Review on Methylene Blue: Its Properties, Uses, Toxicity and Photodegradation

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Abstract: The unavailability of clean drinking water is one of the significant health issues in modern times. Industrial dyes are one of the dominant chemicals that make water unfit for drinking. Among these dyes, methylene blue (MB) is toxic, carcinogenic, and non-biodegradable and can cause a severe threat to human health and environmental safety. It is usually released in natural water sources, which becomes a health threat to human beings and living organisms. Hence, there is a need to develop an environmentally friendly, efficient technology for removing MB from wastewater. Photodegradation is an advanced oxidation process widely used for MB removal. It has the advantages of complete mineralization of dye into simple and nontoxic species with the potential to decrease the processing cost. This review provides a tutorial basis for the readers working in the dye degradation research area. We not only covered the basic principles of the process but also provided a wide range of previously published work on advanced photocatalytic systems (single-component and multi-component photocatalysts). Our study has focused on critical parameters that can affect the photodegradation rate of MB, such as photocatalyst type and loading, irradiation reaction time, pH of reaction media, initial concentration of dye, radical scavengers and oxidising agents. The photodegradation mechanism, reaction pathways, intermediate products, and final products of MB are also summarized. An overview of the future perspectives to utilize MB at an industrial scale is also provided. This paper identifies strategies for the development of effective MB photodegradation systems.

Keywords: methylene blue (MB); photodegradation; toxicity; degradation parameter; mechanism; degradation products

1. Introduction

Dyes are the coloured aromatic organic compounds that absorb light and impart color to the visible region [1,2]. More than 100,000 commercial dyes have been reported worldwide, amounting to approximately $7 \times 10^8$–$1 \times 10^9$ kg/year [3]. William Henry Perkin discovered the first synthetic dye in 1856, naming it Mauveine (an organic aniline dye) [4]. Dyes are applied to the substrates to give them permanent colour, which can resist
fading upon exposure to water, light, oxidizing agents, sweat, and microbial attack [5]. Due to these advantages, various dyes are used in different industries such as textiles, food, rubber, printing, cosmetics, medicine, plastic, concrete, and the paper industry for multiple purposes [6–8]. These industries generate a tremendous amount of wastewater containing carcinogenic and toxic dyes that pollute water, which becomes unfit for human consumption [9]. Among these industries, the textile industry is the most dye-consuming industry utilizing textile dyes, which are highly complex compounds with different structural groups [10]. One of the highest-consuming materials in the dye industry is methylene blue (MB), which is commonly used for colouring silk, wool, cotton, and paper [11–13]. The Scopus database indicates that MB is widely utilized for various applications. The number of articles on MB dye degradation has been continuously increasing since 2010–2020, as shown in Figure 1.

Figure 1. Annual article frequency as indicated by the Scopus database at date 12 January 2022 (Searched with a keyword ‘methylene blue dye degradation’).

Certain literature reviews are reported on the removal of MB via adsorption [14–16] and bioremediation [17]. However, minimal reviews are available on photodegradation of MB, which only describes fundamentals and photocatalysis of MB dye employing various nanocatalytic assemblies [18]. In this review, we discuss the properties, applications, toxicity, and available use methods for the removal of MB, with limitations. Moreover, photodegradation of MB and its advantages, factors affecting parameters, and photodegradation and intermediate products will be reviewed in detail.

MB is an aromatic heterocyclic basic dye [19] having a molecular weight of 319.85 g mol$^{-1}$ [20,21]. MB is a well-known cationic and primary thiazine dye with a molecular formula $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}$, having $\lambda_{\text{max}}$ of 663 nm. It is highly water-soluble, and thus forms a stable solution with water at room temperature [22–25]. MB comes under the class of polymethine dye with an amino autochrome unit and is a positively charged compound [26]. Its chemical name, according to the International Union of Pure and Applied Chemistry (IUPAC), is [3,7-bis(dimethylamino) phenothiazine chloride tetra methylthionine chloride] with colour index (CI) 52015 [27,28]. The model and the structure of the MB molecule are shown in Figure 2 [29], while its different resonance structures are given in Figure 3 [30]. MB is a redox indicator and not a pH indicator [31]. MB was first synthesized by Heinrich Caro in 1800 [32].
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Photodegradation is an advanced and economical technology which utilises solar energy and employs a catalyst (mostly photoactive materials of nano-level size). Various nanomaterials have been reported for this purpose, including ZnS [33], TiO$_2$ [34,35], ZnO [36], hematite [37–39], plasmonic metals (such as gold, silver, platinum) [40,41], Ag$_2$S@TiO$_2$ nanofibers [42] metal vanadates (those of Bi, Ni, Cu, Zn etc.) [43–47], carbon-based catalysts such as graphene and its oxides, and carbon nitrides, [48–51], magnetite nanoparticles (NPs) and iron (III) oxide-based catalysts [52,53]. These systems have demonstrated exceptional results. It is expected that understanding the basics of degradation of MB via this technology will shift the researchers’ attention to a more advanced level of such a technology. Limited reviews are reported on removing MB dye via adsorption [14,15]. Still, there is no specific review on photodegradation of MB by single-component and multi-component photocatalytic systems so far, to the best of the authors’ knowledge. This review collectively highlights the single component and multi-component photocatalytic systems as effective and promising technologies for removing MB from industrial wastewater. The influence of operating parameters on the degradation of MB by various photocatalytic systems is also examined. This review is focused to provide guidelines for developing effective photocatalytic systems for MB degradation from wastewater.

Figure 2. The model and the structure of MB dye molecule [29] (Adapted with permission from the Royal. Society of Chemistry (license ID 1079849-1).

Figure 3. Different resonance structures of MB.

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2. Properties of Methylene Blue

MB is a solid, odourless, dark green powder at room temperature and yields a blue solution when dissolved in water [54,55]. MB have molecular diffusivity (Dmol) of 4.7 × 106 (cm$^2$/s) at 25 °C [56]. The length of MB molecule is 13.82 Å or 14.47 Å, and the width is approximately 9.5 Å [57]. MB dye has a pK$_a$ of 3.8 [58,59]. It is soluble in methanol, 2-propanol, water, ethanol, acetone, and ethyl acetate [60]. Its solubility in water is 43.6 g/L at 25 °C [61]. The melting point ($T_m$) of MB is in the range 100–110 °C [62].

MB has a characteristic deep blue colour in the oxidized state and is colourless in the reduced form; leucoMB [63]. The structure of both forms is represented in Figure 4 [64,65]. The colour of MB depends on its chromophoric and auxochrome groups. The chromophore group of MB is the N–S conjugated system on the central aromatic heterocycle, while the auxochrome group is N-containing groups with lone pair electrons on the benzene ring [66]. In photodegradation and adsorption studies, UV-analysis of MB is very important, as almost all calculations are measured from its UV-Visible spectra. The absorption spectra of the MB reveal the most intense absorption peak at around 664 nm associated with an MB monomer, with a shoulder peak at about 612 nm attributed to MB dimer. An additional two bands appear in the ultraviolet region with peaks around 292 and 245 nm (associated with substituted benzene rings) [67]. These absorption peaks gradually decrease as the photodegradation reaction proceeds [68]. Fourier transform infrared spectroscopy (FTIR) also provides important quantitative and qualitative analysis for the studied dyes. This includes identifying the chemical bonds and functional groups in the study sample. Various FTIR peaks of MB and their assignments are summarized in Table 1.

<table>
<thead>
<tr>
<th>FTIR Transmission Wavenumbers (cm$^{-1}$)</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>3410</td>
<td>-NH/-OH overlapped stretching vibration</td>
</tr>
<tr>
<td>2928</td>
<td>symmetrical stretching C-H of –CH$_2$ band</td>
</tr>
<tr>
<td>1600</td>
<td>C=N central ring stretching</td>
</tr>
<tr>
<td>1482</td>
<td>C=C side ring stretching</td>
</tr>
<tr>
<td>1384</td>
<td>multiple ring stretching</td>
</tr>
<tr>
<td>1590</td>
<td>skeleton stretching vibration of the benzene ring</td>
</tr>
<tr>
<td>1486.4 and 1389</td>
<td>C$_{Ar}$–N stretching</td>
</tr>
<tr>
<td>1320</td>
<td>stretching band of C=O, C-N of amide II</td>
</tr>
<tr>
<td>1572</td>
<td>N–CH$_3$ stretching</td>
</tr>
<tr>
<td>1240 and 1182</td>
<td>stretching vibration of C–N in aromatic amines</td>
</tr>
<tr>
<td>1143</td>
<td>symmetrical stretching band of –COOH</td>
</tr>
<tr>
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<td>bending band of N-H and C-N from the amide III</td>
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<td>skeleton vibration mode of C–S–C</td>
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Table 1. FTIR spectra and assignment of MB [69–71].

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Figure 4. Oxidized and reduced forms of MB.

3. Uses and Applications of Methylene Blue

MB is an attractive molecule with various properties useful for biomedical applications and is used as an effective therapeutic agent to treat anaemia, malaria, and Barrett’s oesophagus [72]. MB has primarily been used in human and veterinary medicine for several diagnostic and therapeutic procedures [73].

MB was the first synthetic antimalarial used during the late 19th and the early 20th centuries against all types of malaria and can also act as a chloroquine sensitizer [74,75]. MB dye is being used for the photodynamic treatment of cancer [76]. It is widely used as a photosensitizing agent for photodynamic inactivation of RNA viruses (including HIV, hepatitis B, and hepatitis C viruses) in plasma [77]. Recent studies have suggested that MB has beneficial effects on memory improvement and Alzheimer’s disease. Presently, it is used clinically in a wide range of medications that treat conditions such as methemoglobinemia, urinary tract infections, plaque psoriasis, thyroid surgery, cancer chemotherapy, and ifosfamide-induced encephalopathy [78,79]. MB served as the leading compound for developing tricyclic antidepressants- chlorpromazine [80]. It has also been used to detect neuroendocrine tumours, such as insulinoma [81].

MB dye has many potential applications in the textile, pharmaceutical, paper, dyeing, printing, paint, medicine, and food industries [82–85]. It is the most common dye in the textile industry [86], and is considered one of the most popular clothing colourants [87]. MB firmly adheres in the interstitial spaces of cotton fibres and is fixed firmly on fabric in the...
textile industry [88]. MB is used to estimate rock swelling, which is used as a quick test to assess the quality of foundry sand in foundries [89]. MB dye is also used as a photosensitizer, an oxidation-reduction indicator, an optical redox indicator in analytical chemistry and in the trace analysis of anionic surfactants [90–92]. It is also used as a potential material in dye-sensitized solar cells [93,94], capacitors [95], sensors [96,97], microbial fuel cells [98], etc.

4. Toxicity of Methylene Blue

Textile industries usually release a large amount of MB dyes in natural water sources, which becomes a health threat to human beings and microbes [99]. MB dye is harmful to human health above a certain concentration due to its substantial toxicity [24]. MB is toxic, carcinogenic, and non-biodegradable and can cause a serious threat to human health and destructive effects on the environment [100,101]. MB causes several risks to human health such as respiratory distress, abdominal disorders, blindness, and digestive and mental disorders [15,102]. It also causes nausea, diarrhoea, vomiting, cyanosis, shock, gastritis, jaundice, methemoglobinemia, tissue necrosis, and increased heart rate, causing the death of premature cells in tissues and skin/eye irritations [103–107]. MB contacts with skin may result in skin redness and itching [108]. The no observed adverse effect level (NOAEL) for the MB in rats was observed to be 25 mg kg\(^{-1}\) [109]. Some of the toxic effects of MB on humans and other animals are represented in Figure 5 [110]. MB discharge into the environment is a significant threat for aesthetical and toxicological reasons. It also reduces light penetration and is a toxic supply to food chains for organisms [111]. MB presence in water bodies, even at a very low concentration, makes highly coloured sub-products. Owing to its high molar absorption coefficient (~8.4 \(\times\) \(10^4\) L mol\(^{-1}\) cm\(^{-1}\) at 664 nm), which reduces sunlight transmittance, it decreases oxygen solubility, affects the photosynthetic activity of aquatic life, and decreases the diversity and aesthetics of the biological community [112–115].

![Harmful effects of the MB dye.](image)
5. Methods of Removal of Methylene Blue

Treatment of wastewater containing MB dye before discharging into the environment is of great importance due to its harmful impacts on water quality and perception [116,117]. Various methods are reported to remove MB and other textile dyes from industrial wastewater. These include adsorption/biosorption [118–123], phytoremediation [124,125], coagulation [126,127] electrocoagulation [56,128], vacuum membrane distillation [129], liquid-liquid extraction [130], ultrafiltration [131–133], nanofiltration [134–136], microwave treatment [137], biodegradation [138–140], hybrid systems [141–144] etc. Due to the thermal and light stability and non-biodegradability, it is tough to degrade MB dye into smaller inorganic molecules by employing common methods [145,146]. Each of these treatment methods has its advantages and constraints in terms of cost and feasibility, efficiency, and environmental impact [147]. Advanced oxidation processes (AOPs) were developed to treat toxic organic pollutants such as MB through strong redox processes with specific radicals generated in this process without generating any additional harmful substances [148–150]. AOPs approaches employed for the photodegradation of MB are ozonation [151,152], UV/H2O2 oxidation [153] electrochemical oxidation/degradation [154,155], catalytic oxidation [156], heterogeneous photo-Fenton [157,158], photocatalytic degradation [159,160], etc. The AOPs treatment methods have certain advantages. The main disadvantages of ozonation are the low solubility of ozone in water, elevated energy costs, and the formation of hazardous byproducts [149]. H2O2 has poor UV light absorption characteristics. Thus, this can be considered as wasting most of the light input. In the Fenton process, the production of sludge that contains iron hydroxide as a byproduct is a major drawback [161]. The main drawback of the electrochemical process is the high operating cost due to the high energy consumption [162]. Among these AOPs methods, photocatalytic degradation methods are the most employed ones to remove MB. Few new photocatalytic degradation techniques are hybrid or integrated by sonocatalysis [163], nanofiltration [141], adsorption [164], and biodegradation [165], etc. These integrated methods were found to be more efficient than a single process alone.

6. Photodegradation of Methylene Blue

Over the last few decades, multi-component photocatalysis of organic pollutants using semiconducting NPs has received increased attention because it is a cost-effective, environmentally-friendly, and easy technique for wastewater treatment containing hazardous pollutants [166–168]. The lower cost of catalysts and the utilization of renewable energy in this technology are much more attractive when compared to other techniques [169].

The oxidation of MB to H2O and CO2 through a photocatalyst is an imperative technique to remove the dye from industrial wastewater [170]. Photodegradation is an oxidation process in which the chemical breakdown of complex molecules transforms into simple, nontoxic, and lower molecular weight fragments due to light exposure [171]. This is an emerging and promising technology for waste effluent treatment, having the capability to decolourize and degrade the dye molecules into simple and nontoxic inorganic species such as CO2 and H2O [172]. The process is performed in the presence of photocatalyst, a semiconductor material activated by adsorbing photons, and can accelerate a reaction without being consumed [173].

MB is a representative organic dye and stable under visible light irradiation [174]. Due to its stability, it cannot be degraded efficiently just by photolysis or catalysis alone. It was reported that 7.9% of MB dye was removed through photolysis after 10 h irradiation time [175], and only 10% degradation of MB occurred after 24 h in the presence of a catalyst without light irradiation [176]. It was also observed that negligible decomposition occurred without a catalyst under visible light [177,178]. Similarly, no degradation was observed in the acidic and neutral medium in the dark and under sunlight irradiation without using a catalyst [179]. In the basic medium, photolysis occurs rapidly because of the formation of the hydroxyl ions, which is a key radical for dye degradation. However, raising the temperature has a negligible effect and under argon, atmosphere degradation...
completely stopped [179]. Photodegradation of MB is an efficient approach because MB can also function as a photocatalyst sensitizer [180]. The small/partial degradation observed in MB without catalysts might be attributed to the photosensitized phenomenon of MB molecules observed after irradiation with different light sources [181,182]. MB can absorb light in the region of 500–700 nm, form singlet and triplet species by electronic transition and intersystem crossing, and undergo self-decomposition to a certain extent [183]. Photolysis of MB dye proceeds in the atmospheric air, which means that the O$_2$ is essential for the degradation. In basic media, *OH radicals form through mono-electronic reduction of MB$^+$ radicals by OH$^-$, *OH reacts with each other to produce H$_2$O$_2$, which is an important active species in degradation processes. Similarly, O$_2$ reacts with excited MB$^*$ radicals and forms O$_2$•$^*$. These photolysis reactions of MB are summarized in the following Equations (1)–(3), as follow:

$$\text{MB}^+ + \text{OH}^- \rightarrow \text{MB}^* + \text{OH}^*$$  \hspace{1cm} (1)

$$2\text{OH}^* \rightarrow \text{H}_2\text{O}_2$$ \hspace{1cm} (2)

$$\text{MB}^* + \text{O}_2 \rightarrow \text{MB}^+ + \text{O}_2\cdot^-$$ \hspace{1cm} (3)

All these reactive radical species take part in the direct photolysis of MB dye [179]. Photodegradation of MB dye in % can be calculated from the Equations (4) and (5):

$$\text{Degradation rate (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100$$ \hspace{1cm} (4)

$$\text{Degradation rate (\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100$$ \hspace{1cm} (5)

where, $C_0$ represents the initial concentration of dye, $C$ stands for dye concentration after the reaction, $A_0$ symbolizes initial absorbance, and $A$ shows the absorbance of dye after the reaction [184]. The absorption is often measured at 664 nm, and absorption intensity decreases with increasing irradiation time [185].

7. Mechanism of Photodegradation of Methylene Blue

The photodegradation of MB proceeds via (i) demethylation; (ii) breaking of the MB central aromatic ring and then the side aromatic rings; (iii) conversion of the fragments produced from the first two steps to intermediates species, such as R-NH$_3^+$, phenol, aniline and aldehydic/carboxylate species; and (iv) conversion of these intermediates to the final products, such as CO$_2$, H$_2$O, SO$_4^{2-}$ and NH$_4^+$ [186]. Most of the reaction intermediates come from the breakage of the aromatic ring of the MB dye. The fragments of dyes are degraded into further reaction intermediates, including aldehyde, carboxylic species, phenols, and amines, which are ultimately converted into H$_2$O, CO$_2$, ammonium ions and sulfate ions [18].

Usually, *O$_2$•$^-$ and *OH radicals are responsible for the degradation of MB and have been determined via ESR measurements under full-spectrum irradiation in H$_2$O and methanol. The results clearly displayed signals with intensity ratios of 1:2:2:1 and 1:1:1:1, which are the characteristic ratios for *OH and *O$_2$•$^-$, respectively. The created e$^-$ and h$^+$ are transferred to the photocatalyst surface. The e$^-$ reduces O$_2$ to superoxide radicals (*O$_2$•$^-$) while the h$^+$ either oxidizes H$_2$O to form *OH or directly oxidizes MB dye. These reactive species (*O$_2$•$^-$, *OH and h$^+$) initiate the redox reactions and degrade MB dye into CO$_2$, H$_2$O, or inorganic ions. Thus, the MB dye solution becomes colourless due to the degradation of aromatic rings [187–189]. Such a mechanism of photodegradation of MB dye can be understood from Figure 6, in which MB dye is degraded using ZnO NPs as a single-component photocatalyst [190]. Similarly, Figure 7 has provided an example of a multicomponent system consisting of Fe$_2$O$_3$/graphene/CuO photocatalyst [191].
Figure 6. Proposed photocatalytic mechanism of ZnO-NPs for the catalytic degradation of MB dye [190].

Figure 7. Postulated mechanism for the photocatalytic activity of Fe$_2$O$_3$/graphene/CuO nanocomposite [191]. Adapted with permission from the Elsevier (License Number 5226930035146).

*OH has been normally recognized as the most important active species for ring-opening and complete degradation of MB dye. The *OH attacks the C–S+=C functional group, which is the initial step of MB degradation. To conserve the double bond conjugation...
that was lost through the transformation from C–S+=C to C–S(=O)–C, the central aromatic ring containing both heteroatoms S and N is opened. Hole-induced H⁺ plays a vital role in forming CH and NH bonds [192–194]. Such splitting of a complex molecule into smaller and highly oxidized intermediate molecules is the primary reason for dye degradation [195]. The FTIR spectroscopy studies suggest that •OH radicals attack the side chains of MB during decomposition pathways, which leads to a demethylation process. The colour change in MB contributes to the protonation in the aromatic ring, and it is most likely a reversible reaction process [196]. The VB holes can also directly attack MB dye. They can degrade it [197,198] due to the high oxidation potential of holes [169], which permits direct oxidation of the dye to reactive intermediates followed by degradation [199].

8. Parameters Affecting Methylene Blue Photodegradation

8.1. Effect of Irradiation Time

The irradiation time and adsorption equilibrium between MB and a photocatalyst are the most critical parameters that controlled photodegradation [200]. The percentage of MB degradation is directly related to the irradiation time, which means degradation increases with increasing irradiation time [201,202]. The distinct absorption peak of MB spectra gradually decreases with the increase in reaction time. It shows a colour change from blue to colourless, and the reduction of MB chromophore is probably the reason for the decrease in absorption spectra [203,204]. The photodegradation of MB initially increases gradually by increasing irradiation time and then becomes constant after a particular time [184]. Figure 8 shows the effect of irradiation time on the photodegradation of MB, which displays the absorptive intensity of MB at 664 nm, and it gradually decreases with the reaction time. The decrease in the concentration of MB dye in the photograph indicates that degradation increases with the irradiation time. [205].

Figure 8. UV-Vis analysis of the photocatalytic degradation of MB by cellulose/GO/TiO₂ hydrogel with the reaction time [205]. Adapted with permission from Royal Society of Chemistry (license ID 1079849-2).
8.2. Light Source and Intensity

Light intensity and radiation wavelength both affect the rate of photocatalytic degradation of pollutants [206]. There are various sources of UV light such as black light tubes, fluorescent tubes, Vis white cold light tubes [207], etc., while the sources of visible light are tungsten halogen lamps (QVF135/500 W) [208] or xenon lamps (500 W) [209], etc. The more energy photons interact with the photocatalysts, the more will be the production of charge carriers and, consequently, the degradation rate will increase [18]. Solar and artificial lights have been used for the photocatalytic degradation of dyes. Still, most commonly, artificial light sources are used to maintain stable intensities and avoid clouding and other environmental issues. Graphene decorated titanium dioxide degraded 87% MB dye under UV light and 40% MB dye under visible light [210]. The degradation efficiency of MB is not satisfactory, and there are still limitations in terms of light source and intensity [211]. This shows that light intensity and exposure times have an immense effect on the rate of photodegradation.

8.3. Effect of Initial Dye Concentration

The photodegradation rate of a dye depends on its concentration, nature, and the presence of other existing compounds in the solution [212]. The adsorption capacity of MB dye is high at lower concentrations because of the availability of more active sites on the surface of the photocatalyst [206]. The photodegradation rate of MB increases by increasing initial dye concentration up to a specific limit and then decreases with further increasing dye concentration [213]. The initial increase in the MB dye degradation rate with increasing initial dye concentration might be due to the rise in the reaction probability between the dye molecules and the •OH radical [214]. Using TiO₂ as a photocatalyst, Pandey et al. [215] observed that increasing the MB concentration beyond the limit (3.00 × 10⁻⁶ M) causes retardation of reaction due to the increased collisions between dye molecules and decreased collisions between the dye and the •OH. Arumugam and Choi [45] also observed such results using a BiVO₄ photocatalyst. They explained that dye molecule adsorption on the photocatalyst surface and the rate of hydroxyl radical formation is high at a lower concentration. The slower degradation rate at higher concentrations is because of the intermediate products of the MB degradation, which have lower light absorbance and would compete with MB for reaction with hydroxyl radicals and thus lower MB degradation rates [216]. The higher MB concentration might serve as an inner filter shunting the light photons away from the surface of the photocatalyst, making oxidative free radicals non-available [217]. It is suggested that the lower photodegradation of MB at higher concentration occurs because of the covering of active sites of photocatalysts by higher dye molecules adsorption, which suppresses the generation of active •OH radicals and increases the screening effect of UV light [218].

8.4. The pH Effect

The pH plays a vital role in the characteristics of dyes and the reaction mechanisms, including hydroxyl radical attack, direct oxidation by the h⁺, and immediate reduction by the conducting band e⁻ [219]. The surface charge of the adsorbent (catalyst) also varies with changing the pH value [220]. MB is a cationic dye and will adsorb on a highly negatively charged photocatalyst [221]. The photodegradation of MB could be tuned with the pH of the medium [222]. In a basic medium, the photocatalyst tends to acquire a negative charge that results in increased adsorption of positively charged dyes because of the rising electrostatic attraction [223]. At lower pH (acidic media), H⁺ as the dominant species competes with the cationic MB dye, which decreases the adsorption of the MB molecules on the surface of the photocatalyst. The non-adsorption of MB on the photocatalyst surface reduces the reaction between the •OH and MB. At higher pH, there is no competition between OH⁻ and MB, as OH⁻ will be repelled by the negatively charged surface of the photocatalyst and will remain in the solution in a large quantity [224,225]. Some photocatalysts such as ZnO may dissolve at lower pH, which decreases MB degradation [226]. The adsorption
of MB on the surface of TiO$_2$ is maximum in the basic medium as it acquires a negatively charged surface, which causes an increase in the electrostatic attraction between the TiO$_2$ particles and the MB molecules [227].

8.5. Effect of Oxidants

The practical way to increase the photodegradation of MB is to add a strong oxidant [228]. H$_2$O$_2$ increases the formation rate of hydroxyl radicals and enhances the degradation of compounds at low concentrations. This is due to the efficient generation of *OH and inhibition of electron-hole pair recombination, as H$_2$O$_2$ is an electron acceptor [229,230]. Hydrogen peroxide is considered one of the most potent oxidizing potential catalysts and produces 2 mol of the *OH (H$_2$O$_2$ + hv = 2*OH), followed by interaction with dye molecules [231]. The efficiency of MB degradation increases by increasing H$_2$O$_2$ amount up to a certain extent and then decreases, which might be due to recombination caused by hydroxyl radicals and the scavenging effect of H$_2$O$_2$ [232]. At higher concentration, H$_2$O$_2$ can scavenge *OH to form *OOH, as shown in Equation (6), which have much lower oxidation capability [233]. Air and KMnO$_4$ are also used as potential oxidizing agents for the photodegradation of MB [234,235]. Citrate ions generate H$_2$O$_2$ via its photolysis and cause a slight increase in the decolourization of MB [236].

\[
H_2O_2 + *OH \rightarrow H_2O + *OOH \tag{6}
\]

8.6. Effect of Radical Scavengers and Ions

In the photodegradation process, hole, hydroxyl and superoxide radicals are the key reactive species participating in organic pollutants degradation [237]. Several radicals’ scavengers are reported to understand the mechanism and the primary active species responsible for the photodegradation of MB [238]. These radicals include ammonium oxalate (h$^+$), t-butanol (*OH), and 1,4-benzoquinone (*O$_2^-$) [239]. Salgado and Valentini [240] used SiO$_2$@TiO$_2$ hybrid spheres as a photocatalyst for MB degradation and applied t-butyl alcohol (*OH scavenger), benzoquinone (*O$_2^-$ scavenger) and ethylenediamine tetraacetic acid (h$^+$ scavenger). It was observed that t-butyl alcohol significantly suppressed the photocatalytic efficiency than other scavengers. They thus suggested that *OH mainly promoted MB degradation. Lee and Park [241] employed $\alpha$-Fe$_2$O$_3$/g-C$_3$N$_4$ nanofilm. They documented the same results that tert-butyl alcohol significantly lowered the degradation rate when H$_2$O$_2$ was added, indicating that the *OH generated by the Fenton reaction is the significant reactant in the MB degradation. Using different scavengers, several researchers also reported that *OH is the main species in MB degradation [242–245]. Bicarbonate is a well-known radical scavenger, but under certain conditions, it enhances the degradation of certain pollutants, as also observed for MB. The reason is that bicarbonate radicals are more stable than *OH, and their oxidation ability is relatively high, making the lifetime of bicarbonate radicals longer than that of *OH and resulting in an enhanced degradation performance [246]. Other important *OH scavengers reported in the literature for photodegradation of MB are acetonitrile [192] and CaCO$_3$ [247].

Inorganic anion tends to coexist with organic pollutants in wastewater effluent and can influence the separation and purification substances represented in the wastewater treatment [248]. The effects of various inorganic anions on the photodegradation of MB in the presence of different photocatalysts are summarized in Table 2.
Table 2. The effect of inorganic anions on photodegradation of MB.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Inorganic Anions</th>
<th>Positive Effect</th>
<th>Negative Effect</th>
<th>Dual Effect</th>
<th>Negligible Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Fe &lt;sub&gt;3&lt;/sub&gt;O &lt;sub&gt;4&lt;/sub&gt;/ graphene composites</td>
<td>NaCl, Na &lt;sub&gt;2&lt;/sub&gt;SO &lt;sub&gt;4&lt;/sub&gt;, NaH &lt;sub&gt;2&lt;/sub&gt;PO &lt;sub&gt;4&lt;/sub&gt;, NaNO &lt;sub&gt;3&lt;/sub&gt;, and NaCO &lt;sub&gt;3&lt;/sub&gt;</td>
<td>SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, H &lt;sub&gt;2&lt;/sub&gt;PO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, CO &lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;</td>
<td>Na &lt;sup&gt;+&lt;/sup&gt;</td>
<td>[248]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag &lt;sub&gt;3&lt;/sub&gt;P &lt;sub&gt;4&lt;/sub&gt;</td>
<td>NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, OH &lt;sup&gt;-&lt;/sup&gt;, NO &lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, HCO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, Br &lt;sup&gt;-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, S &lt;sup&gt;2-&lt;/sup&gt; and PO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;3-&lt;/sup&gt;</td>
<td>OH &lt;sup&gt;-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, Br &lt;sup&gt;-&lt;/sup&gt;, HCO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, S &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>NO &lt;sub&gt;2&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, HCO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, PO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;3-&lt;/sup&gt;, Br &lt;sup&gt;-&lt;/sup&gt;</td>
<td>NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;</td>
<td>[249]</td>
<td></td>
</tr>
<tr>
<td>ZnFe &lt;sub&gt;2&lt;/sub&gt;O &lt;sub&gt;4&lt;/sub&gt;</td>
<td>SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>[250]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cerium-doped SiO &lt;sub&gt;2&lt;/sub&gt;/TiO &lt;sub&gt;2&lt;/sub&gt;</td>
<td>NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;</td>
<td>NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;</td>
<td>NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, Cl &lt;sup&gt;-&lt;/sup&gt;</td>
<td>[251]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>silver ion-doped TiO &lt;sub&gt;2&lt;/sub&gt;</td>
<td>Cl &lt;sup&gt;-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>Cl &lt;sup&gt;-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>Cl &lt;sup&gt;-&lt;/sup&gt;, NO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;-&lt;/sup&gt;, SO &lt;sub&gt;4&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;, CO &lt;sub&gt;3&lt;/sub&gt; &lt;sup&gt;2-&lt;/sup&gt;</td>
<td>[252]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusively, photocatalyst’s type and concentration selectively control radical production and kinetics during photodegradation.

9. Degradation Products of Methylene Blue, Its Identification, and Reaction Pathways

The reactive radicals generated in the single-component and multicomponent photocatalysis are H<sup>+</sup>, •OH, and •O<sub>2</sub>•− oxidize MB dye into CO<sub>2</sub>, H<sub>2</sub>O, and other degradation products [253]. The degradation of MB leads to the formation of harmless CO<sub>2</sub> and conversion of N and S heteroatoms into inorganic ions, such as nitrate, ammonium, and sulfate ions, respectively [194]. The decrease in the maximum absorption peak (664 nm) intensity of MB indicates that the chromophoric group of the MB molecule is completely removed [254]. When the characteristic peak position of MB absorption spectrum centred at 664 nm remains the same during the entire experiment with a decrease in intensity, it indicates the absence of any other chromophore molecules as a by-product [255]. The complete degradation of MB without any intermediate formation can be examined by the disappearance of the λ<sub>max</sub> peak (662 nm) without the appearance of other peaks in the UV–vis spectra [256]. Zhou et al. [257] observed that the exhibited bands at 465 and 292 nm in the UV spectra indicate the formation of by-products, such as Azure A, Azure B, Azure C, MB without any intermediate formation can be examined by the disappearance of the λ<sub>max</sub> peak (662 nm) without the appearance of other peaks in the UV–vis spectra. The blue shifts in the UV spectra of MB indicate the formation of by-products, such as Azure A, Azure B, Azure C, and Thionine [258]. The formation of these compounds occurs through the demethylation of MB and exist in the independent state. N<sup>-</sup>–CH<sub>3</sub> and C<sup>-</sup>–N are broken after the oxidation of Cl<sup>-</sup> to S=O, and the S<sup>-</sup>–C bond in the remaining structure is split to form phenol and aniline-2-sulfonic acid. These organic intermediates in solution were further oxidized until they were finally transformed into CO<sub>2</sub>, H<sub>2</sub>O, Cl<sup>-</sup>, SO<sub>4</sub> <sup>2-</sup>, and NO<sub>3</sub> <sup>-</sup> [262]. Another study indicates that •OH and H<sub>2</sub>O<sub>2</sub> may attract towards the cationic sulfur group and heteroaromatic ring of the MB that induces the opening...
of the central aromatic ring. Thus producing sulfoxide and hydroxylated intermediate products. These sulfoxide groups may further oxidize to sulfone and cause the dissociation of the two rings. Finally, these aromatic compounds decomposed and formed volatile low molecular weight compounds such as $\text{CO}_2$, $\text{H}_2\text{O}$, $\text{NH}_4^+$, $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ ions. The whole systematic degradation process is summarized in Figure 10 [263]. It was also proposed that N–CH$_3$ terminal bonding of MB is the first broken bonding, and CH$_3$ is oxidized to HCOOH or HCHO. The remaining C–N and C–S bonding are continuously broken to form the single ring structures and then finally oxidized to ions such as $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{H}_2\text{O}$, and $\text{CO}_2$ [264]. Similarly, the disappearance of FTIR individual characteristics peaks (Table 1) in photocatalytically treated MB solution indicates the removal of the MB molecule, while the appearance of any new peaks may be due to the formation of mineralized ions [70,265]. In the same way, the decrease in the total organic carbon (TOC) values after photodegradation reactions show the mineralization degree of the MB [266,267]. The HPLC analysis of MB dye at different intervals of reaction time represents chromatograms for azure A, azure B, azure C, and Thionine as intermediates products [268].

Figure 9. Probable reaction steps of MB photocatalytic degradation [67]. Adapted with permission from the Royal Society of Chemistry (license ID 1079849-3).
10. Role of Catalysts

The photodegradation efficiency of MB is significantly influenced by the type of the catalyst and its concentration. As mentioned above, many single-component and multi-component photocatalysts have been successfully employed to achieve maximum degradation efficiency. Some examples are ZnS [33], TiO$_2$ [34,35], ZnO [36], hematite [37–39], plasmonic metals (such as gold, silver, platinum) [40,41,269], metal vanadates (those of Bi, Ni, Cu, Zn, etc.) [43–47], and carbon-based catalysts such as graphene and its oxides, and carbon nitrides, [40,41]. These systems have demonstrated high efficacy in oxidizing MB through redox reactions.

Figure 10. Proposed MB degradation pathway during the photocatalytic process [263]. Adapted with permission from Royal Society of Chemistry (license ID 1080130-1).
For the single component photocatalyst such as TiO$_2$ [35], the redox reactions are initiated by irradiating the photocatalyst with light of suitable photon energy (of energy $\geq$ bandgap of the photocatalyst). This leads to exciting electron from the valence band to the conduction band of the photocatalyst, generating electron-hole pairs. At the photocatalyst surface, the electrons and holes participate in the reduction and oxidation reactions, respectively. The reduction reaction of the conduction band electrons with oxygen produces superoxide anions, while the oxidation reaction of the valence band hole with water molecules produces hydroxyl radicals. The produced superoxide anions and hydroxel radicals can degrade MB. However, the single component photocatalyst such as TiO$_2$ or ZnO [36] suffers from some drawbacks, including the wide bandgap, and the inability to absorb the visible light, which limits its photocatalytic applications to the UV region of the sunlight spectrum. Moreover, the high recombination rate of the photoexcited electron-hole pairs in the single component photocatalyst weakens the dye degradation rate [26–28]. As a result, many studies have been reported on the surface modification of single component photocatalysts such as addition of noble metals, graphene, or carbon to reduce their bandgaps, and electron-hole recombination and hence enhance their photocatalytic performance [270].

Nevertheless, preparing an efficient, wide bandgap photocatalyst is still challenging. Therefore, an efficient strategy for crafting a highly effective photocatalyst is designing a multi-component photocatalyst in which a narrow bandgap photocatalyst composites the wide bandgap photocatalyst. Such a design enhances the absorption of the visible region of the sunlight spectrum, reduces the electron-hole recombination rate, and enhances photocatalytic activity. Table 3 provides selected examples of efficient multi-component photocatalysts for MB degradation from wastewater. On the other hand, the following parameters of the photocatalyst also need to be manipulated and optimized to promote degradation efficiency:

1. Particle size: when the particle size is reduced to the nanoscale level, the specific surface area and the number of the active sites increases.
2. Morphology: morphology is a key that provides the exposed area to sunlight. It is reported that nano rod-like ZnO structures form a high amount of reactive species due to strong absorption and lower recombination [271].
3. Crystallinity: higher crystallinity leads to fewer defects for the recombination of photoexcited electron-hole pairs, and hence improves the overall photocatalytic activity of the catalyst [272].
4. The high surface area associated with more active sites, and dye adsorption capacity.
5. Facet tuning for specific wavelength absorption as in the case of copper and TiO$_2$ based materials that are widely used in relevant applications [273,274].
6. Kinetic directing catalysts, which produce the desired products from the recycled MB degraded products for use, are also important.

Considering these objectives, various parameters of the catalyst need to be manipulated and optimized, including the nanoscale particle size, desirable morphology (1D, 2D or 3D), and crystallinity. A wide range of literature is available on 1D photocatalysts [275], 2-D photocatalysts such as graphene and carbon nitrides [276,277], and 3D materials with octahedral morphologies [273,278]. Table 3 provides selected examples of efficient multi-component photocatalysts for MB degradation from wastewater.
Table 3. Photodegradation of MB over various photocatalysts.

<table>
<thead>
<tr>
<th>Optimized Material and Morphology</th>
<th>Synthesis Method</th>
<th>Light Source</th>
<th>%MB Degraded@Time</th>
<th>Favourable Features</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Cu$_2$V$_2$O$_7$/Zn$_2$V$_2$O$_6$ (1 wt%:5 wt%) Layered morphology</td>
<td>Ultrasonic assisted hydrothermal synthesis</td>
<td>300 Xenon Lamp</td>
<td>98.7%@65 min</td>
<td>Due to the layered morphology of Cu$_2$V$_2$O$_7$, the Zn$_2$V$_2$O$_6$ pellets are distributed evenly, hence facilitate the charge transfer. A large surface area provides more catalytic sites and exposure to light.</td>
<td>[43]</td>
</tr>
<tr>
<td>CuO/Bi$_2$O$_3$ nanocomposite</td>
<td>Impregnation calcination method</td>
<td>UV-C irradiation</td>
<td>88.32%@120 min</td>
<td>Probably due to the synergistic effect between the components of the nanocomposite</td>
<td>[279]</td>
</tr>
<tr>
<td>ZnO-NR/ACF nanocomposites</td>
<td>Hydrothermal method</td>
<td>UV irradiation</td>
<td>99%@120 min</td>
<td>Synergistic effects between ZnO nanorods and activated carbon fibers (ACFs)</td>
<td>[280]</td>
</tr>
<tr>
<td>SnO$_2$-bentonite nanocomposites</td>
<td>Green synthesis</td>
<td>Solar irradiation</td>
<td>100%@300 min</td>
<td>Efficient dye adsorption on bentonite and high surface of immobilized SnO$_2$ on bentonite surface</td>
<td>[281]</td>
</tr>
<tr>
<td>5% PTh/ZnO</td>
<td>Sol-gel and oxidative polymerization techniques</td>
<td>250 W high-pressure mercury lamp</td>
<td>95%@180 min</td>
<td>Perfect synchronization and synergistic effect of both PTh and ZnO</td>
<td>[282]</td>
</tr>
<tr>
<td>TiO$_2$/Seashell composites (23.4% TCAS)</td>
<td>Simple grinding and calcination, followed by the sol–gel process</td>
<td>Natural sunlight</td>
<td>100%@140 min</td>
<td>The elements presents in abalone shell doped into the substitutional sites of TiO$_2$ and act as semiconductors that improved the charge separation efficiency of TiO$_2$.</td>
<td>[283]</td>
</tr>
<tr>
<td>γ-Fe$_3$/Fe$_2$O$_3$/SiO$_2$ (Ar modified)</td>
<td>Single-stage heat-treatment process</td>
<td>UV-light</td>
<td>87.5%@120 min</td>
<td>Combined effects of structure defects, oxygen vacancies, and the formed carbon sheets after PVA decomposition</td>
<td>[284]</td>
</tr>
<tr>
<td>70% CeO$_2$/g-C$_3$N$_4$ Z-scheme heterojunction</td>
<td>Ball milling</td>
<td>UV light irradiation</td>
<td>90.1%@180 min</td>
<td>Stronger UV light response, higher charge carrier separation efficiency and the synergy between adsorption and photocatalysis.</td>
<td>[285]</td>
</tr>
<tr>
<td>g-C$_3$N$_4$/Ca$_2$Fe$_2$O$_5$ heterostructures</td>
<td>Solid-state reaction route</td>
<td>Natural sunlight</td>
<td>95.4%@70 min</td>
<td>Enhance photodegradation efficient due to the mitigation of recombination of photogenerated charge carriers by Type-II heterojunction</td>
<td>[286]</td>
</tr>
<tr>
<td>Flower-like Bi$_2$O$_3$/ZnO heterojunction</td>
<td>Hydrothermal method</td>
<td>Xenon lamp of power 300 W</td>
<td>98.5%@30 min</td>
<td>The product exhibited preferable morphology for the photocatalytic activity</td>
<td>[287]</td>
</tr>
<tr>
<td>Ternary MoS$_2$/Bi$_2$S$_3$/TiO$_2$ heterostructure</td>
<td>Microwave-assisted hydrothermal method</td>
<td>250 W Xenon lamp</td>
<td>99%@4 min</td>
<td>Ultrastiff MB photodegradation is due to introducing multiple pathways of electrons transfer that efficiently suppressed the photoelectron-hole recombination in the heterostructured composite</td>
<td>[288]</td>
</tr>
</tbody>
</table>

11. Summary and Future Perspectives

The presence of MB in natural water is harmful to humans and harms microbes and aquatic life due to its toxic nature. Photodegradation is found to be an effective and economical approach for the complete decolourization and mineralization of MB dye into nontoxic species. The effect of different parameters shows that photodegradation of MB increases with increasing irradiation time, photocatalysts dosage, pH of the medium, oxidants, and decreasing initial dye concentration. The effect of radical scavengers revealed that *OH is the main species in MB degradation. The impact of inorganic anions shows that anions may show the negative, positive or dual effect on the photodegradation of MB, which depends on its concentration and the nature of the photocatalyst. The mechanism and
reactions pathways analysis revealed that MB dye first converted into different intermediate products and then completely mineralized into CO$_2$, H$_2$O, NO$_3^-$, SO$_4^{2-}$ and Cl.

There are a few dimensions that still require thorough investigations to not only effectively remove the MB dyes but also increase their practical usage in various applications.

1. The wettability and optical properties of MB suggest its hydrophobic and strong fluorescent nature. Its emission peak is observed at 686 nm ($\lambda_{\text{em}}$ 665 nm), and this property can be exploited in multiple advanced applications. Due to these rationalities, MB has recently been used as an extrinsic fluorophore to study the micellization behaviour of drug delivery systems, i.e., bile salts (BS) [289]. The fluorescence response was monitored by fluorescence anisotropy at 686 nm, which indicates the MB–BS (MB-bile salt) association supported by the heat of formation values. This definitive study suggests the future potential of MB dyes as extrinsic fluorescence probes [289]. Moreover, the same property (in combination with various NPs) can be used in future imaging/diagnosis and treatment of tumours and other diagnostic applications [290]. Moreover, these properties can aid with optical sensor fabrication, though limited literature is available on the topic.

2. An important unexplored dimension is to utilize modified MB dye in petroleum applications. The fluorescent nature of these materials could be helpful to probe the oil pockets, map the oil transport pathways and investigate various mechanisms, especially at the dead ends of the rock, where the operational conditions and depth hindered the application of the usual investigative techniques.

3. Another critical aspect, which can be further investigated, is to convert the MB to beneficial and viable products via in situ bioconversion approaches. These investigations will not only remove the MB from the aqueous medium but also help to generate a variety of lower molecular products.

4. Lastly, the simple adsorption approach for removal of MB dye needs to rediscover by utilizing modern concepts and materials. The ultimate goal should be to achieve greater efficiency at a cheaper cost. In this regard, various naturally available supports, especially the plant bio sorbents, still possess enough potential. Recently, the fava bean peels *Vicia faba* (FBP), were explored for the removal of methylene blue (MB) dye, a novel ultrasonic-assisted shaking sorption. The comparison with conventional shaking indicates that the MB removal efficiency reached 90% at 50 mg/L of the initial dye concentration for the ultrasonic-assisted sorbents in a remarkably shorter time [58,291].

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