A. Degradation Rhodamine B dye wastewater by sulfate radical-based visible light-fenton mediated by LaFeO₃: Reaction mechanism and empirical modeling. *J. Taiwan Inst. Chem. Eng.* **2020**, *111*, 162–169. [\[CrossRef\]](#)
31. Chen, F.; Zhao, J.; Hidaka, H. Highly selective deethylation of rhodamine B: Adsorption and photooxidation pathways of the dye on the TiO₂/SiO₂ composite catalyst. *Int. J. Photoenergy* **2003**, *5*, 209–217. [\[CrossRef\]](#)
32. Merka, O.; Yarovyi, V.; Bahnemann, D.W.; Wark, M. PH-control of the photocatalytic degradation mechanism of rhodamine B over Pb₃Nb₄O₁₃. *J. Phys. Chem. C* **2011**, *115*, 8014–8023. [\[CrossRef\]](#)

33. Jinisha, R.; Gandhimathi, R.; Ramesh, S.T.; Nidheesh, P.V.; Velmathi, S. Removal of rhodamine B dye from aqueous solution by electro-Fenton process using iron-doped mesoporous silica as a heterogeneous catalyst. *Chemosphere* **2018**, *200*, 446–454. [\[CrossRef\]](#)
34. Li, T.; Du, X.; Deng, J.; Qi, K.; Zhang, J.; Gao, L.; Yue, X. Efficient degradation of Rhodamine B by magnetically recoverable Fe₃O₄-modified ternary CoFeCu-layered double hydroxides via activating peroxymonosulfate. *J. Environ. Sci.* **2021**, *108*, 188–200. [\[CrossRef\]](#)
35. Tan, C.; Gao, N.; Deng, Y.; Deng, J.; Zhou, S.; Li, J.; Xin, X. Radical induced degradation of acetaminophen with Fe₃O₄ magnetic nanoparticles as heterogeneous activator of peroxymonosulfate. *J. Hazard. Mater.* **2014**, *276*, 452–460. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Chen, S.; Ma, L.; Du, Y.; Zhan, W.; Zhang, T.C.; Du, D. Highly efficient degradation of rhodamine B by carbon nanotubes-activated persulfate. *Sep. Purif. Technol.* **2021**, *256*, 117788. [\[CrossRef\]](#)
37. Xu, Y.; Hu, E.; Xu, D.; Guo, Q. Activation of peroxymonosulfate by bimetallic CoMn oxides loaded on coal fly ash-derived SBA-15 for efficient degradation of Rhodamine B. *Sep. Purif. Technol.* **2021**, *274*, 119081. [\[CrossRef\]](#)
38. He, G.-J.; Zhong, D.-J.; Xu, Y.-L.; Liu, P.; Zeng, S.-J.; Wang, S. Highly Efficient Rhodamine B Decolorization by Pyrite/Peroxymonosulfate/Hydroxylamine System. *Water Air Soil Pollut.* **2021**, *232*, 141. [\[CrossRef\]](#)
39. Wang, L.; Guo, X.; Chen, Y.; Ai, S.; Ding, H. Cobalt-doped g-C₃N₄ as a heterogeneous catalyst for photo-assisted activation of peroxymonosulfate for the degradation of organic contaminants. *Appl. Surf. Sci.* **2019**, *467–468*, 954–962. [\[CrossRef\]](#)
40. Anil, G.; Scaria, J.; Nidheesh, P.V. Removal of Synthetic Dye from Aqueous Solution Using MnFe₂O₄-GO Catalyzed Heterogeneous Electro-Fenton Process. *Water* **2022**, *14*, 3350. [\[CrossRef\]](#)
41. Dhiwaha, A.T.; Maruthamuthu, S.; Marnadu, R.; Sundararajan, M.; Manthrammel, M.A.; Shkir, M.; Sakthivel, P.; Minnam Reddy, V.R. Improved photocatalytic degradation of rhodamine B under visible light and magnetic properties using microwave combustion grown Ni doped copper ferrite spinel nanoparticles. *Solid State Sci.* **2021**, *113*, 106542. [\[CrossRef\]](#)
42. Miao, W.; Liu, Y.; Wang, D.; Du, N.; Ye, Z.; Hou, Y.; Mao, S.; Ostrikov, K.K. The role of Fe-Nx single-atom catalytic sites in peroxymonosulfate activation: Formation of surface-activated complex and non-radical pathways. *Chem. Eng. J.* **2021**, *423*, 130250. [\[CrossRef\]](#)
43. Yang, S.; Wu, P.; Liu, J.; Chen, M.; Ahmed, Z.; Zhu, N. Efficient removal of bisphenol A by superoxide radical and singlet oxygen generated from peroxymonosulfate activated with Fe⁰-montmorillonite. *Chem. Eng. J.* **2018**, *350*, 484–495. [\[CrossRef\]](#)
44. Liu, Y.; Guo, H.; Zhang, Y.; Tang, W.; Cheng, X.; Li, W. Heterogeneous activation of peroxymonosulfate by sillenite Bi₂₅FeO₄₀: Singlet oxygen generation and degradation for aquatic levofloxacin. *Chem. Eng. J.* **2018**, *343*, 128–137. [\[CrossRef\]](#)
45. Kang, S.; Hwang, J. CoMn₂O₄ embedded hollow activated carbon nanofibers as a novel peroxymonosulfate activator. *Chem. Eng. J.* **2021**, *406*, 127158. [\[CrossRef\]](#)
46. APHA. *Standard Methods for Examination of Water and Waste Water*, 22nd ed.; American Public Health Association: Washington, DC, USA, 2012.
47. Liu, Y.; Lan, Q.; Sun, S.; Yang, Q. Synergistic oxygen vacancy-rich CuO/visible light activation of peroxymonosulfate for degradation of rhodamine B: Fast catalyst synthesis and degradation mechanism. *RSC Adv.* **2022**, *12*, 2928–2937. [\[CrossRef\]](#) [\[PubMed\]](#)
48. Marinescu, C.; Ben Ali, M.; Hamdi, A.; Cherifi, Y.; Barras, A.; Coffinier, Y.; Somacescu, S.; Raditoiu, V.; Szunerits, S.; Boukherroub, R. Cobalt phthalocyanine-supported reduced graphene oxide: A highly efficient catalyst for heterogeneous activation of peroxymonosulfate for rhodamine B and pentachlorophenol degradation. *Chem. Eng. J.* **2018**, *336*, 465–475. [\[CrossRef\]](#)
49. Tabit, R.; Amadine, O.; Essamlali, Y.; Dânoun, K.; Rhihil, A.; Zahouily, M. Magnetic CoFe₂O₄ nanoparticles supported on graphene oxide (CoFe₂O₄/GO) with high catalytic activity for peroxymonosulfate activation and degradation of rhodamine B. *RSC Adv.* **2018**, *8*, 1351–1360. [\[CrossRef\]](#)
50. Roy, D.; Poddar, N.; Singh, M.; Neogi, S.; De, S. Photocatalytic degradation of rhodamine-B by visible light assisted peroxymonosulfate activation using the Z-scheme MIL-100(Fe)/Bi₂S₃ composite: A combined experimental and theoretical approach. *New J. Chem.* **2022**, *46*, 10728–10745. [\[CrossRef\]](#)
51. Cherifi, Y.; Addad, A.; Vezin, H.; Barras, A.; Ouddane, B.; Chaouchi, A.; Szunerits, S.; Boukherroub, R. PMS activation using reduced graphene oxide under sonication: Efficient metal-free catalytic system for the degradation of rhodamine B, bisphenol A, and tetracycline. *Ultrason. Sonochem.* **2019**, *52*, 164–175. [\[CrossRef\]](#)
52. Liu, Y.; Guo, H.; Zhang, Y.; Tang, W.; Cheng, X.; Liu, H. Activation of peroxymonosulfate by BiVO₄ under visible light for degradation of Rhodamine B. *Chem. Phys. Lett.* **2016**, *653*, 101–107. [\[CrossRef\]](#)
53. Pang, Y.; Ruan, Y.; Feng, Y.; Diao, Z.; Shih, K.; Hou, L.; Chen, D.; Kong, L. Ultrasound assisted zero valent iron corrosion for peroxymonosulfate activation for Rhodamine-B degradation. *Chemosphere* **2019**, *228*, 412–417. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Cheng, J.; Wei, N.; Wang, Y.; Long, Y.; Fan, G. Direct transformation of bulk cobalt foam into cobalt nanoparticles encapsulated in nitrogen-doped carbon nanotubes for peroxymonosulfate activation toward rhodamine B degradation. *Sep. Purif. Technol.* **2021**, *277*, 119441. [\[CrossRef\]](#)
55. Di, J.; Jamakanga, R.; Chen, Q.; Li, J.; Gai, X.; Li, Y.; Yang, R.; Ma, Q. Degradation of Rhodamine B by activation of peroxymonosulfate using Co₃O₄-rice husk ash composites. *Sci. Total Environ.* **2021**, *784*, 147258. [\[CrossRef\]](#) [\[PubMed\]](#)

56. Zang, T.; Wang, H.; Liu, Y.; Dai, L.; Zhou, S.; Ai, S. Fe-doped biochar derived from waste sludge for degradation of rhodamine B via enhancing activation of peroxymonosulfate. *Chemosphere* **2020**, *261*, 127616. [[CrossRef](#)]
57. Li, Y.; Li, D.; Fan, S.; Yang, T.; Zhou, Q. Facile template synthesis of dumbbell-like Mn₂O₃ with oxygen vacancies for efficient degradation of organic pollutants by activating peroxymonosulfate. *Catal. Sci. Technol.* **2020**, *10*, 864–875. [[CrossRef](#)]
58. Pham, H.H.; You, S.J.; Wang, Y.F.; Cao, M.T.; Pham, V.V. Activation of potassium peroxymonosulfate for rhodamine B photocatalytic degradation over visible-light-driven conjugated polyvinyl chloride/Bi₂O₃ hybrid structure. *Sustain. Chem. Pharm.* **2021**, *19*, 100367. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.