Review

Dynamics of Diffusion- and Immobilization-Limited Photocatalytic Degradation of Dyes by Metal Oxide Nanoparticles in Binary or Ternary Solutions

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Abstract: Photocatalytic degradation employing metal oxides, such as TiO2 nanoparticles, as catalysts is an important technique for the removal of synthetic dyes from wastewater under light irradiation. The basic principles of photocatalysis of dyes, the effects of the intrinsic photoactivity of a catalyst, and the conventional non-fundamental factors are well established. Recently reported photocatalysis studies of dyes in single, binary, and ternary solute solutions opened up a new perspective on competitive photocatalytic degradation of the dyes. There has not been a review on the photocatalytic behavior of binary or ternary solutions of dyes. In this regard, this current review article summarizes the photocatalytic behavior of methylene, rhodamine B, and methyl orange in their binary or ternary solutions. This brief overview introduces the importance of the dynamics of immobilization and reactivity of the dyes, the vital roles of molecular conformation and functional groups on their diffusion onto the catalyst surface, and photocatalytic degradation, and provides an understanding of the simultaneous photocatalytic processes of multiple dyes in aqueous systems.

Keywords: synthetic dyes; titania nanoparticle; photocatalytic degradation; mechanism

1. Introduction

The charming colors of the world originate from the light absorption and/or emission of natural and synthetic dyes. Due to their attractiveness, these coloring agents are applied in all products used in daily life, and throughout history, they have been utilized especially in textile clothes, fabrics, paints, and foods. In ancient times, coloring agents were based on natural dyes from plants and animals. Synthetic dyes have been intensively used since their discovery in the nineteenth century [1]. The production and use of synthetic dyes are continuously increasing, and in dying industries, these man-made dyes have taken over natural dyes due to their brighter colors and relatively low production costs. Another important reason is their stable colors, which can last for long periods of time. In addition to having bright colors, synthetic dyes dissolve easily in water, resulting in easier and cheaper manufacturing processes for the coloration of papers, plastics, leather, and foods and the formation of strong chemical bonds with cottons, fabrics, polymers, and food ingredients. There are about $10^5$ varieties of dyes, and around 10% of them are used for coloring cottons, fabrics, polymers, and food and/or printing [2,3], with their consumption rate being about 36 kilotons per year [4,5]. Notably, over 50% of the global consumption of dyes caused an increase in dye contamination in water systems, particularly in developing regions of Asia [6].
Although textile, paper, leather, plastic, and rubber industries, in principle, handle their respective effluents using treatment or storage systems, it was believed that up to 20% of the effluent is released into wastewater and leached into the surrounding urban areas by rainfall. The dye effluents are resistant to microbial attack, persist in the environment, prevent light penetration, and lower the rate of photosynthesis, thus decreasing dissolved oxygen levels, increasing the biochemical oxygen demand, and resulting in negative effects on living organisms in the water systems [7]. The large-scale production and large industries utilizing toxic dyes on a massive scale eventually cause the contamination of water systems and soil [8]. This extensive environmental pollution is highly poisonous to the ecosystem and decreases agricultural productivity.

As dyes are mutagenic, carcinogenic, and toxic, they have chronic effects. Many dye effluents have been associated with several acute health risks, such as hepatocarcinoma, splenic sarcomas, occupational asthma, and bladder cancer, causing chromosomal aberrations and nuclear anomalies in animal cells [9]. Therefore, the removal of them from wastewater before discharging them into the water systems is imperative [8–11], and removing the dye effluents from wastewater could protect the water systems from harmful pollution, and could recycling the spent water in the dyeing processes [11]. Although synthetic dyes are resistant to many extreme conditions and cannot be removed using any conventional wastewater treatments, research efforts have been devoted to the development of biological, physical, and chemical methods [12]. Among the successful methods, adsorption, photocatalysis, and ozonation have attracted great attention for eliminating organic pollutants from wastewater due to their high removal efficiency, sustainability, and selectivity [13–15].

Adsorption has been predominantly considered as the most promising and favorable method for removing synthetic dyes from wastewater because of its simple technological operation, as this method provides a simple route, operates at room temperature, and achieves relatively high removal efficiency [16]. In this sense, activated carbon, silica gel, polymeric ion exchange resins, and their nanocomposites and aerogels have been widely used as adsorbents to remove a wide variety of dyes [17–21]. Although these materials are considered excellent adsorbents due to their surface hydrophobicity, high surface area, well-developed porous structure, and special surface reactivity [17,18], the process to produce them is often rather expensive and forms secondary contaminated products. The selection of adsorbent material becomes the most essential consideration in any adsorption process. As a result, low-cost, sustainable, and renewable adsorbents have been intensively explored [22].

Although agricultural wastes and clays account for the most explored materials for cost-effective adsorbents, their adsorption ability to remove dyes is much lower than other materials, such as composites and biopolymers [23,24]. The main reason is that, unlike the adsorption of gasses, which is strongly governed by the surface area and porous structure of the absorbents, the adsorption of dyes relies mainly on the intermolecular hydrogen bonding and electrostatic interactions between the functional groups on the adsorbent surface and dyes, as well as the conformational flexibility of the adsorbent when dispersed in water [25]. Therefore, the search for new sustainable adsorbents for the removal of dyes and their ability to be regenerated is still a research challenge [26,27]. Most importantly, the adsorption process from wastewater should be optimized toward the simultaneous removal of dyes from industrial effluents, which often contain multiple contaminants [11,27–31]. Similarly, biological methods are cost-effective, excellent at reducing odor and color, and environmental-friendly [32,33]. However, these methods still require strict and inflexible control of temperature and pH; otherwise, the synthetic dyes will take a long time to degrade and a large amount of sludge will need to be disposed of in the process [33]. Another important point that remains an issue is the application of biological methods in the removal of high concentrations of organic wastes.

On the other hand, heterogeneous photocatalysis has been demonstrated to be more desirable in the removal of dyes from wastewater [34,35]. The photocatalysis can be operated
using UV or white light in water treatment systems at ambient temperature and pressure conditions. This method shows several advantages in the decolorization of wastewater due to the low cost, easy waste disposal, environmental friendliness [36], and highly efficient photocatalytic degradation [15]. Most importantly, the removal of dyes using photocatalysis has been claimed to produce nontoxic or less harmful by-products [37–40].

Although most of the studies of photocatalysis of dyes have been reported since the discovery of titanium oxide (TiO₂) in the early 1970s, important contributions to the understanding of this particular field were developed since the earliest establishment of photocatalysis in water treatment systems [41]. The research on the phenomenon of photocatalysis is continuously established to explore either new photocatalysts, new types of dyes, new concept of photocatalysis, or the photodegradation mechanism of the synthetic dyes. In general, all the contributions have developed knowledge of the photocatalysis of dyes. It is well-known that the removal of dyes is due to their consecutive chemical reactions with photochemically generated hydroxyl (OH•) and oxygen (O₂•−) radicals, resulting in the degradation of dyes on the surface of the catalyst [42,43]. It is conceivable that the rate and efficiency of photocatalytic degradation of dyes depend on many factors; most of them are the intrinsic photoactivity of the catalyst [44], the dynamics of immobilization and the reactivity of the dyes with the photogenerated radicals on the surface of the catalyst [45]. These aspects of the photocatalytic degradation of the dyes are still deficient, while one could always consider the conventional non-fundamental factors, such as irradiation time, the ratio between dye concentration and the catalyst dosage, and the mediation of oxidative agents. This current review article summarizes the vital roles of the crystal structure of catalysts in their photocatalytic activity. It also highlights the molecular conformation and functional groups of synthetic dyes that affect the rate and efficiency of photocatalytic degradation of the dyes based on recently reported photocatalysis of dyes in single, binary, and ternary solute solutions. Therefore, the objective of this review article is to provide an insight into the importance of the dynamics of immobilization dyes (which are attributed to their molecular conformation and functional groups) on their diffusion onto the catalyst surface and their photocatalytic degradation.

2. Metal Oxide Semiconductors as Photocatalysts

The photophysical processes in photocatalysts are depicted in Figure 1. In general, photocatalysts are regarded as harvesting visible and/or near UV light energy to promote the separation of charge carriers and to utilize them to degrade dyes. Most of the studies have, therefore, been focused on metal oxide semiconductors due to their good photoactivity, relatively low bandgap, biologically and chemically inert nature, strong catalytic activity, high charge mobility and long charge carrier diffusion length, low cost, and non-toxicity [46,47]. In this sense, when the sizes of catalysts are in nanometer scales, the photocatalytic activity of the metal oxide semiconductors should be greatly increased.

With a bandgap energy of around 3.0–3.5 eV, the photocatalytic activity of TiO₂, ZnO, Mn₃O₄, CeO₂, BiVO₄, and BiOI/Bi₂WO₆ nanoparticles (NPs) has been intensively investigated. These catalysts absorb photon energy in the UV region less than 420 nm [48–51], and hence, their photocatalytic activity relies on UV light irradiation. This is advantageous for the degradation of the dyes that absorb photon light in the visible region, as the UV light irradiation can solely excite the catalyst and the spontaneous photolysis of the dyes can be avoided. As the bandgap of the metal oxides can be modified by incorporating a small number of metallic dopants, many researchers have successfully engineered the bandgap energy so that the metal oxide NPs could have absorption in the visible region, allowing the utilization of visible light or sunlight. By using this band engineering strategy, a large group of visible-light-responsive metal-oxide-based catalysts have been synthesized, as have been summarized in a number of review articles [52,53]. This means that these types of metal oxide NPs can be excited by visible light, in contrast to TiO₂, ZnO, Mn₃O₄, CeO₂, BiVO₄, and BiOI/Bi₂WO₆ NPs, which are limited by UV light excitation. As dyes also absorb photon
energy in the visible region, their photocatalytic degradation on visible-light-responsive metal-oxide-based catalysts should compete with their spontaneous photolysis [54,55].

Many studies have been focused on finding new metal oxides or incorporating metallic dopants in the metal oxides as photocatalysts. It should be noted that the photocatalytic activity of metal oxide NPs, which depends on the charge carrier separation, allowing electron and hole transfers to generate OH• and O2• radicals [42,56], must be explained by the redox reaction of the charge carriers with water molecules and solvated oxygen. Therefore, the potentials of oxidation–reduction of the valence band and the conduction band with respect to those of H2O and O2 should be evaluated. In this sense, the metal oxide materials are expected to have a redox potential of the photogenerated conduction band to be more negative in order to reduce adsorbed O2 to superoxide. Simultaneously, the redox potential of the photogenerated valence band hole has to be positive to produce OH• radicals in order to subsequently oxidize the organic pollutant [57,58]. For instance, the high photocatalytic activity of TiO2 NPs has a reduction potential (~0.5 V vs. NHE) lower than O2 (~0.33 vs. NHE), allowing the electron transfer to generate a superoxide radical (O2•−), and an oxidation potential (+2.7 V vs. NHE) higher than H2O (+2.53 V vs. NHE), allowing a hole transfer to generate a hydroxyl radical (OH•) [42]. It is obvious that the redox potentials of TiO2 make it a promising photocatalyst, though the O2•− and OH• radicals are not spontaneously generated upon photoexcitation. The most important factor for the formation of the radicals is the mobility of the charge carrier inside the catalyst [54,56]. The crystal structure of the catalyst plays an important role in accelerating the charge carrier mobility and in suppressing the recombination of an electron–hole. With this in mind, Luttrell et al. pointed out that, among the different crystal phases of TiO2 crystals, the anatase phase has the best performance in suppressing the recombination of an electron–hole [56], as has been experimentally observed [59].

The O2•− and OH• radicals are generated by an exciton and hole after their migration onto the catalyst surface [56], which are then involved in the oxidative reaction of synthetic dyes [60]. The photocatalytic activity of TiO2 NPs could be improved by enhancing the rate of immobilization of dyes onto the catalyst surface and by suppressing the electron–hole recombination by designing them in the form of composites with polymers [61], clay minerals [62], and ZnS shell structures [63]. In the presence of TiO2 NPs as catalysts, regardless of their crystalline phase, the photocatalytic degradation rate of synthetic dyes

Figure 1. A schematic illustration of the photophysical processes in photocatalysts. BQ and TBA stand for benzoquinone and tert-butyl alcohol.
has been found to depend on diffusion, immobilization, and oxidation reactions with \( \text{O}_2^* \) and \( \text{OH}^* \) radicals on the catalyst surface [64]. In this sense, there are many metal oxides that exhibit low photocatalytic activity because of the exciton-hole recombination. Such recombination results in low quantum efficiency and, hence, a low probability of generating \( \text{O}_2^* \) and \( \text{OH}^* \) radicals on the catalyst surface. The other important parameter is the surface area of the catalyst. It has been revealed that the photocatalysis is an ultrafast process [65], which requires the dyes to be in chemical contact with the radicals on the catalyst surface. This means that if the diffusion of the synthetic dyes onto the catalyst surface is much slower than the radical formation, the generated radicals are dissolved in the solution and such solvated radicals will quickly decay into non-reactive species; thus, no photocatalytic degradation reaction occurs. This results in the breakdown of the conjugated system of the dyes to produce final products such as \( \text{CO}_2, \text{H}_2\text{O} \) and other small organic molecules [66–68].

It is very interesting to highlight the effect of a dopant on the electron–hole recombination. In several photocatalytic studies, the bandgap engineering has been successfully performed by the incorporation of metallic dopants, thus lowering the bandgap energy, which has been claimed to optimize the photoexcitation utilizing visible light or sunlight and enhance the photocatalysis of dyes [69]. However, many reports stated otherwise [70,71]. The latter is rationalized by considering that defects in the crystalline structure due to the incorporation of metallic dopants create trapping states (or dopant states), enhancing the rate of the electron–hole recombination. This has also been clearly demonstrated in the photocatalytic conversion of acetic acid to carbon dioxide on metal-doped graphitic carbon [72].

Photocatalysis can be assisted by the presence of a small amount of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) due to its good capability of oxidizing the photogenerated electron on the catalyst surface to form an \( \text{OH}^* \) radical [73,74]. The peroxide dissociation is also accelerated under UV light irradiation, and eventually leads to the formation of \( \text{OH}^* \) radicals in the solution that readily oxidizes and degrades the dyes [74]. Therefore, in the presence of \( \text{H}_2\text{O}_2 \), in addition to the photocatalysis process on the catalyst surface when irradiated with light energy, direct oxidation by the formation of an \( \text{OH}^* \) radical in the solution also contributes to the degradation of synthetic dyes, although the direct degradation produces different mechanisms and products from those resulted from the photocatalysis process. The degradation of dyes due to the spontaneous dissociation of \( \text{H}_2\text{O}_2 \) is relatively slow and inefficient. Nevertheless, the additional \( \text{H}_2\text{O}_2 \) in the photocatalysis is used to examine if the formation of \( \text{O}_2^* \) and \( \text{OH}^* \) radicals are the rate-determining step of the photocatalytic degradation of dyes.

It is conceivable that, due to their photoactivity, the catalysts should always generate electron–hole pairs. After their migration onto the catalyst surface, depending on the redox potential of the catalysts, the exciton and hole could form the \( \text{O}_2^* \) and \( \text{OH}^* \) radicals [56]. Radical scavengers intentionally added into the mixture of dyes with photocatalysts in an aqueous system, such as tert-butanol and benzoquinone, which scavenge \( \text{OH}^* \) and \( \text{O}_2^* \) radicals, respectively, inhibit the oxidation reaction of the dyes. The mechanism of photocatalytic degradation of dyes is therefore evaluated based on the observation of whether the degradation efficiency of the dyes is affected by the additional radical scavengers or not. The bottom line is to find out which kinds of radicals are formed by the catalysts and which kinds of radicals play a role in the oxidative decomposition of the dyes.

Another important successful approach is the combination of the photocatalysis with sonication [75,76]. The additional treatment by applying 20–1000 kHz ultrasonic waves in the photocatalysis has been demonstrated to induce cavitation bubbles, which could generate \( \text{H}^* \) and \( \text{OH}^* \) radicals, enhancing the degradation of organic dyes. It should be understood that, in this so-called sonophotocatalysis, the intrinsic photocatalytic activity of catalysts and photocatalytic degradation of hydrophilic dyes are unchanged. However, the additional sonication is very useful in degrading hydrophobic compounds in wastewater containing multiple synthetic dyes via sonolysis [75,76].
As mentioned above, owing to their good photoactivity and suitable bandgap with the incident light excitation, metal oxides such as TiO$_2$, ZnO, WO$_3$, Mn$_3$O$_4$, CeO$_2$, and BiVO$_4$ NPs are excellent photocatalysts. These photoactive metal oxides have some advantages of being easy to manufacture into a variety of morphologies and nanostructures (such as nanospheres, nanorods, nanowires, and nanofibers), abundant, and inexpensive [77]. In addition to their suitable redox potential to reduce or oxidize oxygen and water, the reusability and stability of photocatalytic materials have also been of interest [78]. In this sense, some of the metal oxides suffer from several drawbacks. For instance, TiO$_2$ and ZnO NPs are amphoteric and have poor chemical stability at high pH of a medium [79], BiVO$_4$ and Fe$_3$O$_3$ NPs have poor charge carrier mobility in the crystal lattice and slow oxygen kinetics on the particle surface, whereas WO$_3$ NPs undergo peroxidation and photocorrosion during the photocatalytic process [80]. Nevertheless, as the crystal structure and the surface of the mentioned metal oxides remain unchanged after the photoexcitation and washing with water, the photoactive catalysts can be recovered, regenerated, and reused [81]. Recycling of the nanostructured photocatalysts from electronic waste, such as printed circuit boards and batteries, has also opened up a new pathway of photocatalysis of recalcitrant dyes to be more efficient in terms of synthesis cost, environmental risks, electronic waste valorization, and waste disposal management [82].

3. Synthetic Dyes

Most of the synthetic dyes utilized by the textile clothes, fabrics, paints, and foods available in the market are categorized as chromophoric or auxochromic dyes. These dyes are classified into direct dyes, reactive dyes, indigo dyes, mordant dyes, nitro dyes, azo dyes, sulfonate dyes, basic dyes, and acidic dyes, depending on their chemical structure and their functional groups [9,83,84]. Common chromophoric dyes include azo (-N=N-), carbonyl (-C=O), ethenyl (-C=C-), nitro (-NO$_2$ or =NO-OH), imino (-C=N-), thiocarbonyl (-CH=S), nitroso (-N=O) moieties. Auxochromic dyes are related to their functional groups, such as amino (-NH$_2$), carboxylic (-COOH), sulphonyl (-SO$_3$H), alkoxy (-OR), hydroxyl (-OH), and quinoid rings [9,85]. The number of functional groups present in dyes is responsible for the intensity of color. Amongst these chemically synthesized dyes, azo dyes containing auxochromes are widely used by textile, paper, leather, plastic, and rubber industries in large quantities, e.g., 60–70% of the total synthetic dyes, due to their push–pull effect on intramolecular electron delocalization and, hence, intense light absorption, bright emission, and excellent speed properties [9,83,84,86]. The azo dyes are well-known for their good solubility in water and their harmful impacts on aquatic organisms [87] and human health [88] when discharged directly into water systems.

In the literature, there are still no reports of the effluents of synthetic dyes that are mixed in industrial wastewater, but it is believed that textile industries may use multiple coloring agents at the same time in the dyeing process and produce multiple dyes in their wastewater [11]. Although the impacts of water containing multiple dyes have also not been reported, one could consider that possible synergistic effects of the dye effluents might cause more harmful health effects than wastewater of single solute solutions of dyes. The multiple dyes also have different photocatalytic degradation reactions due to their chemical structures and functional groups. In many studies, auxochromic dyes are demonstrated to undergo photocatalytic degradation reaction easily [37–40]. As it has been discussed in the literature for methylene blue, rhodamine B, crystal violet, and auramine O, the auxochromatic dyes become unstable upon reaction with O$_2^*$ and OH* radicals and undergo N-demethylation or N-deethylation through successive oxidation reactions [37–40]. The conjugated structure of the dyes is destructed via various intermediates into small volatile compounds, such as CO$_2$, NH$_2$, and NH$_4^+$, which may gasify and escape from the solution [37–40,89].

Comparing the rate and efficiency of the photocatalytic degradation of different auxochromic dyes is not an easy task because of the different photocatalytic setups and experimental conditions in each reported paper. By comparing the photocatalytic degra-
dation of six different auxochromic dyes, i.e., methylene blue, rhodamine B, crystal violet, methyl violet, brilliant green, and malachite green, Zulmajdi et al. reported that although the dyes have slightly different degradation rates, they have almost similar efficiencies, and all of them can be completely depleted [15]. However, this finding still does not resolve the factors that control the photocatalytic degradation of auxochromic dyes, which could be related to their chemical structures. The important findings are given by the photocatalytic degradation behavior of methylene blue and rhodamine B in the binary solute solution [45] and methylene blue, methyl orange, and rhodamine B in the ternary solute solution [90], ensuring all the experimental conditions are the same. It was revealed that the dyes with planar structure and smaller size have a faster rate and a higher efficiency of photocatalytic degradation [45,90]. This provides an interpretation that the rate and efficiency of photocatalytic degradation of dyes are controlled by their diffusion in the solution and their immobilization dynamics onto the catalyst surface, in addition to the potential energy barrier of the oxidation reaction of the dyes.

4. Parameters Affecting the Rate of Photodegradation of Dyes

In heterogeneous photocatalysis, a typical experimental setup should consist of a suitable light source (UV lamp, visible lamp, or natural light source such as sunlight), magnetic stirrer, and a reactor or petri dish containing a dye solution, photocatalyst, and a magnetic bead. Although sunlight is naturally available in abundance, which can be regarded as an alternative cost-effective light source, artificial UV irradiation provides better reproducible results than sunlight with a higher degradation efficiency of dyes [91]. As mentioned above, the use of UV irradiation in photocatalysis could minimize the spontaneous photolysis of dyes.

As mentioned above, the intrinsic properties of photocatalysts, including the crystallinity and surface chemistry, play a role in the photocatalytic activity of metal oxide catalysts. In addition, it is well-known that catalysts with smaller particle sizes, which have a higher surface-to-volume ratio, have higher photocatalytic activity. In this sense, the energy band structure remains intact, suggesting that the particle size does not change the electronic structure of the catalyst; however, one could consider that the surface phonon is enhanced, and the excited energy is highly confined. Therefore, it is also widely accepted that the particle size determines the charge-carrier dynamics. In this sense, the electron–hole recombination tends to reduce in the catalysts with smaller sizes, and hence, their photocatalytic activity is enhanced [92,93].

The performance of catalysts and photocatalytic degradation of dyes in single, binary, or ternary solute solutions are also determined by several conventional non-fundamental parameters, such as the irradiation time, initial concentration, catalyst dosage, and temperature. The effect of irradiation time is used to decipher the photocatalytic degradation kinetics. Based on the assumption that dyes degrade according to the first-order kinetic reaction, as described by the Langmuir–Hinshelwood (L–H) model [94–96], the kinetics of the heterogeneous photocatalytic degradation of each dye is usually evaluated by a single exponential decay function, as given by

\[ C_t = C_0 \exp(-k_{\text{obs}}t) \]

where \( k_{\text{obs}} \) is the observed photocatalytic degradation rate constant and is determined from the single exponential decay of \( C_t \) as a function of irradiation time, \( t \). It should be noted that this L–H model is, however, a simplified process of photocatalysis, which involves complex multistep processes. The most important consideration of this model is that there is no interaction between dyes in solution, and all of them would be completely degraded, regardless of the \( k_{\text{obs}} \) value. In other words, the dyes will reach 100% efficiency of photocatalytic degradation. In fact, in many cases, the dyes are not completely degraded, and thus have lower photodegradation efficiency (\( \eta \)), much lower than 100%, even under elongated continuous light irradiation. In this sense, it is proposed that the degradation reaction of dyes involves many transition states and various intermediates, or the reaction
undergoes different pathways so that there is a backward reaction, and the photocatalytic degradation eventually reaches an equilibrium. By comparing the effects of the conventional non-fundamental parameters on the photocatalytic degradation of dyes, such as $k_{obs}$ and $\eta$, in their single solutions and in binary or tertiary solutions, as summarized in Table 1, one could anticipate simultaneous photocatalysis of the multiple dyes with respect to their individual photocatalytic degradation.

Table 1. Photocatalytic experimental conditions and observed photocatalytic degradation efficiency and rate of methylene blue, rhodamine B, and methyl orange in their single solute, binary, or ternary solutions.

<table>
<thead>
<tr>
<th>Experimental Conditions</th>
<th>Single Solute Solution</th>
<th>Binary or Ternary Solutions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6.7</td>
<td>Concentration:</td>
<td>Methylene blue</td>
<td>$\eta = 93.1%$</td>
</tr>
<tr>
<td></td>
<td>Methylene blue</td>
<td>$= 2.0 \times 10^{-5} \text{ M}$</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td></td>
<td>Rhodamine B</td>
<td>$= 2.0 \times 10^{-5} \text{ M}$</td>
<td>Catalyst: TiO$_2$</td>
</tr>
<tr>
<td></td>
<td>0.25 g/L</td>
<td>Irradiation time:</td>
<td>180 min</td>
</tr>
<tr>
<td>pH 6.5</td>
<td>Concentration:</td>
<td>Methylene blue</td>
<td>$\eta = 99.9%$</td>
</tr>
<tr>
<td></td>
<td>Methylene blue</td>
<td>$= 1.56 \times 10^{-5} \text{ M}$</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td></td>
<td>Rhodamine B</td>
<td>$= 1.04 \times 10^{-5} \text{ M}$</td>
<td>Methyl orange</td>
</tr>
<tr>
<td></td>
<td>Methyl orange</td>
<td>$= 1.53 \times 10^{-5} \text{ M}$</td>
<td>Catalyst: BaTiO$_3$/Bi$_2$WO$_6$</td>
</tr>
<tr>
<td></td>
<td>0.03 g/L</td>
<td>Irradiation time:</td>
<td>120 min</td>
</tr>
</tbody>
</table>

As has been reported in many photocatalysis of dyes in single or binary solute solutions, the initial concentration of the dyes affects their photocatalytic degradation. It is rational to consider that higher initial concentration of dyes generates a competitive effect of the dye molecules to diffuse in close vicinity to the catalyst surface. As a result, their photodegradation rate decreases. It is also noteworthy that high initial concentration of dyes can hinder light penetration into the solution. This so-called screen effect may reduce the number of incident photons to excite the catalysts. Therefore, the removal rate tends to decrease exponentially with the initial dye concentration at the same irradiation time [97].

It was noted that an increase in catalyst dosage results in an increase in photodegradation rate up to a certain weight and saturates at high catalyst dosages [34]. An increase in catalyst dosage also indicates a larger surface area, which provides more exposure for $O_2^-$ and $OH^+$ radicals. Because the dye degradation rate is directly proportional to the mass of photocatalyst, above the established saturation point, the reaction rates may be decelerated. This can be suggested due to the prevention of light from penetrating into the solution due to an agglomeration of the photocatalyst, and as a consequence of overdosing, the number of radicals is decreased, thus resulting in a decrease in photocatalytic performance [15,98].

The effect of temperature on photocatalytic degradation can be considered as an important factor in term of diffusion. In many photocatalysis studies of dyes in single and binary solute solutions, increasing the reaction temperature in the range of 10–50 $^\circ$C enhances $k_{obs}$ [45,89], suggesting that, within this temperature range, the photocatalytic degradation rate was increased due to higher diffusion of the dyes onto the catalyst.
surface [99,100]. Based on the temperature-dependent $k_{\text{obs}}$, one could always determine the activation energy ($E_a$) of the photocatalytic degradation using the Arrhenius equation;

$$k_{\text{obs}} = A \exp\left(-\frac{E_a}{RT}\right)$$

(2)

where $A$ is the pre-exponential factor, $R$ is the gas constant, and $T$ is the temperature. In this sense, the $E_a$ value just reflects an average energy barrier and thermodynamic favorability of the photocatalytic degradation reaction of individual dyes, but it is not necessarily that of the oxidation reaction between the dyes and the generated $O_2^\bullet$ and $OH^\bullet$ radicals.

The effect of pH on photocatalytic degradation has been explored, but it is not straightforward, as the pH of the medium affects the chemical properties of both catalysts and dyes. In particular, charge on dyes and the characteristics of the catalyst surface can be modified by pH. Consequently, the diffusion and photocatalytic degradation of the dyes, as well as the reaction mechanism of the photoinduced dye degradation, are affected, as summarized by Reza et al. [101]. In this sense, the interaction between the dyes and the catalyst surface, and hence, the dynamics of the immobilization and reactivity of the dyes with the photogeneration on the surface of the catalyst, are modified. The pH also shows a pronounced effect on the electrostatic interaction between dyes and the catalyst surface. Abdellah et al. [102], Suhaimi et al. [45], and Kong et al. [89] reported that the photocatalytic degradation of methylene blue, rhodamine B, and auramine O on TiO$_2$ NPs generally increased at a pH value of 3 to 7. In this sense, these results are explained by considering the pKa of the dyes and the point of zero charge of anatase TiO$_2$ NPs (pH 6.1) [103]. Thus, TiO$_2$ NPs have a positive charge at low pH and gain a negative charge at pH > 6.1 towards alkalinity, modifying the electrostatic interactions and dynamics of immobilization of dyes on the catalyst surface. It is interesting to note that Suhaimi et al. showed a similar effect of pH on the photocatalytic degradation of methylene blue and rhodamine B in a binary solution, suggesting that each dye maintains its respective diffusional mass transfer onto the catalyst surface over a wide range of pH [45].

In other studies, the dynamics of immobilization of dyes has been anticipated, so that the effect of the adsorption of the dyes on their photocatalytic degradation was evaluated after keeping the mixture of dyes with TiO$_2$ NPs in an aqueous system in the dark [104]. In this sense, the photocatalytic degradation of dyes effectively occurred after the mixture was kept for 48 h in the dark, suggesting that deposition of the dyes onto the catalyst surface due to the adsorption process played an important role. In other words, photocatalysis of the preexisting dyes on the catalyst surface due to Le Chatelier’s equilibrium principle improves the degradation efficiency. However, during the photocatalytic degradation, it would be more reasonable to consider the dynamics of immobilization rather than the adsorption of the dyes onto the catalyst surfaces, as the adsorption–desorption equilibrium should be disrupted under light irradiation.

5. The Effect of Magnetism of the Photocatalyst in the Photocatalytic Activity

Recently, the effect of the magnetic field on the photocatalytic degradation of dyes on TiO$_2$ NPs has been reported by Bian et al. [104]. For instance, an applied magnetic field of as low as 0.28 T enhances the degradation rate of methyl orange by 24% as compared with that under zero magnetic field [104]. It was revealed that the macroscopic and microscopic structures of the TiO$_2$ catalysts are unchanged in the presence or in the absence of a magnetic field, suggesting that the enhanced degradation of the dyes is due to an increase in the photocatalytic process rather than to the nature of the catalyst. Firstly, under an applied magnetic field, the recombination of the photogenerated electron–hole could be suppressed, and thus the charge carriers migrate onto the catalyst surfaces more efficiently [105]. Moreover, the applied magnetic field could polarize the chemical bonds on the catalyst surfaces and induce the Lorentz force on the generated charge carriers [106].

As a result, the applied magnetic field accelerated the movement of charge carriers and the adsorption or immobilization of dyes onto the catalyst surfaces, leading to higher degradation rate of the photocatalysis of the dyes [104].
It is noteworthy that the magnitude of the Lorentz force is linearly related to the magnetic field intensity. Thus, the electron–hole recombination, the migration of charge carriers, the adsorption of dyes onto the catalyst surfaces, and hence, the photocatalytic degradation of dyes are influenced by the intensity of the applied magnetic field [107,108]. A relatively high magnetic field intensity has been revealed to suppress the degradation of dyes. One possible explanation is that the formations of O$_2$$^•$ and OH$^•$ radicals on the catalyst surface are interrupted by the strong Lorentz force exerted on the charge carriers so that the oxidation reaction of the immobilized dyes does not occur. In addition to the magnetic field intensity, the diffusion length of the charge carriers in the crystal structure of the catalyst should also be considered. In this sense, Bian et al. estimated that the diffusion length of the generated electron and hole in a TiO$_2$ lattice is approximately 10 nm [104]. Therefore, the effect of the Lorentz force exerted on the charge carriers should be more obviously observable when the particle size of TiO$_2$ is around 10 nm or less, which is comparable to the diffusion length of the generated electron and hole. This conclusion has been demonstrated in the study reported by Bian et al. [104].

6. Diffusion of Dyes onto the Catalyst Surface

With the assumption that the degradation of dyes is proportional to the external mass transfer, the diffusion of dyes onto the catalyst surface can be analyzed based on the time-dependent photocatalytic degradation of the dyes in single, binary, or ternary solute solutions. Among the established diffusion models, the Weber–Morris intraparticle model provides the rate and profile of the external mass transfer of dyes onto the catalyst surface [109];

$$C_0 - C_t = k_i t^{1/2} + C$$  \hspace{1cm} (3)

Here, $k_i$ is the diffusion rate, and $C$ is the boundary layer thickness on the catalyst surface.

The profile of external mass transfer of dyes was deduced based on the plot of the intraparticle model. Typically, a fast diffusion and effective degradation of the dyes was observed at an early irradiation time, followed by a slower diffusion at longer irradiation times until the dyes in the solution reached an equilibrium. Extrapolation of the Weber–Morris plot at time zero can provide an interpretation of the boundary layer thickness as well as the different diffusion rate of dyes in the solution and on the catalyst surface.

The diffusion of dyes in solution should be related to their respective hydrodynamic size, as reflected by their diffusion constant ($D$) value (see Table 1). As the photocatalytic degradation depends on the diffusion and migration of dyes onto the catalyst surface, the diffusion-limited rate constant ($k_D$) of the dyes should be proportional to their respective $D$ value, as given by the generalized Smoluchowski equation:

$$k_D = 4\pi\sigma D$$  \hspace{1cm} (4)

Here, $\sigma$ is the encounter distance. Consequently, the $k_{obs}$ or $k_i$ value of the dyes is positively related to the respective $D$ value.

By comparing the $k_{obs}$ value of each dye in a single solute solution and those in binary or ternary solute solutions, one could interpret the role of the molecular and conformational structures of the dyes with the rate and efficiency of their photocatalytic degradation. With this in mind, Suhaimi et al. suggested that the planar conformation and relatively smaller size of methylene blue, as reflected by its higher $D$ value, are the reasons for its domination in photocatalytic degradation over rhodamine B in the binary solution of these dyes [45]. Similar findings have been reported by Wang et al. in the photocatalytic degradation of the ternary solution of methylene blue, rhodamine B, and methyl orange using a novel BaTiO$_3$/Bi$_2$WO$_6$ heterojunction photocatalyst, where the photodegradation performance was dominated by methyl orange [90]. Recently, Kong et al. pointed out that the non-planar structure of auramine O, with a torsion angle between its two aromatic ring systems being $\sim$40°, and the non-favorable dimethylamino groups attached to the aromatic rings for
hydrogen bonding interactions to approach the surface of TiO$_2$ NPs are the reasons for the low $k_{obs}$ value of this dye [89].

Based on the above argument, one could anticipate that the catalytic degradation of organic pesticides on photocatalysts should also be governed by the diffusion of the pesticides onto the catalyst surfaces [110]. However, the photocatalytic degradation of the organic pesticides was suppressed by the presence of activated carbon support [111]. The organic compounds are well adsorbed and fill up the pore structures on the surfaces of the activated carbon/TiO$_2$ composites NPs. The adsorption then hinders the diffusion of the organic compounds onto the catalyst surfaces. This has also been supported by the lower degradation of organic pesticides at their higher concentrations, which acts as a driving force in the adsorption process, most probably due to the faster saturation of the composite surfaces [112].

7. Conclusions

The heterogeneous photocatalysis, which is initiated by light radiation in the presence of metal oxide nanoparticles, has been proven as one of the promising methods for the removal of a large variety of dyes. This brief review focuses on the photocatalytic degradation of dyes for evaluating their overall rate and efficiency based on recently reported photocatalysis of the dyes in single, binary, and ternary solute solutions. While the basic principles of photocatalysis of dyes are explained, the effects of the intrinsic photoactivity of catalyst and the conventional non-fundamental factors are elucidated in detail. The importance of the dynamics of immobilization and reactivity of the dyes with the photogenerated radicals on the surface of the catalyst has been highlighted. The diffusion of dyes onto the catalyst surface is reflected by the average degradation rate of the dyes and can be analyzed based on the degradation kinetics. By comparing the degradation kinetics and diffusion of the dyes, it is revealed that those with planar conformation and smaller size dominate in photocatalytic degradation in their binary or ternary solutions. Overall, this current review article emphasizes the vital roles of the molecular conformation and functional groups of synthetic dyes in their photocatalytic degradation. Nevertheless, further studies of the molecular structure, steric hindrance, diffusion, immobilization onto the catalyst surface, and synergetic-photosensitization effect of the dyes are some plausible factors to be explained and still remain a research challenge in photocatalysis. Another challenge in the future is the recovery, regeneration, and reuse of the photoactive catalysts, as their crystal structures and surfaces should remain unchanged after the photoexcitation. Moreover, deriving nanostructured metal oxides from electronic waste, such as printed circuit boards and batteries, is a challenging research area and opens up a new pathway of photocatalysis of recalcitrant dyes to be more efficient in terms of synthesis cost, environmental risks, electronic waste valorization, and waste disposal management, so that the photocatalysis keeps its record as the cleanest and most eco-friendly process to remove dyes from wastewater.

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