


Photochemical degradation of bromocresol green dye by UV/Co²⁺ process via activation of peroxymonosulfate: a mechanistic approach

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ABSTRACT

This study is focused on the application of the ultraviolet/peroxymonosulfate/cobaltous cation (UV/PMS/Co²⁺) (cobalt II ion) system for the successful degradation of bromocresol green (BCG) dye in an aqueous solution. The influences of different variables like initial PMS concentration, pH of the media, and catalyst dose in terms of BCG degradation were studied. Furthermore, the effectiveness of the UV/PMS/Co²⁺ system for the degradation of BCG was performed in different water systems (i.e., deionized water, tap water, and industrial wastewater). UV and UV–PMS systems alone contributed 13 and 67%, respectively, in the degradation of BCG with the k_{app} values of 0.006 and 0.0297 min⁻¹, respectively. It was observed that by the incorporation of Co²⁺ in the UV–PMS system, the degradation of BCG was significantly increased from 67 to 98% with the corresponding increase in k_{app} values to 0.0931 min⁻¹. The scavenger results revealed the SO₄^{-•} and •OH radicals are the dominant species involved in the BCG removal. The toxicity data showed that the UV/PMS/Co²⁺ method considerably reduced the toxicity of textile effluent. In addition, seven BCG degradation products (DPs) have been identified experimentally using gas chromatography–mass spectrometry (GC-MS). In conclusion, the UV/PMS/Co²⁺ procedure can be used to effectively cleanse and detoxify wastewater.

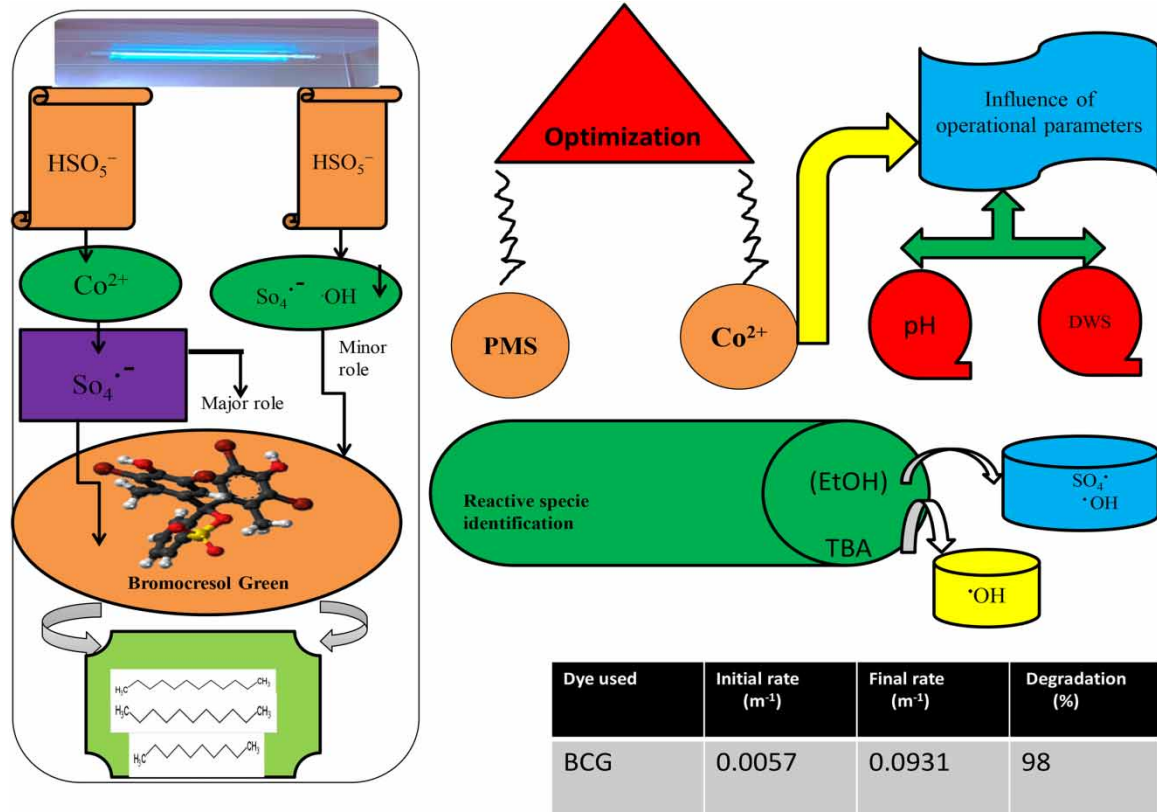
Key words: advanced oxidation processes (AOPs), cobalt ions, peroxymonosulfate (PMS), toxicity, wastewater

HIGHLIGHTS

- To the best of our knowledge, this is the first article on photocatalytic elimination of BCG by the UV/Co²⁺ process.
- The addition of the green oxidant, peroxymonosulfate, synergistically improved the degradation process.
- The mechanistic approach was conducted for the photocatalytic elimination of BCG by the UV/Co²⁺ process.
- The toxicity evaluation was performed.

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GRAPHICAL ABSTRACT



1. INTRODUCTION

Almost 15% of the estimated 7×10^5 – 1×10^6 metric tons of various dyes generated each year ends up as wastewater. One of the most significant dyes among them is bromocresol green (BCG) (Onu *et al.* 2022). This dye is an anionic dye from the triphenylmethane family that is extremely soluble in water and barely biodegradable (Onu *et al.* 2022; Nawaz *et al.* 2023). It is used in the textile industry and to detect liver and kidney failure by measuring the concentration of serum albumin. Moreover, it serves as a pH indicator and a tool for DNA tracing. BCG is pale brown in an acidic environment and dark green in an alkaline environment (Onu *et al.* 2022). In aqueous solution, it ionizes to produce a mono-anionic form that, at a higher pH, can deprotonate to produce the dye's resonance-stabilized blue di-anionic form (Onu *et al.* 2022). When compared with other dye effluents, BCG shows a comparatively higher level of stability. Its difficult aromatic structure makes biodegradation of this substance nearly impossible (Onu *et al.* 2022). As a result, it is extremely toxic to aquatic and terrestrial life even at low doses, which can sometimes result in malignant diseases. Advanced oxidation processes (AOPs) primarily entail producing $\cdot\text{OH}$, a potent and non-selective oxidant (Khan *et al.* 2023a) that can be created alone and by various arrangements of the reagents used in AOPs, such as Fenton's reagents [i.e., H_2O_2 and $\text{Fe}(\text{II,III})$] and combinations of O_3 , TiO_2 , and H_2O_2 with ultraviolet (UV) radiation for destroying a variety of harmful contaminants including BCG dye (Moorjani & Gohil 2021). AOPs can replace the lengthy reaction times (from a few days to minutes) associated with biodegradation technologies; however, powerful AOPs do not produce the same results on imperative degradation, and certain AOPs, particularly Fenton processes, always discharge a certain quantity of sludge, which poses an issue that is worse than the degradation (Weng *et al.* 2023). Due to their distinctive properties, sulphate radical-based AOPs (SR-AOPs) are currently receiving an enormous amount of attention (Zhao *et al.* 2022). A strong oxidant with a higher oxidation potential (2.5–3.1 V), the sulphate radical ($\text{SO}_4^{\cdot-}$) is produced when the peroxy-bond of either one of persulfate (PS) or peroxymonosulfate (PMS) breaks during the activation of the aforementioned compounds (Lin *et al.* 2022; Sayed *et al.* 2022; Khan *et al.* 2023b). Due to the tendency to interact with organics upon electron transfer, sulphate radical has a half-life that is greater than the hydroxyl radical (30–40 s versus 20 ns), whereas the latter operates non-selectively and prefers to

participate in all reactions equally (Ghanbari & Moradi 2017). To produce a sulphate radical, PMS must be broken down with the assistance of an activator. These are the primary classes under which PMS activators are divided: UV, heat, ultrasonic (US) (Wang *et al.* 2023), transitional metals, carbon catalyst, and electron conduction (Wang *et al.* 2021; Bethi *et al.* 2023; Honarmandrad *et al.* 2023). The transitional metals have been heavily used to activate the oxidant and create free radicals that will cause organic compounds to degrade (Wang *et al.* 2021). Because of certain limitations of heterogeneous photocatalysis, such as slow reaction kinetics and incomplete solubility, the focus on homogeneous photocatalysis has increased. Since both the target pollutant and the homogeneous catalyst are in the same phase, high catalytic activity can be attained here. On the photocatalytic decomposition of BCG employing UV/PMS/cobalt photocatalyst homogeneously, limited research has been done. To the best of our knowledge, no studies have been done to assess the UV/PMS/cobalt combined ability to degrade BCG dye or to measure its activity in doing so. Here, the chemical oxidizing agents used in homogeneous catalysis frequently including UV/PMS in conjunction with Co^{2+} will produce the reactive species sulphate and hydroxyl radicals. The aim of our presented investigation is to assess the viability of the decolorization and degradation of BCG using the Co^{2+} /PMS oxidative procedure with an incredibly less amount of Co^{2+} and PMS. In this, a different oxidation dynamics approach of substitution was undertaken using Co^{2+} /PMS in response to the aforementioned issues. In the current investigation, PMS was first activated through UV, then further through cobalt ions, and it was then used to decolorize BCG.

In the present work, UV/PMS/ Co^{2+} advanced oxidation technology based on $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ is proposed to degrade BCG dye in aqueous media. This study investigated the effects of various parameters on dye removal, including irradiation time, PMS dosage, catalyst dosage, and pH study and aimed to find out reactive radicals. The primary goal of the current work is to use an effective technique for the degradation of BCG from aqueous medium using the Co^{2+} /PMS process. Furthermore, the process's effectiveness needs to be increased, optimizations of oxidant and cobalt were carried out. Besides, the effectiveness of the process was examined through pH of the aqueous media and a different water system. Scavenger experiments were carried out to determine the main reactive species that was involved in the degradation process.

2. MATERIALS AND METHODS

2.1. Chemicals

During experimental work, analytical grade chemicals were used. BCG ($\text{C}_{21}\text{H}_{14}\text{Br}_4\text{O}_5\text{S}$) was bought from BDH Chemicals Ltd. Oxone ($\text{KHSO}_5 \cdot 0.5\text{KHSO}_4 \cdot 0.5\text{K}_2\text{SO}_4$), which is the source of the oxidant PMS (HSO_5^-), was acquired from sigma Aldrich. Sodium hydroxide and hydrochloric acid (HCl 37%) were provided by Scharlau. Ethanol ($\text{C}_2\text{H}_5\text{OH}$ 99.8%), methanol (CH_3OH 99.85%) n-hexane C_6H_{14} , and ter-butanol ($\text{C}_4\text{H}_{10}\text{O}$) were supplied by Scharlau. For the purpose of creating the working solution, ultra-pure water with a resistivity of 18.2 M Ω cm was collected from the deionized water.

2.2. Instrumentation

Model GDX-SVISPL Spectro Vis plus spectrophotometer with 1 cm quartz cuvettes were used to determine the peak wavelength to collect data for the solution of the BCG dye. For photocatalytic degradation, UV-254 lamp was used as a source of radiation for the activation of the oxidant and catalyst for mineralization of BCG. The degradation by-products (DP) of BCG were examined by gas chromatography–mass spectrometry (GC–MS), using QP.2010 plus, Shimadzu, Japan, with DB-5MS column (30 m 0.25 mm, 0.25 m). The operating conditions of GC–MS were set as reported in our earlier research work (Khan *et al.* 2023b).

2.3. Collection of water samples

To examine the efficiency of the UV/PMS/ Co^{2+} in industrial wastewater (IWW), samples were collected from the Janana Da Malucho Textile Mill Ltd, Kohat district, Kohat, Pakistan.

2.4. Ecotoxicity assessment

The toxicity assessment of BCG and its DPs was performed by a computational program, Ecological Structure Activity Relationship (ECOSAR) (Gohar *et al.* 2023). The detailed procedure is reported elsewhere (Gohar *et al.* 2023).

3. RESULTS AND DISCUSSION

3.1. Photolysis of BCG

To examine the stability of BCG under UV light, photolysis of BCG was performed. Despite the fact that UV light has the ability to significantly degrade most of the organic molecules, in this study only 13% degradation of BCG was achieved in 30 min with the k_{app} value of 0.0053 min^{-1} as shown in Figure 1 and Figure 1 inset, respectively. BCG exhibits a comparatively strong level of stability as compared with other dyes. Due to its complex aromatic structure, this chemical is essentially incapable of degrading (Onu *et al.* 2022). It was also reported that BCG dye decolorizes very slowly as compared with the other dyes in the presence of UV-C (Kanchana & Vijayalakshmi 2020). This could be due to the presence of the sulphonate group as well as the bromo ring substitution in the structure of BCG dye molecule, which needs a longer time for degradation under UV-C light. Therefore, it has been found difficult to significantly degrade BCG dye by direct UV photolysis. Hence, PMS (oxidant) and Co^{2+} , as catalyst, were introduced into the system to boost the degradation of BCG dye.

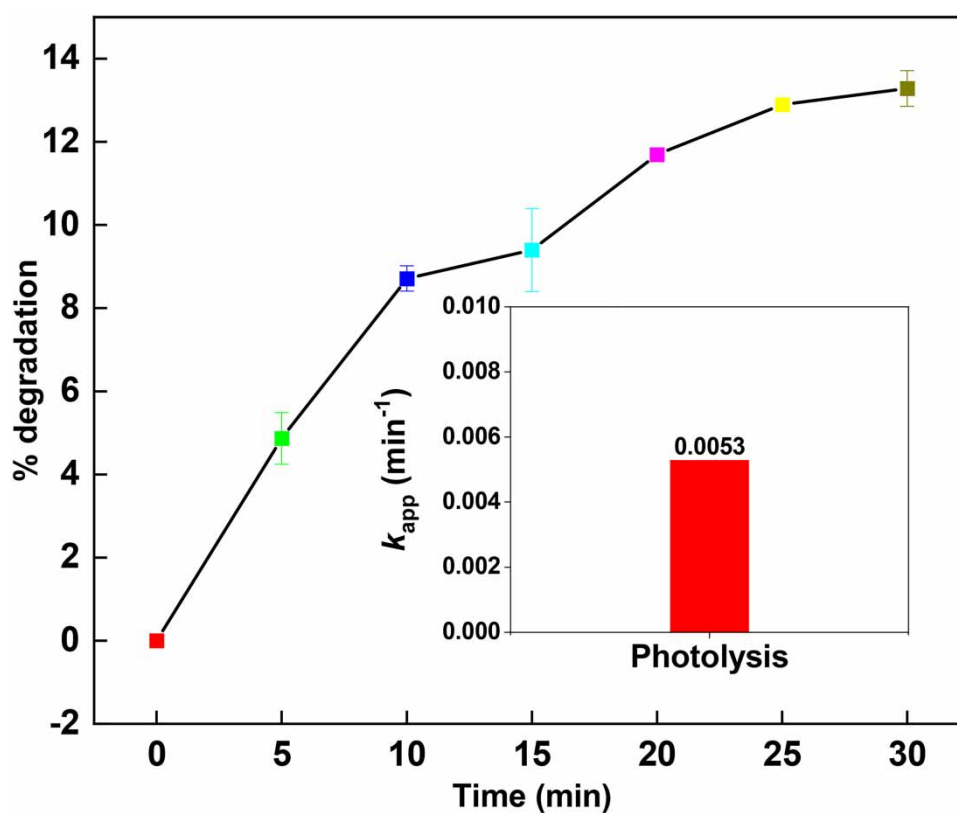


Figure 1 | Photolytic degradation of BCG under UV light: experimental conditions [BCG] = 0.12 mM, radiation source = UV lamp (15 W), radiation time = 30 min.

3.2. Effects of operating parameters on the photocatalytic degradation of BCG by UV/PMS/ Co^{2+} process

3.2.1. Effect of PMS on the photocatalytic degradation of BCG

Although PMS is a powerful oxidant thermodynamically, its direct reactivity with the bulk of contaminants is too slow, demanding activation (Ghanbari & Moradi 2017). Moreover, by generating protons, PMS can also change the pH of a solution. After activation of PMS, $\text{SO}_4^{\bullet-}$ is produced and plays a prominent role in the degradation of the contaminants (Ghanbari & Moradi 2017). So, to enhance the photocatalytic degradation of BCG, it was inevitable to introduce some reactive species. For this purpose, $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ were introduced in the system through PMS addition. The influence of PMS (0.1–0.9 mM) on the photocatalytic degradation of BCG under UV irradiation is shown in Figure 2. The results revealed that increasing the amount of PMS caused an increase in BCG degradation because of high concentration of $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ production. The resultant $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$, which are powerful oxidants, immediately attack and degrade the target pollutant into DPs. It is clear that at

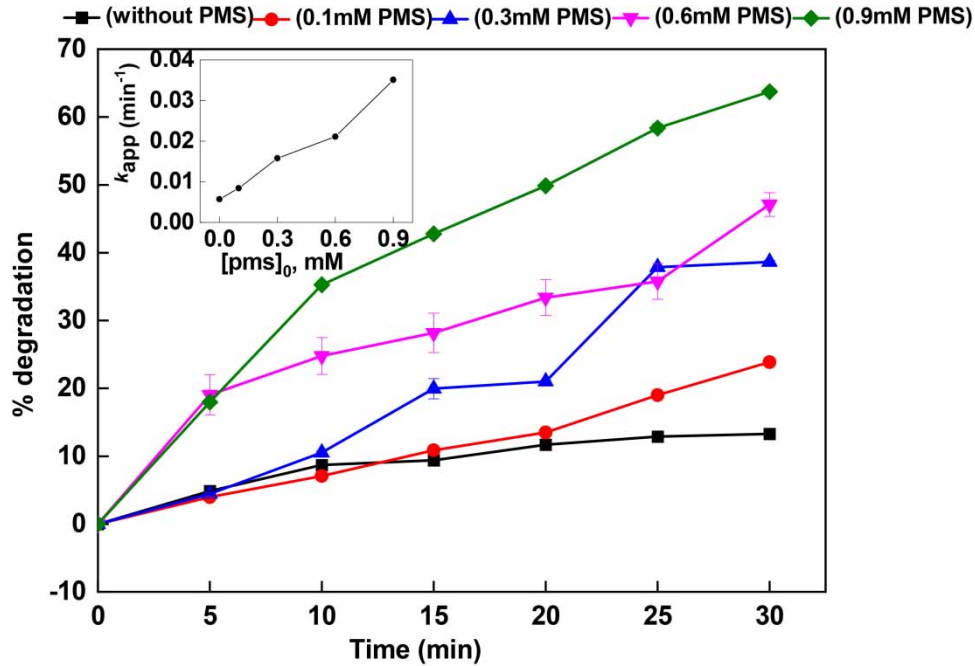


Figure 2 | Effect of PMS dosage under UV light radiation. Experimental conditions BCG = 0.12 mM, radiation source = UV lamp (15 W), radiation time = 30 min at different concentrations of PMS = 0.1, 0.3, 0.6, and 0.9 mM.

reaction time of 30 min, the degradation was raised from 13% (no PMS) to 23% (0.1 mM PMS), 38% (0.3 mM PMS), 47% (0.6 mM PMS), and 63% (0.9 mM PMS) (Figure 2). The corresponding k_{app} values for 0.0, 0.1, 0.3, 0.6, and 0.9 mM PMS were 0.005, 0.006, 0.012, 0.022, and 0.0297 min^{-1} , respectively (Figure 2, inset). In the case of PMS photo activation, using UV wavelength of 254 nm of electromagnetic emission gives sufficient energy for the splitting of the peroxy-bond in the PMS structure, and caused the formation of $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$, which then attacked the target contaminants, thus causing its degradation (Equations (1)–(3)) (Ghanbari & Moradi 2017).



Similarly, Sharma *et al.* (2015) examined UV-C/PMS oxidative degradation of bisphenol A (BPA) in aqueous media. In their study, using 0.66 mM PMS resulted in a BPA removal effectiveness of 96.7%. Their findings also showed that increased PMS concentration caused BPA degradation to rise due to high concentrations of $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ generation.

Moreover, in the present study, the $[\text{oxidant}]_0/[\text{pollutant}]_0$ ratio was 0, 2.5, 5, and 7.5. The aforementioned discussions and results indicate that the higher the $[\text{oxidant}]_0/[\text{pollutant}]_0$ ratio, the stronger the degradation performance of UV/PMS process towards BCG in the aquatic system.

3.2.2. Effect of Co^{2+} ions on the photocatalytic degradation of BCG

Numerous studies have been conducted on the divalent cobalt ion (Co^{2+}) as a Fenton-like catalyst for the oxidation of organic contaminants. Using the redox couple $\text{Co}^{2+}/\text{Co}^{3+}$ [$E^0(\text{Co}^{3+}/\text{Co}^{2+}) = +1.92 \text{ V}$] (Penas-Garzon *et al.* 2021), most research has been centred on the activation of PS ($\text{S}_2\text{O}_8^{2-}$) or PMS (HSO_5^-) to produce sulphate and hydroxyl radicals (Equations (4) and (5)) (Zhou *et al.* 2022; Gu *et al.* 2023).



According to Anipsitakis and Dionysiou (2004), the Co^{2+} ion demonstrated the best catalytic activity for PMS activation among numerous transition metal ions, including, Cu^{2+} , Fe^{2+} , Mn^{2+} , Ce^{2+} , and Ni^{2+} . The increased catalytic activity of Co^{2+} may be attributed to its higher standard of reduction potential ($E^0 = 1.92 \text{ V}$) compared with $\text{Fe}^{3+}/\text{Fe}^{2+}$ ($E^0 = 0.77 \text{ V}$), $\text{Ce}^{4+}/\text{Ce}^{3+}$ ($E^0 = 1.72 \text{ V}$), $\text{Mn}^{3+}/\text{Mn}^{2+}$ ($E^0 = 1.54 \text{ V}$), $\text{Cu}^{2+}/\text{Cu}^+$ ($E^0 = 0.153 \text{ V}$), and $\text{V}^{4+}/\text{V}^{3+}$ ($E^0 = 0.34 \text{ V}$) (Ghanbari & Moradi 2017). Furthermore, the high catalytic activity of Co^{2+} could be related to the electronic configuration of Co^{2+} and the interaction between Co^{2+} and PMS. Ji *et al.* (2015) studied the cobalt-catalysed peroxymonosulfate (Co(II)/PMS) routes of atrazine (ATZ) decomposition. In their study, for the removal of ATZ in aqueous solution, Co(II)/PMS was shown to be more effective than Fe(II)/PMS. Similarly, the emphasis of our investigation was the activation of PMS by cobalt ions.

The influences of varying concentrations of Co^{2+} (0.00017, 0.00102, and 0.00153 mM) on the photocatalytic degradation of BCG were investigated while keeping the dye concentration at 0.12 mM and the PMS concentration at 0.9 mM constant. Figure 3 shows that the percentage of degradation of BCG increased from 63% to 65, 85, and 98% with the corresponding increase in Co^{2+} concentration from 0 mM to 0.00017, 0.00102, and 0.00153 mM, respectively. Figure 3 inset indicates the k_{app} values increased from 0.0297 min^{-1} to 0.0393, 0.0657, and 0.0931 min^{-1} , with the corresponding increase in Co^{2+} concentration from 0 mM to 0.00017, 0.00102, and 0.00153 mM, respectively. As mentioned previously (Equations (6)–(9)), the oxidation of Co^{2+} can activate HSO_5^- , resulting in $\text{SO}_4^{\bullet-}$ and Co^{3+} , which can then be regenerated via Equation (7). Because of the $\text{Co}^{2+}/\text{Co}^{3+}$ cycle, HSO_5^- might be continually activated in the $\text{Co}^{2+}/\text{PMS}$ system (Chen *et al.* 2019). The experimental results revealed that the Co(II)/PMS combination was more effective for BCG. Co(II) is thought to act as a catalyst during PMS activation (Equations (7)–(9)), and Co(II) regeneration is thought to occur via reduction (Equations (8) and (9)) (Huang *et al.* 2009).

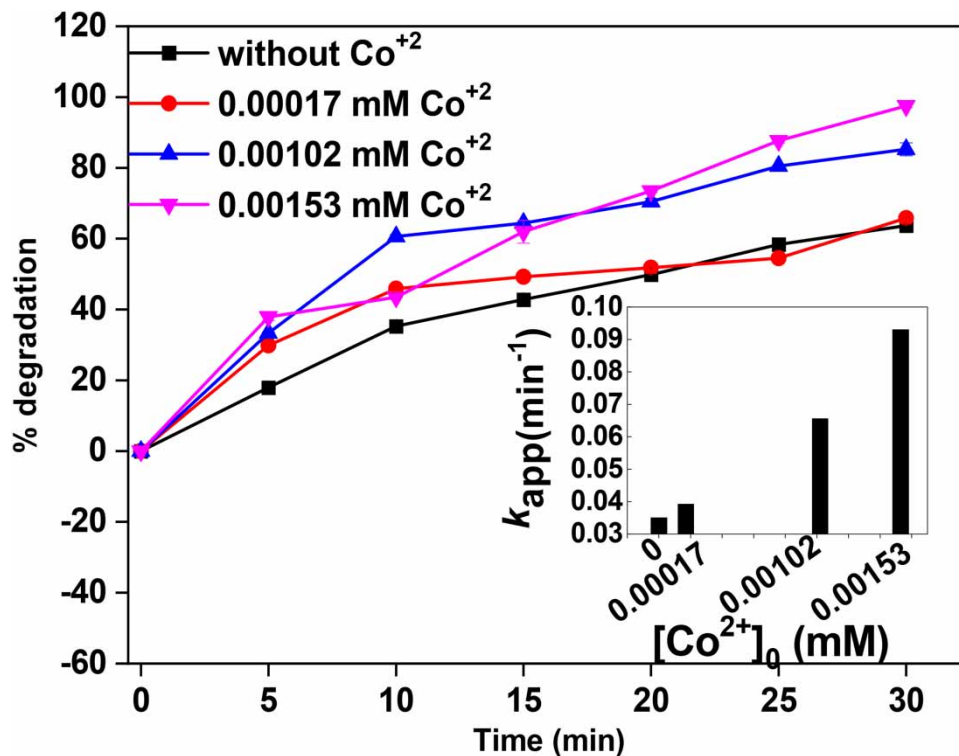


Figure 3 | Photocatalytic degradation of BCG under UV light radiation. Experimental conditions BCG = 0.12 mM, PMS = 0.9 mM, irradiation time = 30 min, and radiation source = UV lamp (15 W).

The synergy factor of UV/PMS Co^{2+} was 3.13 times UV/PMS and 17.56 times the UV process.

3.2.3. Effect of pH on the degradation of BCG

The importance of pH in photocatalytic processes cannot be overstated. So, to investigate the influence of pH on BCG degradation, various pH tests were carried out. NaOH and HClO_4 were used to modify the pH of the solutions. The effects of various acidic, basic, and neutral media on the photocatalytic degradation of BCG by UV/PMS/ Co^{2+} are shown in Figure 4. UV/PMS/ Co^{2+} degraded nearly 78 and 98% of BCG at pH 3.48 and 5.0, respectively (Chaleshtori *et al.* 2013). However, at pH = 7 and 8, the percentage of degradation of BCG was significantly reduced to 53 and 44%, respectively. The decrease in degradation of BCG at pH 7 and 8 is likely caused by the lower reactivity of Co^{2+} hydroxo complex during higher pH reactions with PMS radicals and is therefore likely to have a negative impact. Comparable results were also shown by Huang *et al.* (2009). In their study, the degradation of reactive black B increased significantly as the solution pH increased from 3.5 to 5, whereas it decreased significantly as the pH of the solution increased from 6 to 8.4. Moreover, it also provides evidence that $\text{SO}_4^{\bullet-}$ is stable at acidic conditions ($\text{pH} \leq 5.0$) and therefore plays a prominent role in the degradation of BCG.

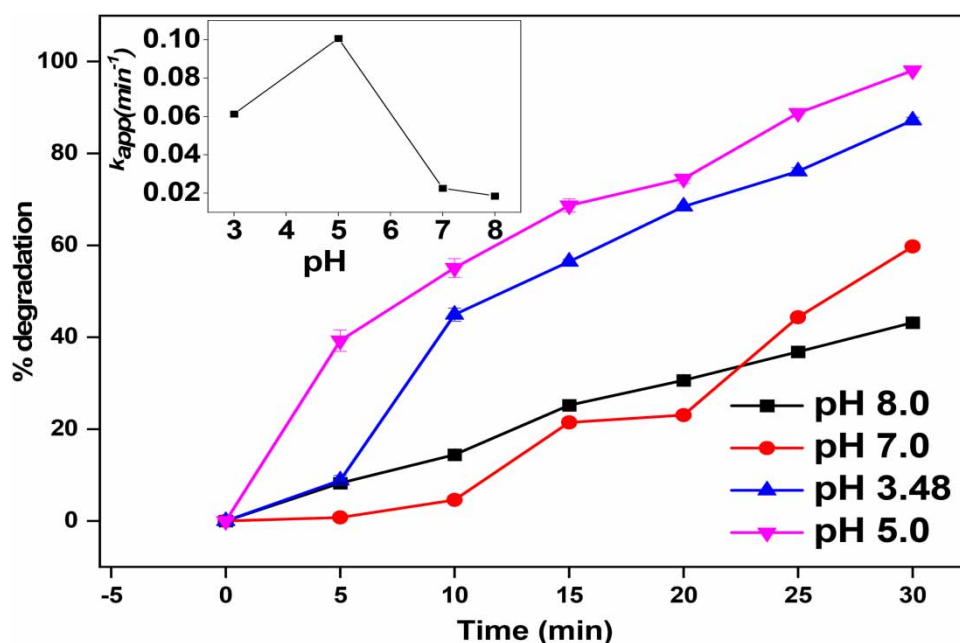
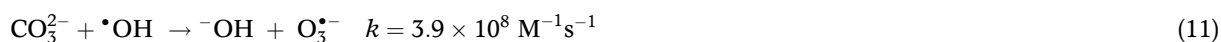
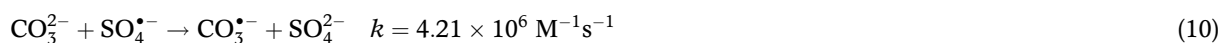


Figure 4 | Photocatalytic degradation of BCG under UV light radiation. Experimental conditions BCG = 0.12 mM, PMS = 0.9 mM, Co^{2+} = 0.0153 mM, irradiation time = 30 min, radiation source = UV lamp (15 W) at various pH.

3.3. Photocatalytic degradation of BCG in various water systems

The photocatalytic degradation of BCG was also carried out in tap water (TW), IWW, and distilled water (DW). Figure 5 demonstrates the photocatalytic degradation of BCG in various water systems using Co^{2+} -aided PMS. The removal efficiency of the UV/PMS/ Co^{2+} system for degradation of BCG was in the order of $\text{DW} > \text{TW} > \text{IWW}$ and the corresponding k_{app} values of 0.931 (DW), 0.352 (TW), and 0.0152 (IWW) min^{-1} (Figure 5; Inset). In the case of TW, the presence of modest quantities of dissolved carbonate (CO_3^{2-}), sulphate SO_4^{2-} , and chloride (Cl^-) ions, which act as scavengers for $\cdot\text{OH}$ and $\text{SO}_4^{\bullet-}$, causes the lowering in degradation of BCG (Equations (10)–(15)) (Bibi *et al.* 2022). Carbonate ions, however on reaction with $\text{SO}_4^{\bullet-}$ also result in the formation of $\text{CO}_3^{\bullet-}$, which can show reactivity towards certain pollutants depending on their structure and functionality (Rayaroth *et al.* 2023). When compared with TW, the inclusion of a significant amount of NaCl in IWW produces a significant decrease in percent degradation of BCG in aqueous media.



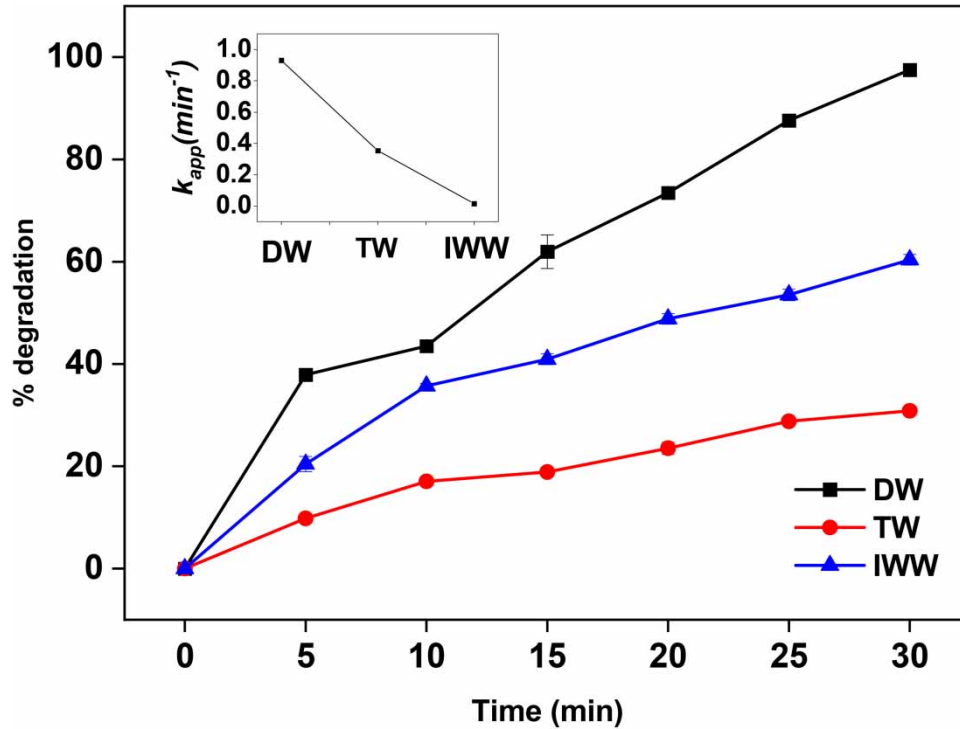
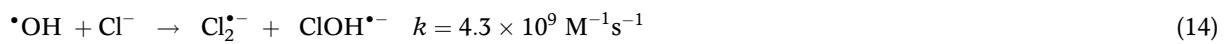
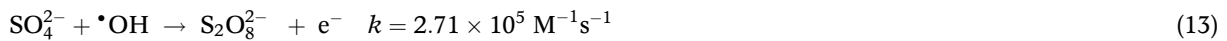
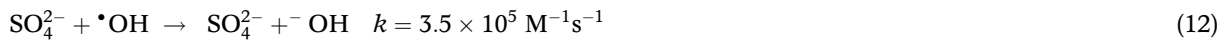


Figure 5 | Photocatalytic degradation of BCG under UV light radiation. Experimental conditions BCG = 0.12 mM, PMS = 0.9 mM, Co^{2+} = 0.0153 mM, irradiation time = 30 min, radiation source = UV lamp (15 W) in various water systems.



3.4. Identification of reactive species

When PMS is activated, the chemical reaction produces $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. Peroxymonosulfate radical ($\text{SO}_5^{\cdot-}$) is also formed, but its activity is minor in comparison with that of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. Different radical scavengers were used in quenching studies to investigate the principal reactive species. According to the literature, ethanol (EtOH) is a strong scavenger for both $\cdot\text{OH}$ ($k = 1.2 - 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) and $\text{SO}_4^{\cdot-}$ ($k = 1.6 - 7.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$), whereas tert-butanol (TBA) is a good scavenger for $\cdot\text{OH}$ ($k = 3.8 - 7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) but not for $\text{SO}_4^{\cdot-}$ ($k = 4.0 - 9.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) (Khan *et al.* 2020). It can be seen from Figure 6 that in the absence of any scavengers, 98% degradation was obtained with k_{app} value of 0.027 min^{-1} at a reaction time of 30 min. However, in the presence of 0.5 mM TBA and 0.5 mM EtOH, the percentage of degradation of BCG was reduced to 61% ($k_{\text{app}} = 0.017 \text{ min}^{-1}$) and 26% ($k_{\text{app}} = 0.0090 \text{ min}^{-1}$), respectively (Figure 6; Inset). Thus, it can be concluded that in addition to $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ also plays a prominent role in the photocatalytic degradation of BCG by the UV/PMS/ Co^{2+} process.

4. ANALYSING THE BY-PRODUCTS OF BCG'S DEGRADATION, ITS ROUTES, AND ITS ECOTOXICITY

4.1. BCG by-products and potential degradation pathways

The GC-MS analysis reported the formation of five DPs for BCG using the UV/PMS/ Co^{2+} system. Figure 7 indicates the possible degradation pathways for BCG contaminant. The degradation of this dye by the attack of $\cdot\text{OH}$ and/or $\text{SO}_4^{\cdot-}$ is mainly due to substitution, hydrogen abstraction, and electron transfer, in addition to unsaturated bond and elimination reactions. It has been well reported in the literature that $\text{SO}_4^{\cdot-}$ normally attacks through electron transfer reactions and $\cdot\text{OH}$ frequently attacks through hydrogen abstraction and addition reactions.

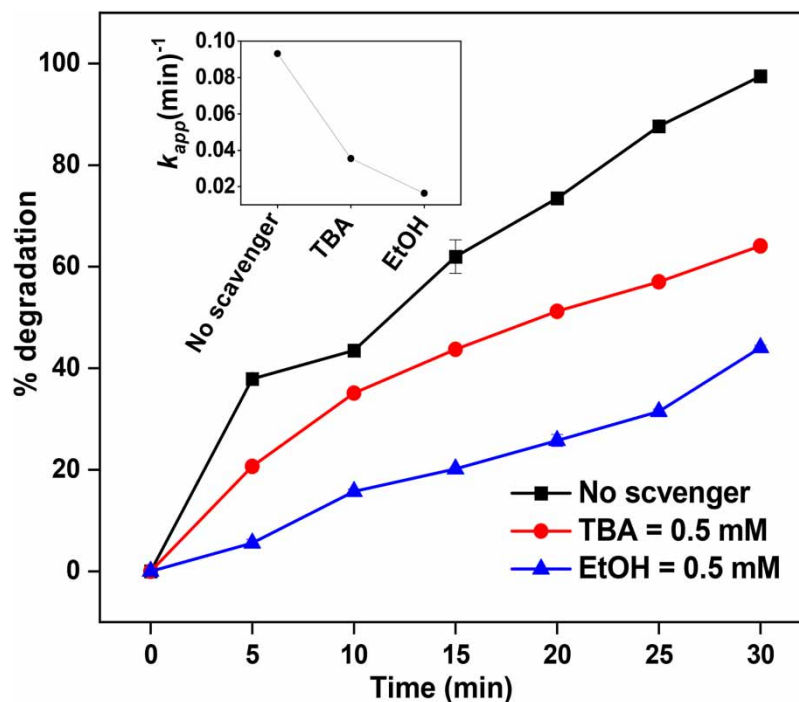


Figure 6 | Effect of different scavengers under UV light radiations. Experimental conditions. BCG = 0.12 mM, PMS = 0.9 mM, Co^{2+} = 0.153 mM, EtOH = 0.5 mM, TBA = 0.5 mM, irradiation time = 30 min, radiation source = UV lamp (15 W).

To make the degradation mechanism clearer, it is divided into two different paths, i.e., path-I and path-II depending on the structure of the by-products and nature of its atoms. It can be seen from the path-I that the BCG molecule could be degraded into DP1 ($m/z = 184.09$) via elimination and subsequent addition reactions of BCG by $\cdot\text{OH}$ and/or $\text{SO}_4^{\cdot-}$. The DP1 is then converted to DP2 by elimination and/or substitution reactions of DP1 by $\cdot\text{OH}$ and/or $\text{SO}_4^{\cdot-}$. The DPs presented in parenthesis (DP3 and DP4) were not observed during GC/MS analysis and can be formed by elimination reactions followed by re-arrangement of DP2.

4.2. Ecotoxicity assessment of BCG and its degradation by-products

The toxicity of BCG and the DPs formed during its degradation were analysed by using computational investigation through ECOSAR towards the aquatic organisms. The analysis is based on the measurement recommended by the European Union and the Chinese hazard evaluation for the emergence of new chemical species (Gul *et al.* 2020). The toxic nature, e.g., harmless, harmful, toxic, or very toxic of BCG and its DPs, towards different aquatic organisms is revealed in Table 1. It could be seen from the table that BCG is very toxic towards all the organisms. Thus, its removal from the aquatic media is of vital importance. Likewise, DP1 also shows toxic behaviour towards all the organisms, but its toxicity values suggest that it is less toxic than the parent BCG molecule. Moreover, DPs such as DP2, DP3, and DP4 display least or no toxicity levels towards the different aquatic organisms compared with the parent BCG contaminant. Most importantly, DP4 shows no acute toxicity towards daphnia and also no chronic toxicities were observed towards algae and daphnia. Hence, it could be suggested from the toxicity evaluation that further study is needed for the applied treatment technique that might turn the degradation path towards harmless DP4 formation. Although, it can be concluded from the values of different toxicities of all the DPs that these are less/not toxic than the BCG molecule, which confirms the success of this degradation study.

5. ENVIRONMENTAL IMPLICATION

The activation of PMS by green and environmentally friendly methods has gained increasing attention worldwide. In this work, UV/ Co^{2+} has been applied as an activator for PMS. The UV/PMS/ Co^{2+} at ambient temperature can effectively degrade BCG and lead to less toxic/no toxic degradation by-products. Furthermore, the proposed technology was equally efficient in all types of water systems (DW, TW, IWW). This confirms the practical application of the proposed technology.

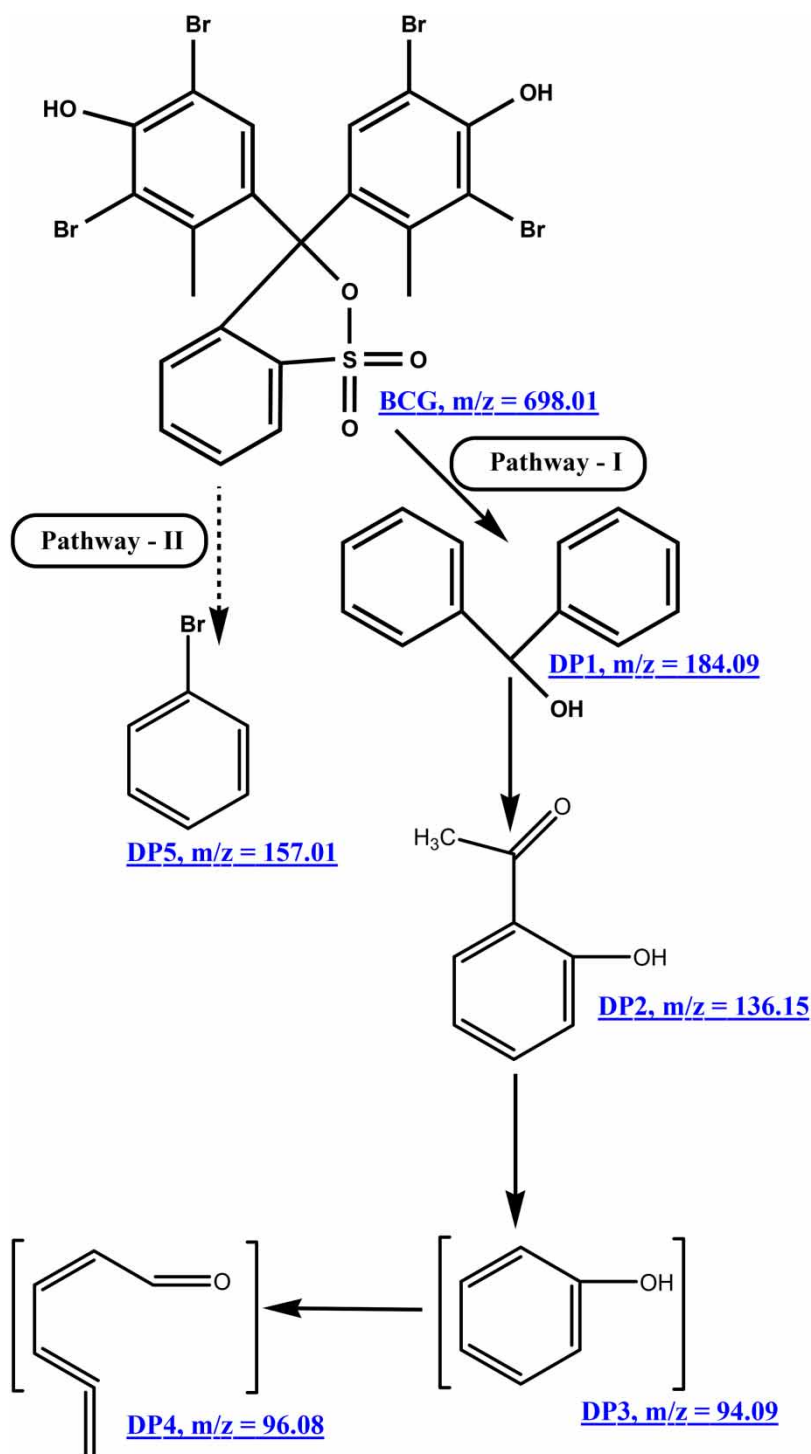


Figure 7 | Possible degradation pathways of BCG using the UV/PMS/Co²⁺ system.

6. CONCLUSIONS

Textile wastewater loaded with a dye contaminates water resources and raises hazardous toxic levels in the environment. These effluents cause acute toxicity to the water body, which directly or indirectly enter the food chain. Dye effluents in wastewater must be treated using effective dye removal procedures before being discharged into the environment. It was proven that AOPs can be utilized as an efficient method for the degradation of dye-containing wastewater because they make it possible to combine UV irradiation, catalysts, and oxidants to form hydroxyl radicals ($\cdot\text{OH}$) and $\text{SO}_4^{\cdot-}$ radicals in solutions. It has been confirmed that AOPs are a very competitive technology for treating water and eliminating organic contaminants, particularly

Table 1 | Eco-toxicity evaluation of BCG and its DPs towards aquatic organisms (measured in mg L⁻¹)

compound	Acute toxicity			Chronic toxicity			
	Organism			Organism			
	m/z	Fish (LC ₅₀) Duration 96 h	Daphnia (LC ₅₀) Duration 48 h	Green Algae (EC ₅₀) Duration 96 h	Fish (ChV)	Daphnia (ChV)	Green Algae (ChV)
BCG	698	0.035	0.039	0.006	0.0007	0.005	0.011
DP1	184.09	13.2	11.1	6.37	1.36	2.21	3.89
DP2	136.15	19.4	8.31	1.71	1.92	0.905	3.60
DP3	94.09	27.7	9.64	2.40	2.61	0.969	4.53
DP4	96.08	0.264	1.13E+4	2.22E+3	0.041	440	127
DP5	157.01	20.8	12.8	13.4	2.24	1.57	4.19

The acute toxicities according to the European Union criteria: toxic (violet), very toxic (red), harmful (yellow), and not harmful (green) (specified in Annex VI of Directive 67/548/EEC). While the Chinese hazard evaluation standards for new chemical substances (HJ/T154-2004) are used to evaluate chronic toxicities.

dyes. Water containing dyes can be effectively treated using a variety of AOPs, including photocatalysis, photolysis, UV/H₂O₂, UV/O₃, photo-Fenton, Fenton-like sonolysis, electrochemical oxidation, and ozonation. The present use of photolysis and the Fenton-like process, which are among the efficient AOPs, for the degradation of wastewater containing dye was comprehensively examined in this research. The research proved that using UV light and a Fenton-like process (UV/PMS/Co²⁺) has the ability to completely degrade BCG dye in wastewater. This was made possible by the simultaneous occurrence of oxidation and reduction events. The photocatalytic degradation of the BCG was found to be influenced by pH, the dye initial concentration, catalyst loading, and so on. It is particularly efficient to use a low concentration of materials, which successfully leads to the destruction of BCG dye. The significant future element is scaling up an energy-efficient, economical, and sustainable method for the total mineralization of BCG dye from water using hybrid AOPs. With increasing population, scarcity of water pushes the whole world to use wastewater. So, this approach opened and analysed novel and socioeconomic aspects to degraded BCG dye by up to 97% within 30 min. The synergistic effect of PMS with cobalt ion and UV worked swiftly and in an environmentally friendly and cost-effective manner. This research offered fresh perspectives on the quick and secure decomposition of organic contaminants in wastewaters. Comprehensive analysis of the latest developments in several homogenous AOPs has been accomplished. The effectiveness of individual and merged AOPs in degrading different contaminants was discussed. We investigated the effects of different experimental factors on the AOPs, including oxidant amount, flow rates, solution pH, substrate concentrations, light intensity, and water matrix. Under the right circumstances, combined AOPs significantly increased the rate at which they degraded by producing more reactive radicals. For effective elimination, an ideal solution and oxidant dosage were reported.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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